Kinetic study of hydrolysis of benzoates. Part XXII.† Variation of the *ortho* inductive, resonance and steric terms with temperature in the alkaline hydrolysis of substituted phenyl benzoates in aqueous 2.25 M Bu_4NBr

2 PERKIN

Vilve Nummert and Mare Piirsalu

Institute of Chemical Physics, Tartu University, EE2400 Tartu, Jakobi 2, Estonia

Received (in Cambridge, UK) 14th June 1999, Accepted 14th December 1999

The second order rate constants k_2 (M^{-1} s^{-1}) for the alkaline hydrolysis of *meta*-, *para*-, and *ortho*-substituted phenyl benzoates $C_6H_5CO_2C_6H_4$–X (X = H, 3-Cl, 3-CH_2, 3-NH_2, 3-NO_2, 4-F, 4-NO_2, 2-Cl, 2-F, 2-CH_3, 2-OCH_3, 2-NO_2) in 2.25 M aqueous *n*-Bu_4NBr have been measured spectrophotometrically at various temperatures (15, 25, 30, 40, 50 °C). The log *k* values were treated using both the modified Fujita–Nishioka and the Charton three-parameter correlation equations. The $\sigma°$, σ_I, $\sigma_R°$, E_s^B scales were used as the measure of the ordinary polar, inductive, resonance, and steric components of the substituent effects. $E_s^B = (\log k_X - \log k_H)_{H^+}$, where k_X and k_H are the rate constants of the acidic hydrolysis for *ortho*-substituted and unsubstituted phenyl benzoates in water at 50 °C. The modified Fujita–Nishioka and Charton treatments gave the excellent and identical results. The susceptibility to the induction effect of *ortho*-substituents was found to be about 0.2 units of the ρ scale smaller [$(\rho_I)_{ortho} = 1.80$] than that for *meta*- and *para*-substituents [$(\rho°)_{m,p} = 2.03$], in the alkaline hydrolysis of substituted phenyl benzoates in 2.25 M aqueous *n*-Bu_4NBr at 50 °C. Also in this solution, the variation of the susceptibility to the inductive and the resonance effects with temperature for the *ortho*-derivatives appeared slightly smaller than that for *para*-derivatives. During the transition from water to 2.25 M aqueous Bu_4NBr the susceptibility of the *meta*- and *para*-substituent polar effect $(\rho°)_{m,p}$ was found to increase by about 1.0 units, but the susceptibility to the inductive effect of *ortho*-substituents was enhanced only by about 0.5 units of the ρ_I scale at 50 °C. The variation of the inductive term of *ortho*-substituents with both solvent and temperature was found to be half that for *para*-substituents. Variation of the inductive term of *ortho*-substituents with the solvent and temperature by the same extent had earlier been found for the alkaline hydrolysis of substituted phenyl tosylates, though the ratio of the susceptibilities to the polar influence of *meta*-, *para*-, and *ortho*-substituents in water differed two-fold. The steric term of *ortho*-substituents for 2.25 aqueous *n*-Bu_4NBr was found to be independent of temperature and nearly equal to the steric term for water.

Introduction

We have for some time been engaged in an investigation of substituent effects, especially of the *ortho*-effect (*i.e.* the difference $\log k_o^X - \log k_p^X$, where k_o^X and $\log k_p^X$ are the rate constants for the *ortho*- and *para*-substituted derivatives) dependent upon temperature and medium. For the further extension of our studies on substituent effects, in the present paper the kinetics of the alkaline hydrolysis of substituted phenyl benzoates $C_6H_5CO_2C_6H_4$–X (X is the substituent in the *meta*-, *para*- or *ortho*-position) in 2.25 M aqueous Bu_4NBr at various temperatures has been studied. Earlier[1] we have studied the substituent effects dependent on temperature in the alkaline hydrolysis of substituted phenyl tosylates $CH_3C_6H_4SO_2OC_6H_4$–X in 2.25 M Bu_4NBr solution. The aim of our work was to compare the variation of substituent effects with both temperature and solvent in the alkaline hydrolysis of benzoates and tosylates.

The main purpose of our work was to follow the variations of the *ortho*-inductive, -resonance, and -steric terms with temperature, during the transition from water to 2.25 M aqueous Bu_4NBr. The contributions of the inductive, resonance and steric terms we separated from the total *ortho* substituent effect, using for the data processing the Fujita and Nishioka method,[2] which enabled the simultaneous use of data for *ortho*-, *meta*- and *para*-substituted derivatives. For comparison, the log *k* values for *ortho*-substituted derivatives were processed according to the modified Charton[3,4] three-parameter equation as well.

The linear free energy relationship of Hammett[5] type that has been used to correlate the vast numbers of rate and equilibrium data for reactions of *meta*- and *para*-substituted benzenes is not usually applicable to similar reactions of *ortho*-substituted benzenes. The peculiar behavior of *ortho*-substituted benzenes is called the "*ortho*-effect", and is caused by proximity effects, such as proximity electric effects, primary and secondary steric effects, hydrogen bonding, specific solvation effects and other intramolecular interactions. Numerous attempts have been made to separate quantitatively the terms which influence the reactivity of *ortho*-substituted benzenes.[2–22]

Hammett[4] considered that, in the absence of proximity effects (mainly the steric effect), the polar effect of *ortho*-substituents ought to be the same as the polar effect of *para*-substituents. Assuming this to be true, the difference $\log k_o^X - \log k_p^X$ is often used as the measure of the *ortho*-effect.

Taft[6] attempted to separate the total *ortho*-substituent effect into contributions of the polar and steric effects using eqns. (1) and (2). In eqns. (1) and (2) k_X and k_H are the rate constants for

$$\log (k_X/k_H)_B \equiv 2.48\,\sigma_o^* + E°_S \qquad (1)$$

$$\log (k_X/k_H)_A \equiv E°_S \qquad (2)$$

substituted and non-substituted benzoate esters, respectively, A and B indicate acidic and basic hydrolysis, respectively, σ_o^* is the polar *ortho*-substituent constant and $E°_S$ is a steric

---

† For Part XXI, see ref. 34.

DOI: 10.1039/a904741g

parameter characteristic of the *ortho*-substituent. The Taft polar $\sigma_o{}^*$ substituent constants appeared nearly equal to the polar substituent constants σ for *para*-substituents defined by Hammett. It should be remembered that the steric constants E°_S were defined by Taft on the basis of the kinetic data for carboxylic esters containing *ortho*-substituents in the acyl part.

According to Charton[3] the total *ortho* substituent effect could be separated into inductive, resonance and steric components. He treated 265 sets of reactivity data for *ortho*-substituted compounds according to eqn. (3), where

$$\log k = \alpha\sigma_I + \beta\sigma_R + \psi r + \text{const} \qquad (3)$$

σ_I and σ_R are the inductive and resonance substituent constants and r is a parameter for the steric effect based on the van der Waals radius of the substituent. Charton concluded that in a general case, *ortho*- and *para*-electrical effects might be expected to differ in both magnitude and composition. He considered that only in an exceptional case is the *ortho*-electrical effect identical with that in the *para* position. Charton[15] demonstrated that the steric constants E°_S defined by Taft [eqn. (2)] are not a function of the steric effects of the *ortho*-substituents and that they are almost completely a measure of the resonance effect. Charton concluded that the effect of *ortho*-substituents in the alkaline hydrolysis of *ortho*-substituted benzoates is determined only by the electrical substituent effect and is generally independent of steric effects. The Charton analysis was criticised by Shorter[7] because the compounds with the bulkiest substituents (*t*-Bu, CF_3, I, NO_2), as well as the non-substituted compound, had been systematically excluded from the correlations.

Fujita and Nishioka[2] correlated the data for 44 sets according to an equation that enabled them to treat the data for the *ortho*-substituted derivatives simultaneously with the *meta*- and *para*-substituted derivatives. In the case of *ortho*-substituted derivatives the additional proximity and steric scales were included [eqn. (4)].

$$\log k_{o,m,p} = \rho\sigma_{o,m,p} + \delta E_s^{ortho} + fF_{ortho} + c \qquad (4)$$

In eqn. (4) E_S are the steric parameters proposed by Kutter and Hansch,[23] determined using the average van der Waals radii r of the substituent, F is the proximity polar scale of Swain and Lupton,[24] nearly equal to the σ_I scale proposed originally by Taft. In eqn. (4) the unsubstituted derivative (X = H) was used as the standard. At the data processing according to eqn. (4) the values of the adjustable constant c appeared practically identical to the corresponding log k value for the unsubstituted derivative. Fujita and Nishioka used for non-symmetrical NO_2 and Ph-substituents two values of E_s calculated for the group being coplanar with or perpendicular to the reaction site. They used the maximum steric effect for the 2-NO_2 substituent (coplanar dimension) in the esterification, acidic, and basic hydrolysis of esters. None of those data sets included the 2-OCH_3 derivative. Fujita and Nishioka[2] considered that the definition $\sigma_{ortho} \equiv \sigma_{para}$ could underestimate the inductive component of the *ortho*-substituents. They included the additional proximity scale to take into consideration the possible difference in inductive effect of the *ortho*-substituents in comparison with that of *para*-substituents.

Concentrated quaternary ammonium salts, mainly aqueous Bu_4NBr, has been of great interest as a medium for the study of organic reactions during the last twenty years. The presence of organic electrolytes like Bu_4NBr increases the solubility of organic compounds in water considerably.[25] Electrophilic solvating power of aqueous solutions of Bu_4NBr decreases very significantly with an increase in the concentration of Bu_4NBr. The electrophilic solvating power for highly concentrated (3 M or ≈30 molal) aqueous solutions of Bu_4NBr reaches the level which is characteristic of the dipolar aprotic solvent DMSO, or of the pure liquid quaternary salt, $C_6H_5COO[(C_5H_{11})_4N]$.[26]

Steigman and Sussman[27] determined the pK_a values for *ortho*-, *meta*- and *para*-substituted benzoic acids in 7.75 M aqueous tetra-*n*-butylammonium bromide. They found that the *ortho*-effect disappeared for *ortho*-substituted benzoic acids and that the steric effect was not observed in the ionization of a hindered phenol when the solvent was 7.75 M aqueous *n*-Bu_4NBr. We demonstrated[1] that the additional positive *ortho*-inductive effect in the alkaline hydrolysis of substituted phenyl tosylates $CH_3C_6H_4SO_2OC_6H_4$–X diminished considerably, but did not disappear, while solvent composition was changed from water to 2.25 M aqueous Bu_4NBr. When studying the kinetics of the alkaline hydrolysis of *ortho*-substituted phenyl benzoates in 2.25 M aqueous Bu_4NBr at 50 °C[28] the *ortho*-effect was observed to be considerably more negative than in water.

In earlier papers we studied the *ortho*-effect dependence on temperature in the alkaline hydrolysis of substituted phenyl benzoates in water[39–32] and in an 80% aqueous DMSO.[33–35] We determined the dependence of the additional induction term for *ortho*-substituents on temperature for the alkaline hydrolysis of substituted phenyl tosylates in water,[36] in 80% aqueous DMSO[36–40] and in 2.25 M aqueous Bu_4NBr.[1,36,41] The correlation of the log k values with the polar σ° constants were excellent in both the alkaline hydrolysis of *meta*- and *para*-substituted phenyl benzoates and tosylates. When we processed the data for *ortho*-substituted phenyl tosylates together with *meta*- and *para*-substituted derivatives at a single temperature, we used, in addition to the σ° constants, the additional induction σ_I scale[42] as substituent parameters for *ortho*-substituted derivatives. In the alkaline hydrolysis of substituted benzoates we included the additional induction σ_I and the steric $E_s{}^B$ scales (see Table 2) as a measure of the *ortho*-effect. We defined the steric constants for *ortho*-substituents $E_s{}^B$, using the data of the acidic hydrolysis of substitued phenyl benzoates in water at 50 °C[38–31] ($E_s{}^B = \log k_{H^+}{}^X - \log k_{H^+}{}^H$ where $k_{H^+}{}^X$ and log $k_{H^+}{}^H$ are the rate constants in the acidic hydrolysis for *ortho*-substituted and non-substituted phenyl benzoates, respectively). By definition the steric constants $E_s{}^B$ are similar to the Taft steric E°_S constants, but our steric constants $E_s{}^B$ we determined for *ortho* substituents in the phenyl part of phenyl benzoates.

It should be mentioned that for *meta*- and *para*-substituents, the log k values of both the benzoate and tosylate reaction series correlate with the σ° substituent constants, but the susceptibility to the polar substituent effect in water exhibited a two-fold difference, *i.e.* $[(\rho^\circ)_{m,p}]_{Tos}/[(\rho^\circ)_{m,p}]_{Bens} \approx 2$. In water[28,36] the sensitivity to the inductive effect of *ortho*-substituents was found to be 1.5 times stronger than that of *para*-substituents (and the additional induction term); both the tosylate and benzoate alkaline hydrolysis reaction series exhibited a two-fold difference as well. In water, the dependence of the induction term of *ortho*-substituents on temperature appeared about two times larger than that for *para*-substituted derivatives. In water, it was found that the term of the additional inductive effect disappeared (*i.e.* the induction term for *ortho*-substituents and for *para*-substituents became identical) at 500 K in the alkaline hydrolysis of both benzoates[29] and tosylates.[36]

Though the polar substituent effect in the tosylate and benzoate reaction series differs in water about two-fold, an equal change was observed in the ρ° value when going from water to some other medium.[43–45]

Similarly the substituent-dependent change in both the activation energies and the log A values was found to be of the same magnitude for both the benzoate and tosylate alkaline hydrolysis reaction series upon changing from water to 80% DMSO solution, though the susceptibility of substituents to the polar effect in water differs two-fold.[34]

The present work was undertaken to study the influence of substituent effects, especially the *ortho*-inductive term, dependent on temperature in the alkaline hydrolysis of substituted phenyl benzoates in 2.25 M aqueous Bu_4NBr.

In the literature, there are, to our knowledge, no kinetic data on the alkaline hydrolysis of substituted phenyl benzoates in 2.25 M aqueous Bu_4NBr within a wide temperature range. The rates of the alkaline hydrolysis of substituted phenyl benzoates in 2.25 M aqueous Bu_4NBr solution for *meta*-, *para*-, and *ortho*-substituted derivatives have previously been measured only at a single temperature.[28,46]

Experimental

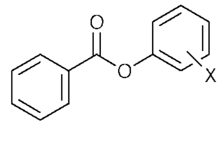
The preparation procedure and characteristics of the substituted phenyl benzoates and the technique of kinetic measurements are described in refs. 28, 29, 41, 46 and 47. As the reagent, 0.017 M tetrabutylammonium hydroxide was used. A carbon dioxide-free hydroxide solution was prepared from 10% aqueous Bu_4NOH ("Chemapol", reagent for polarography) by passing the hydroxide solution through an anion-exchange column (Amberlite IRA-400) in an argon atmosphere. The salt, Bu_4NBr ("pure" grade, Reachim, Moscow), was purified by a triple recystallization from acetone, precipitated by ether and dried under vacuum.

For kinetic measurements the spectrophotometric method was applied.[47] Reaction was followed using a Beckman DU-8 spectrophotometer and a device CF-4A supplied with a photoelectric multiplier and a recorder of the LP type. The spectrophotometer CF-4A was equipped with a jacketed cell compartment (specially made from brass for kinetic measurements) through which water was circulated from a bath, maintaining the temperature within ±0.05 °C. The wavelengths used are given in Table 1.

The kinetic measurements were carried out under pseudo-first-order conditions with alkali excess. To avoid the influence of salt effect on the kinetic measurements, a constant alkali concentration (0.0175 M) was used.

The pseudo-first order rate constants, k_1, were determined by a least squares computer program. The second-order rate constants were calculated by dividing the pseudo-first order rate constant k_1 by the alkali concentration. The measurements for each benzoate were repeated 3–6 times and the arithmetic means of the corresponding second order rate constants k_2 were calculated.

In the present paper the second order rate constants k_2 ($M^{-1}\ s^{-1}$) for the alkaline hydrolysis of phenyl benzoates were measured spectrophotometrically at various temperatures in 2.25 M aqueous Bu_4NBr for the following *meta*-, *para*-, and *ortho*-substituted phenyl benzoates:



X = H (25, 30, 40, 50 °C), 3-Cl (25, 30, 40, 50 °C), 4-F (15, 25, 30, 40, 50 °C), 3-CH_3 (25, 30, 40, 50 °C), 3-NH_2 (25, 30, 40, 50 °C), 3-NO_2 (25, 30, 40, 50 °C), 4-NO_2 (15, 25, 40, 50 °C), 2-Cl (15, 25, 30, 40, 50 °C), 2-F (15, 25, 30, 40, 50 °C), 2-CH_3 (25, 30, 40, 50 °C), 2-OCH_3 (25, 30, 40, 50 °C), 2-NO_2 (15, 25, 40, 50 °C).

The k_2 values, the number of measurements and the wavelength λ used at spectrophotometric kinetic measurements are given in Table 1.

Discussion

Data processing

In the present work the log k values of the alkaline hydrolysis of substituted phenyl benzoates in 2.25 M aqueous Bu_4NBr at various temperatures were treated according to eqns. (5)–(8):

$$T = \text{const},\ \text{X} \neq \text{const}:$$

$$\log k_{m,p} = \log k_o + (\rho^\circ)_{m,p}\sigma^\circ \qquad (5)$$

$$\log k_{m,p,ortho} = \log k_o + (\rho^\circ)_{m,p,ortho}\sigma^\circ + (c_\mathrm{I})_{ortho}\sigma_\mathrm{I} + \delta_{ortho}E_\mathrm{s}^\mathrm{B} \qquad (6)$$

$$\log k_{ortho} - 1.2E_\mathrm{s}^\mathrm{B} = \log k_o + (\rho_\mathrm{I})_{ortho}\sigma_\mathrm{I} + (\rho_\mathrm{R})_{ortho}\sigma_\mathrm{R}^\circ \qquad (7)$$

$$T \neq \text{const},\ \text{X} = \text{const}:$$

$$\log k = \log A - (E/2.3RT) \qquad (8)$$

Eqn. (7) is the modified Charton three-parameter correlation eqn. (9), where the steric term $\delta_{ortho}E_\mathrm{s}^\mathrm{B}$, constant at all temperatures studied, is subtracted from the log k values before data processing.

$$\log k_{ortho} = \log k_o + (\rho_\mathrm{I})_{ortho}\sigma_\mathrm{I} + (\rho_\mathrm{R})_{ortho}\sigma_\mathrm{R}^\circ + \delta_{ortho}E_\mathrm{s}^\mathrm{B} \qquad (9)$$

The susceptibility to the steric effect $\delta_{ortho} = 1.2$ was used as the mean value of δ_{ortho} calculated according to eqn. (6) at all temperatures for 2.25 M aqueous Bu_4NBr and water.

The log k values for the *meta*- and *para*-substituted derivatives were treated according to eqn. (5). Eqn. (6) is the Fujita and Nishioka[2] modified equation for the simultaneous use of data for *ortho*-, *meta*-, and *para*-substituted derivatives. We included for *ortho*-derivatives in eqn. (6) the Taft σ_I scale[42] instead of the proximity polar scale F of Swain and Lupton[24] used by Fujita and Nishioka. The term $(c_\mathrm{I})_{ortho}\sigma_\mathrm{I}$ in eqn. (6) represents the additional inductive effect of *ortho*-substituents compared with that for *para*- and *meta*-substituents. The total sensitivity to the inductive effect of *ortho*-substituents, detected according to eqn. (6) could be represented as the sum $(c_\mathrm{I})_{ortho} + (\rho^\circ)_{m,p,ortho}$ [according to Taft $\sigma^\circ = \rho_\mathrm{I}\sigma_\mathrm{I} + \rho_\mathrm{R}\sigma^\circ_\mathrm{R}$, where $\rho_\mathrm{I} = \rho_\mathrm{R} = 1$ and $\rho_\mathrm{I} = (\rho_\mathrm{I})_m = (\rho_\mathrm{I})_p$]. The data for only the *ortho*-substituted derivatives were treated according to eqn. (7) to compare the susceptibilities obtained for the inductive, resonance and steric terms for *ortho*-substituents with those determined with the simultaneous use of data for *ortho*-, *meta*-, and *para*-substituted derivatives [eqn. (6)]. In the data processing, according to eqn. (7), the log k value for the unsubstituted derivative (X = H) as standard was included besides the *ortho*-substituted derivatives. The activation parameters, the activation energy E and log A values were calculated according to the Arrhenius eqn. (8).

In an earlier paper[29] the kinetic data for the alkaline hydrolysis of substituted phenyl benzoates in water at a constant temperature were treated according to eqns. (5), (6) and (8). In the present paper the results of the data treatment according to eqn. (7) are reported as well.

In the data processing according to eqn. (5)–(8) the second order rate constants k_2 of the alkaline hydrolysis of substituted phenyl benzoates in 2.25 M aqueous Bu_4NBr at various temperatures, reported in Table 1, were used. The analogous data for water were taken from the literature.[32]

The data treatment was carried out on a PC/XT 486 computer, using a multiple parameter linear least squares (LLSQ) procedure.[48,49] According to the data treatment procedure the program carried out the preliminary automatic exclusion of statistically non significant argument scales, granting minimally required orthogonality of these scales. The resulting set of scales includes only those significant on the level 0.95 and meeting the orthogonality requirement. As a criterion of satisfactory orthogonality, the relationship $(s^\circ)_j < s^\circ$ is employed, where s° is the normalized standard deviation from the hyperplane of the regression and $(s^\circ)_j$ is the normalized standard deviation for the j-th regression coefficient. The normalization was obtained by dividing the corrected values and arguments by the square roots

Table 1 The second order rate constants k_2 for the alkaline hydrolysis of substituted phenyl benzoates $C_6H_5CO_2C_6H_4$–X in 2.25 M aqueous Bu_4NBr at various temperatures[a]

X	λ[b]/nm	T/°C	k_2[c]/M^{-1} s^{-1}	log (k_2/M^{-1} s^{-1})	n/n_0[d]	Notes
H	292.5	25	0.0801 ± 0.0012	−1.096	3/3	
		30	0.128 ± 0.003	−0.893	3/3	
		40	0.303 ± 0.013	−0.518	3/3	
		50	0.593 ± 0.033	−0.227	4/4	
			0.625 ± 0.011	−0.204	3/4	
3-Cl	293	25	0.462 ± 0.012	−0.335	3/3	
		30	0.682 ± 0.002	−0.166	5/5	
		40	1.42 ± 0.08	0.152	4/4	
		50	3.10 ± 0.04	0.491	4/4	
4-F	306	15	0.0858 ± 0.0053	−1.066	5/5	
		25	0.232 ± 0.009	−0.634	3/3	
		30	0.326 ± 0.007	−0.487	4/4	
		40	0.736 ± 0.029	−0.133	4/4	
		50	1.460 ± 0.081	0.164	4/4	
3-CH_3	296	25	0.0658 ± 0.0013	−1.182	3/3	
		30	0.0932 ± 0.0094	−1.031	5/5	
		40	0.233 ± 0.008	−0.633	3/3	
		50	0.502 ± 0.010	−0.299	3/3	
3-NH_2	266	25	0.0343 ± 0.0033	−1.465	3/3	
		30	0.0545 ± 0.0014	−1.264	3/3	
		40	0.116 ± 0.002	−0.935	3/3	
		50	0.261 ± 0.003	−0.583	3/3	
3-NO_2	430	15	1.79 ± 0.23	0.253	6/6	
		25	3.40 ± 0.34	0.531	6/6	
		40	8.29 ± 0.75	0.918	7/7	
		50	14.7 ± 0.8	1.167	6/6	[e]
4-NO_2	404	15	3.67 ± 0.34	0.565	4/4	
		25	7.15 ± 0.41	0.854	7/7	
		40	18.0 ± 1.3	1.255	3/3	[e]
		50	28.3 ± 1.45	1.452	7/7	[e]
2-F	292.5	15	0.0556 ± 0.0026	−1.255	4/4	
		25	0.166 ± 0.014	−0.780	3/3	
		30	0.194 ± 0.024	−0.712	4/4	
			0.218 ± 0.008	−0.661	3/4	
		40	0.549 ± 0.003	−0.260	3/3	
		50	1.07 ± 0.04	0.029	3/3	
2-Cl	303	15	0.0804 ± 0.0109	1.095	4/4	
		25	0.202 ± 0.016	−0.695	3/3	
		30	0.238 ± 0.021	−0.623	4/4	
			0.254 ± 0.020	−0.596	3/4	
		40	0.618 ± 0.057	−0.209	4/4	
			0.667 ± 0.040	−0.176	3/4	
		50	1.20 ± 0.02	0.079	3/3	
2-CH_3	298	25	0.0236 ± 0.0005	−1.627	3/3	
		30	0.0352 ± 0.0028	−1.453	4/4	
			0.0380 ± 0.0009	−1.420	3/4	
		40	0.101 ± 0.001	−0.996	3/3	
		50	0.208 ± 0.014	−0.682	4/4	
2-OCH_3	298	25	0.0110 ± 0.0001	−1.959	3/3	
		30	0.0191 ± 0.0006	−1.719	3/3	
		40	0.0523 ± 0.0011	−1.281	3/3	
		50	0.106 ± 0.003	−0.975	4/4	
2-NO_2	427	15	0.583 ± 0.033	−0.231	5/5	[e]
		25	1.26 ± 0.10	0.100	7/7	[e]
		40	3.05 ± 0.05	0.484	7/7	
		50	5.99 ± 0.21	0.777	8/8	

[a] Bu_4NOH concentration 0.0175 M was used, except where indicated otherwise. [b] λ = the wave length used in kinetic measurements (nm). [c] k_2 = the arithmetic mean value of the second order rate constants (M^{-1} s^{-1}). [d] The denominator, n_0, reflects the total number of data involved in the calculations of the arithmetic mean value for the second order rate constant k_2 and the numerator, n, equals the number of the remaining k_2 values after exclusion of significantly deviating rate constants. [e] Bu_4NOH concentration 0.00875 M was used.

Table 2 Substituent parameters used for correlations and values of characteristics for cross-correlations $R^2(E_s^B,\sigma)$ and $R^2(\sigma_I,\sigma)$

X	$\sigma^{o\,a}$	$\sigma_I^{\,b}$	$\sigma_R^{o\,c}$	$E_s^{B\,d}$
H	0	0	0	0
4-NO_2	0.81	0	—	0
3-NO_2	0.71	0	—	0
3-Cl	0.37	0	—	0
4-F	0.21	0	—	0
3-CH_3	−0.07	0	—	0
3-NH_2	−0.14	0	—	0
2-NO_2	0.81	0.63	0.19	−0.374
2-Cl	0.28	0.47	−0.20	−0.243
2-F	0.21	0.52	−0.35	−0.155
2-CH_3	−0.14	−0.05	−0.10	−0.264
2-OCH_3	−0.15	0.25	−0.41	−0.308
2-$N(CH_3)_2$	−0.44	0.10	−0.54	−0.425
$R^2(E_s^B,\sigma)$	−0.200	−0.140	−0.136	
$R^2(E_s^B,\sigma)^e$	−0.053	0.020	−0.244	
$R^2(\sigma_I,\sigma)$	0.586		−0.163	
$R^2(\sigma_I,\sigma)^e$	0.572		−0.249	

[a] See ref. 50. [b] See ref. 42. [c] See ref. 51. [d] See ref. 28. [e] Data set does not include 2-$N(CH_3)_2$ substituent.

of the corresponding dispersions. Significantly deviating points were excluded using a Student criterion. Exclusion of the significantly deviating points was performed on different confidence levels of the "t" test. In the present work the results of the data treatment are given mainly on the confidence level 0.99.

The "recommended" values of σ^o from the Tables[50] and the Taft σ_I and σ_R^o constants[42,51] were used. $E_s^B = (\log k_{H^+}^X - \log k_{H^+}^H)$, where $k_{H^+}^X$ and $k_{H^+}^H$ are the rate constants for the acidic hydrolysis of *ortho*-substituted and unsubstituted phenyl benzoates, respectively, in water at 50 °C.[28,31] The values of the substituent parameters used are listed in Table 2. The cross-correlations among independent variables for the *ortho* substituents NO_2, Cl, F, CH_3, OCH_3, $N(CH_3)$ and for the unsubstituted derivative (X = H), characterized by values $R^2(E_s^B,\sigma^o_p)$, $R^2(E_s^B,\sigma_I)$, $R^2(E_s^B,\sigma^o_R)$, $R^2(\sigma_I,\sigma^o{}_{;p})$, $R^2(\sigma_I\sigma^o_R)$ in Table 2, appeared not to be significant.

We compared the values of E_s^B with the steric constants E_s proposed by Kutter and Hansch,[23] determined using the average van der Waals radii r, and correlated E_s^B constants according to eqn. (10). The E_s^B constants do not correlate with the

$$E_s^B = (E_s^B)_H + cE_s \qquad (10)$$

steric constants, E_s, reported by Kutter and Hansch, when the substituents 2-NO_2, 2-F, 2-Cl, 2-CH_3, 2-OCH_3, 2-$N(CH_3)_2$ and the unsubstituted derivative (X = H) are included (R = 0.450). When we omit the data for the 2-OCH_3 and 2-$N(CH_3)_2$ substituents from the correlation and use the maximum value of E_s for the 2-NO_2 substituent as the Kutter and Hansch E_s steric substituent constant, there exists the correlation given by eqn. (11), where n_0 is the total number of data subjected to the

$$E_s^B = (-0.065 \pm 0.039)(E_s^B)_H + (0.137 \pm 0.029)E_s \qquad (11)$$
$$R = 0.918,\ s = 0.055,\ n/n_0 = 5/5$$

regression data treatment and n is the number of points remaining after the exclusion of significantly deviating points. The scale E_s^B does not correlate with the Taft resonance substituent constants of σ^o_R ($\sigma^o_R = \sigma^o - \sigma_I$). The Kutter and Hansch E_s steric parameters correlate with resonance substituent constants σ^o_R only if the unsubstituted derivative is excluded from the correlation [eqn. (12)].

$$E_s = (-1.73 \pm 0.148) - (3.00 \pm 0.47)\sigma^o_R \qquad (12)$$
$$R = 0.943,\ s = 0.26,\ n/n_0 = 6/7$$

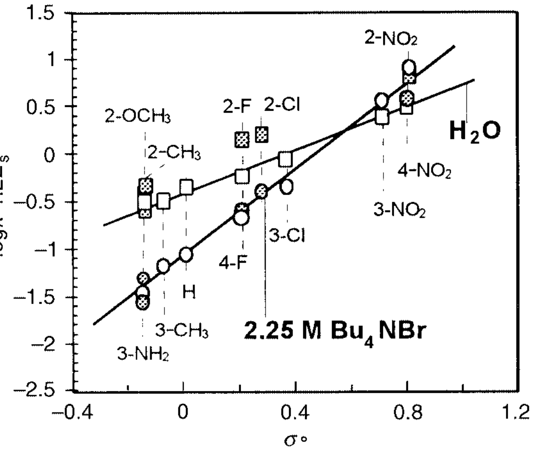


Fig. 1 Relationship between the ($\log k - 1.2E_s^B$) values and substituent constants σ^o for the alkaline hydrolysis of substituted phenyl benzoates $C_6H_5CO_2C_6H_4$–X in 2.25 M Bu_4NBr aqueous solution and in water at 25 °C.[32] Shaded circles and squares denote *ortho*-substituted derivatives.

In the correlation the substituents 2-NO_2, 2-F, 2-Cl, 2-CH_3, 2-OCH_3, 2-$N(CH_3)_2$ and the non-substituted derivative (X = H) were included. The point for the non-substituted derivative was excluded during the data processing. The scale E_s^B does not correlate with the Taft resonance substituent constants of σ^o_R. Comparison of the two steric scales, E_s^B and the Kutter and Hansch E_S steric constants, show that the E_s^B constants are more suitable in the alkaline hydrolysis of substituted phenyl benzoates.

When calculating according to eqn. (6) it was assumed that $\sigma^o_{para} = \sigma^o_{ortho}$. It was supposed that the inductive effect of *ortho*-substituents should differ from that for *para*-substituents, but the resonance from the *ortho*-position is equal to the resonance from the *para*-position. We assumed that in the case of 2-$N(CH_3)_2$-substituent the resonance contribution would equal zero and in the data treatment we added the correction $\rho^o\sigma^o_R$.

The results of the statistical data treatment according to eqns. (5)–(7) for the alkaline hydolysis of substituted phenyl benzoates in 2.25 M aqueous Bu_4NBr are listed in Table 3. The analogous results for water are given in Table 4. The values of activation energies E (kJ mol^{-1}) and log A found according to eqn. (8) are reported in Table 5.

Fig. 1 illustrates the relationship between the ($\log k - 1.2E_{s\,(ortho)}^B$) values and the σ^o constants for the alkaline hydrolysis of substituted phenyl benzoates $C_6H_5CO_2C_6H_4$–X in 2.25 M aqueous Bu_4NBr and in water at 25 °C. In Fig. 2 the relationship between the log k values and the ($1/T$) term for the same reaction is shown. Fig. 3 illustrates the variation of the activation energies E with the substituent constants σ^o. The dependence of log A on σ^o is shown in Fig. 4.

The comparison of the predicted log k values for the alkaline hydrolysis of substituted phenyl benzoates in 2.25 M Bu_4NBr solution at 40 °C and the experimental log k values are shown in Table 6 (Fig. 5). The log k_{calc} values are calculated according to eqn. (6) in Table 3 $(\log k_{calc})_{m,p,ortho} = -0.517 + (2.02\sigma^o)_{m,p,ortho} + (1.34E_s^B)_{ortho}$, the experimental log k_{obs} values are from Table 1. We found for the relation: $\log k_{calc} = a + b\log k_{obs}$: $a = -0.00184 \pm 0.029$, $b = 0.986 \pm 0.038$, $R = 0.992$, $s = 0.098$.

Comparison of 2.25 M Bu_4NBr solution and water

The substituted phenyl benzoates studied are very slightly soluble in water. The addition of Bu_4NBr to water increases the solubility of esters considerably relative to pure water (salting-in effect[25]). In aqueous Bu_4NBr solution the difference in the UV spectra for an ester and the corresponding phenolate ion, used in kinetic measurements, appeared also more significant than in water. For that reason kinetic measurements were

Table 3 Results of the treatment of log k values for the alkaline hydrolysis of substituted phenyl benzoates $C_6H_5CO_2C_6H_4$–X in 2.25 M aqueous Bu_4NBr according to eqns. (5)–(7) at various temperatures

t/°C	Eqn.	log k_o	ρ^o	$(c_I)_{ortho}$[a] or $(\rho_I)_{ortho}$	$(\rho_R)_{ortho}$	δ_{ortho}	R	s[b]	n/n_0[c]	Notes
50	5	−0.237 ± 0.026	2.03 ± 0.06	—	—	—	0.997	0.05	7/7	
	6	−0.207 ± 0.073	1.97 ± 0.08	−0.15 ± 0.16	—	1.15 ± 0.26	0.993	0.083	12/12	
	6	−0.202 ± 0.042	1.94 ± 0.07	0	—	1.33 ± 0.17	0.993	0.083	12/12	
	7	−0.190 ± 0.045		1.80 ± 0.21	1.76 ± 0.26	(1.20)	0.981	0.129	6/6	
40	5	−0.566 ± 0.036	2.16 ± 0.08	—	—	—	0.996	0.075	7/7	
	6	−0.523 ± 0.093	2.05 ± 0.09	−0.19 ± 0.20	—	1.11 ± 0.33	0.991	0.104	12/12	
	6	−0.517 ± 0.053	2.02 ± 0.08	0	—	1.34 ± 0.21	0.991	0.104	12/1	
	7	−0.491 ± 0.106	—	1.82 ± 0.21	1.78 ± 0.26	(1.20)	0.981	0.131	6/6	
25	5	−1.106 ± 0.032	2.34 ± 0.07	—	—	—	0.997	0.068	7/7	
	6	−1.073 ± 0.090	2.27 ± 0.09	−0.10 ± 0.20	—	1.34 ± 0.32	0.993	0.101	12/12	
	6	−1.070 ± 0.049	2.25 ± 0.08	0	—	1.47 ± 0.20	0.993	0.101	12/12	
	7	−1.079 ± 0.133	—	2.09 ± 0.26	2.05 ± 0.32	(1.20)	0.977	0.165	6/6	
15	5	−1.535 ± 0.054	2.55 ± 0.10	—	—	—	0.988	0.066	4/4	[d]
	6	−1.431 ± 0.100	2.35 ± 0.10	−0.26 ± 0.19	—	1.18 ± 0.34	0.994	0.097	9/9	[e]
	6	−1.414 ± 0.068	2.28 ± 0.10	0	—	1.52 ± 0.24	0.994	0.104	9/9	[e]
	7	−1.420 ± 0.056	—	2.01 ± 0.11	1.87 ± 0.14	(1.20)	0.995	0.069	6/6	[d,e]

[a] $(c_I)_{ortho}$ = the susceptibility to the additional *ortho*-inductive effect in eqn. (6), confidence level 0.99. [b] s = standard deviation. [c] n_0 = the total number of data subjected to the regression data treatment, n = the number of points remaining after exclusion significantly deviating points. [d] The log k for unsubstituted derivative was calculated from the relationship between the log k values and the (1/T) term. [e] The log k values for 2-OCH_3 and 2-CH_3 derivatives were calculated from the relationship between the log k values and the (1/T) term.

Table 4 Results of the treatment of log k values for the alkaline hydrolysis of substituted phenyl benzoates $C_6H_5CO_2C_6H_4$–X in water according to eqns. (5)–(7) at various temperatures[a]

T/°C	Eqn.	log k_o	ρ^o	$(c_I)_{ortho}$[b] or $(\rho_I)_{ortho}$	$(\rho_R)_{ortho}$	δ_{ortho}	R	s[c]	n/n_0[d]	Notes
60	5	0.435 ± 0.034	0.90 ± 0.17	—	—	—	0.936	0.070	5/5	
	6	0.434 ± 0.055	0.90 ± 0.08	0.31 ± 0.12	—	0.77 ± 0.17	0.985	0.053	10/10	
	7	0.531 ± 0.038	—	1.26 ± 0.07	0.89 ± 0.09	(1.20)	0.994	0.047	6/6	
50	5	0.200 ± 0.025	1.01 ± 0.05	—	—	—	0.988	0.057	11/11	
	6	0.222 ± 0.026	0.97 ± 0.03	0.54 ± 0.05	—	0.97 ± 0.03	0.997	0.039	17/17	
	6	0.221 ± 0.024	0.96 ± 0.03	0.54 ± 0.05	—	1.19 ± 0.08	0.996	0.036	16/16	[e]
	7	0.214 ± 0.031	—	1.52 ± 0.06	1.01 ± 0.07	(1.20)	0.994	0.041	7/7	
	7	0.217 ± 0.025	—	1.50 ± 0.05	0.94 ± 0.06	(1.20)	0.998	0.031	6/6	[e]
40	5	−0.079 ± 0.035	0.99 ± 0.06	—	—	—	0.987	0.062	7/7	
	6	0.081 ± 0.041	1.02 ± 0.04	0.44 ± 0.09	—	1.23 ± 0.13	0.998	0.050	13/13	
	6	−0.077 ± 0.046	1.02 ± 0.04	0.42 ± 0.10	—	1.17 ± 0.17	0.993	0.052	12/12	[e]
	7	0.023 ± 0.029	—	1.47 ± 0.04	1.05 ± 0.04	(1.20)	0.999	0.023	7/7	
	7	−0.011 ± 0.012	—	1.44 ± 0.02	1.03 ± 0.03	(1.20)	0.999	0.032	6/6	[e]
30	5	−0.261 ± 0.051	1.11 ± 0.10	—	—	—	0.983	0.086	5/5	[f]
25	5	−0.372 ± 0.028	1.04 ± 0.07	—	—	—	0.986	0.068	8/8	
	6	−0.363 ± 0.050	1.08 ± 0.06	0.53 ± 0.11	—	1.24 ± 0.16	0.999	0.078	15/15	
	6	−0.381 ± 0.054	1.07 ± 0.06	0.54 ± 0.11		1.18 ± 0.16	0.990	0.075	14/14	[e]
	7	−0.355 ± 0.05	—	1.58 ± 0.09	1.08 ± 0.10	(1.20)	0.994	0.061	7/7	
	7	−0.347 ± 0.021	—	1.53 ± 0.04	0.93 ± 0.05	(1.20)	0.999	0.027	6/6	[e]
15	5	−0.671 ± 0.025	1.14 ± 0.06	—	—	—	0.987	0.070	14/14	
	6	−0.670 ± 0.041	1.15 ± 0.05	0.54 ± 0.10	—	1.17 ± 0.15	0.991	0.075	20/20	
	6	−0.676 ± 0.027	1.15 ± 0.03	0.44 ± 0.07	—	0.92 ± 0.11	0.996	0.043	19/19	[e]
	7	−0.661 ± 0.062	—	1.72 ± 0.13	1.20 ± 0.13	(1.20)	0.995	0.107	7/7	
	7	−0.675 ± 0.040	—	1.71 ± 0.08	0.98 ± 0.10	(1.20)	0.996	0.049	6/6	[e]

[a] The statistical data treatment according to eqn. (5) and (6) were performed earlier, see ref. 29. [b] $(c_I)_{ortho}$ = the susceptibility to the additional *ortho*-inductive effect in eqn. (6), confidence level 0.99. [c] s = standard deviation. [d] n_0 = the total number of data subjected to the regression data treatment, n = the number of points remaining after exclusion of significantly deviating points. [e] Data for the 2-$N(CH_3)_2$ derivative were excluded before data treatment. [f] Estimated on the bases of data published in ref. 56.

taken in Bu_4NBr solutions rather than in water or in solutions of inorganic salts where the solubility of esters is lower than in water.

The alkaline hydrolysis of aryl benzoates is regarded as following the addition tetrahedral intermediate path.[52–55] Good correlation of data with σ^o constants for 2.25 M Bu_4NBr solution (Table 3) and water solution (Table 4) indicate the absence of the additional Ar–O resonance effect in the case of p-NO_2 substituent. Such a result is in accord with the two stage $B_{Ac}2$ mechanism for the hydrolysis of aryl benzoates, while the formation of the tetrahedral intermediate by addition of the hydroxide ion to the carbonyl carbon atom of the ester $[R–CO(OH)–OR]^-$ is considered rate limiting.[53–56] Decomposition of the intermediate by loss of the arene oxide ion should be much more rapid than reversion to the ester by loss of the more basic and poorer leaving group, the hydroxide ion. The positive ρ^o

Table 5 The values of log A and activation energy, E (kJ mol^{-1}), for the alkaline hydrolysis of substituted phenyl benzoates $C_6H_5CO_2C_6H_4$–X in 2.25 M aqueous Bu_4NBr calculated according to eqn. (8)

X	E/kJ mol^{-1}	log A	R	s_0	n/n_0[a]	Notes
H	65.90 ± 1.42	10.46 ± 0.24	0.999	0.037	4/4	
3-Cl	60.64 ± 4.41	10.28 ± 0.23	0.999	0.039	4/4	
4-F	62.13 ± 1.76	10.22 ± 0.30	0.998	0.065	5/5	
	60.92 ± 1.55	10.02 ± 0.26	0.999	0.043	4/4	[b]
3-CH_3	65.69 ± 2.22	10.31 ± 0.37	0.998	0.058	4/4	
	64.48 ± 0.63	10.12 ± 0.11	0.999	0.014	3/3	[c]
3-NH_2	64.37 ± 1.22	9.80 ± 0.21	0.999	0.013	4/4	
	64.64 ± 1.34	9.86 ± 0.22	0.999	0.029	3/3	[c]
3-NO_2	46.31 ± 1.35	8.67 ± 0.30	0.999	0.048	4/4	
4-NO_2	45.64 ± 1.35	8.84 ± 0.23	0.999	0.021	4/4	
2-F	61.71 ± 1.97	10.01 ± 0.33	0.998	0.063	5/5	
2-Cl	60.04 ± 5.32	9.75 ± 0.90	0.995	0.092	5/5	
2-CH_3	70.42 ± 2.55	10.72 ± 0.43	0.998	0.063	4/4	
2-OCH_3	73.02 ± 3.77	10.85 ± 0.64	0.996	0.090	4/4	
	71.80 ± 2.13	10.63 ± 0.25	0.999	0.042	3/3	[d]
2-NO_2	50.48 ± 1.45	8.92 ± 0.31	0.998	0.022	4/4	
3-Cl	80.35 ± 7.20	10.68 ± 1.09	0.992	0.124	3/3	[e]
2-NO_2	65.60 ± 5.50	9.73 ± 0.87	0.990	0.144	4/4	[f]
2-OCH_3	95.41 ± 5.92	11.45 ± 0.91	0.994	0.107	4/4	[g]
2-CH_3	98.04 ± 10.52	11.98 ± 1.62	0.990	0.184	4/4	[h]

[a] n_0 = the total number of data subjected to the regression data treatment, n = the number of points having remained after exclusion of significantly deviating point, confidence level 0.99. [b] The value of log k at 15 °C was excluded before data treatment. [c] The values of log k at 25, 40 and 50 °C were included. [d] The value of log k at 40 °C was excluded before data treatment. [e] The activation energy, E, and log A for the alkaline hydrolysis of 3-chlorophenyl tosylate in 2.25 M Bu_4NBr aqueous solution (ref. 1). The value of log k at 50 °C was excluded before data treatment. [f] The activation energy, E, and log A for the alkaline hydrolysis of 2-NO_2 phenyl tosylate in 2.25 M Bu_4NBr aqueous solution.[1] At 30 °C log $k = -1.635$ was used. [g] The activation energy, E, and log A for the alkaline hydrolysis of 2-OCH_3 phenyl tosylate in 2.25 M aqueous Bu_4NBr.[1] [h] The activation energy, E, and log A for the alkaline hydrolysis at 2-CH_3 phenyl tosylate in 2.25 M aqueous Bu_4NBr.[1] At 30 °C log $k = -3.800$ used.

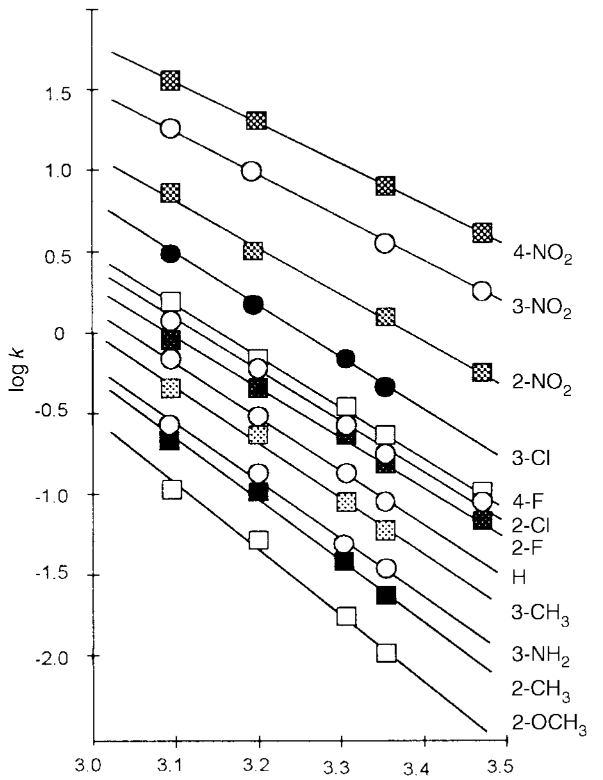


Fig. 2 Relationship between the log k values and (1/T) term for the alkaline hydrolysis of substituted phenyl benzoates $C_6H_5CO_2C_6H_4$–X in 2.25 M aqueous Bu_4NBr.

values, found for the alkaline hydrolysis of substituted phenyl benzoates in water and in 2.25 M Bu_4NBr, indicate that electron-withdrawing groups stabilize the intermediate by delocalisation of the fractional negative charge in the activated complex. The electron-donating groups destabilize the intermediate with negative charge or stabilize the ground state of esters by decreasing the fractional positive charge on the carbonyl carbon atom of esters.

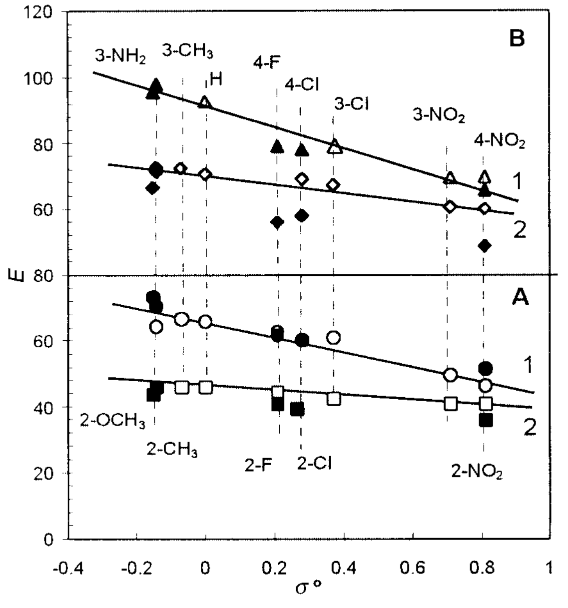


Fig. 3 Dependence of activation energies E(kJ mol^{-1}) on substituent constants σ^o for the alkaline hydrolysis of substituted phenyl benzoates $C_6H_5CO_2C_6H_4$–X (A) and phenyl tosylates[36] $CH_3C_6H_4SO_2OC_6H_4$–X (B) in 2.25 M aqueous Bu_4NBr solution (plot 1) and in water[29] (plot 2). Shaded characters denote *ortho*-substituted derivatives.

For most substituted phenyl benzoates the rate constants for alkaline hydrolysis decrease considerably when going from water to 2.25 M aqueous Bu_4NBr. The second order rate constant for non-substituted benzoate at 25 °C was found to be about 0.6 log k units lower than the corresponding value in water. The log k_2 value for the p-NO_2 substituted derivative in 2.25 M Bu_4NBr solution is, by approximately 0.3 log k units, higher than that for water due to an increased polar substituent effect in 2.25 M Bu_4NBr solution. The addition of Bu_4NBr to water causes the decrease in both the relative permittivity ε and

Table 6 The predicted values log k_{calc} and the experimental values log k_{obs} for 2.25 M aqueous Bu_4NBr at 40 °C

X	log k_{calc}[a]	log k_{obs}[b]	Δlog k[c]
4-NO_2	1.119	1.255	0.126
3-NO_2	0.917	0.918	−0.001
3-Cl	0.230	0.152	−0.078
4-F	−0.093	−0.133	−0.040
H	−0.517	−0.518	−0.001
3-CH_3	−0.658	−0.633	+0.025
3-NH_2	−0.800	−0.935	−0.135
2-NO_2	0.618	0.484	−0.134
2-Cl	−0.277	−0.209	0.068
2-F	−0.301	−0.260	0.041
2-CH_3	−1.154	−0.996	0.158
2-OCH_3	−1.233	−1.281	−0.048

[a] log k_{calc} was calculated using eqn. (6) for 40 °C (Table 3), $(\log k_{calc})_{m,p} = -0.517 + 2.02\sigma^o$ and $(\log k_{calc})_{ortho} = -0.517 + 2.02\sigma^o + 1.34E_s^B$. [b] log k_{obs} is the experimental log k value of the second rate order constant at 40 °C given in Table 1. [c] Δlog k = log k_{obs} − log k_{calc}.

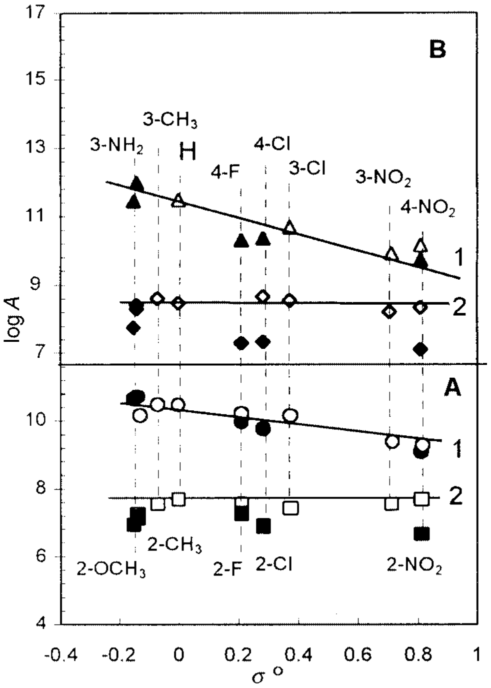


Fig. 4 Dependence of log A values on substituent constants σ^o for the alkaline hydrolysis of substituted phenyl benzoates $C_6H_5CO_2C_6H_4$ (A) and phenyl tosylates[36] $CH_3C_6H_4SO_2OC_6H_4$-X (B) in 2.25 M aqueous Bu_4NBr (plot 1) and in water (plot 2). Shaded characters denote *ortho*-substituted derivatives.

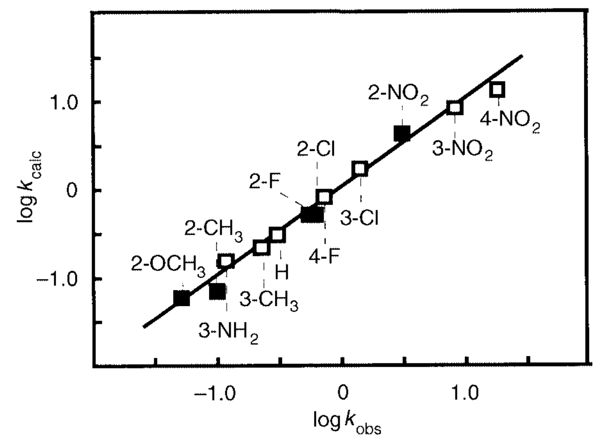


Fig. 5 Plot of log k_{cal} *vs.* log k_{obs}. log k_{calc} were calculated using eqn. (6) for 40 °C (Table 3). $(\log k_{calc})_{m,p} = -0.517 + 2.02\sigma^o$ and $(\log k_{calc})_{ortho} = -0.517 + 2.02\sigma^o + 1.34\ E_s^B$, log k_{obs} are the log k values of experimental values of the second order rate constants at 40 °C given in Table 1.

the electrophilicity E-parameter of solution. For 2.25 M aqueous Bu_4NBr at 25 °C, $\varepsilon = 19.5$[57] (for 1 M aqueous Bu_4NBr at 25 °C, $\varepsilon = 50.6$[58] and for 2 M Bu_4NCl at 25 °C, $\varepsilon = 25$[59]) and the electrophilicity parameter $E = 9.4$.[57] In the magnitudes of its electrophilicity E-parameter and relative permittivity ε, 2.25 M aqueous Bu_4NBr is similar to 80% aqueous dimethyl sulfoxide (DMSO) ($E = 7.9$[60] and $\varepsilon = 47.9$[61] for 90% aqueous DMSO solution). In spite of these similar properties, the rate of alkaline hydrolysis of the non-substituted phenyl benzoate varies in the opposite direction when going from water to aqueous Bu_4NBr or DMSO. As mentioned above, the second order rate constant for the non-substituted derivative decreases 0.6 log k units on changing from water to 2.25 M aqueous Bu_4NBr. On changing from water to 80% DMSO[34] the log k value for the alkaline hydrolysis of non-substituted phenyl benzoate appeared to increase by 0.9 log k units. According to electrostatic theories[62] reaction between a dipolar molecule and a charged ion should be dependent on the magnitude of the relative permittivity of the solvent. It seems clear that in the present case the variation of the alkaline hydrolysis rate with solvent could not be ascribed to the change in the relative permittivity of solvent alone. The rate enhancement in aqueous DMSO in the low water concentration range has been attributed to an increase in the activity of hydroxide ions caused by their reduced solvation by water in the presence of an aprotic solvent which has a strong attraction for water molecules.[63–65] The strong DMSO–water interaction significantly reduces the number of "free" water molecules available for the solvation of hydroxide ions. The lack of solvation of OH^- in DMSO solution makes it better nucleophile and increases its reactivity.

Steigman and Sussman hypothesized[66] that the hydroxy ion in aqueous n-Bu_4NBr salt solution has a higher activity coefficient and is more basic than in pure water solution, while water is strongly organized into hydrogen-bonded clusters in concentrated aqueous solutions of n-Bu_4NBr. The presence of tetraalkyl ammonium salt strengthens the structure of water[58,59,66,67] and the electrophilic solvating power of water decreases. It has been determined that the structure of the clathrate hydrate of n-Bu_4NBr salt contains on average 32.8 molecules of water. Water molecules in the presence of n-Bu_4NBr associate into strongly hydrogen-bonded structures and the number of non-bonded water molecules able to take part in electrophilic interactions decreases. In the presence of organic salt n-Bu_4NBr increases the solubility of organic compounds in water[25] (salt-in effect), whereas in the presence of inorganic salts the solubility of organic molecules is reduced (salt-out effect). Salting-in was explained in terms of an association between the non-electrolyte and the quaternary ammonium ions.

We assume that in the alkaline hydrolysis of benzoates in n-Bu_4NBr solution, the ester molecules in the ground state are more stabilized by hydrophobic solvation (with the organic part of quaternary ammonium ions) and the tetrahedral intermediate is less solvated than is the case in water. In 2.25 M Bu_4NBr solution the negatively charged intermediate could not be stabilized due to the reduced electrophilic activity of water molecules in concentrated aqueous solution of Bu_4NBr. The large Bu_4N^+ ions are also not able to stabilize charged intermediates to the same extent as do water molecules in pure water. While the transition state in the alkaline hydrolysis has a greater hydrogen bond acceptor capacity than esters in the ground state, they are stabilized by solvation relatively better in the protic media.

The decrease in the rate of hydrolysis of phenyl benzoate in 2.25 M Bu_4NBr solution and the enhanced Arrhenius parameters E and log A, relative to water solution, are in accord with the enhanced stabilization of the ground state with the solvation. The activation energy, E, for the alkaline hydrolysis of phenyl benzoate in water was found to be 45.8 kJ mol^{-1} and log $A = 7.67$.[29] The activation energy, E, and log A values increase by 20 kJ mol^{-1} and 3 units of log A, respectively. The behaviour of E and A are mainly the result of changes in the solvation of reactants and activated complex.[68] The orientation of solvent molecules round the solute involves an increase of order, *i.e.* decrease of entropy of the reacting system. If the activated complex is solvated, its entropy is lowered. Solvation of one or both of the reactants enhances the difference between the energy level of the activated complex and the energy level of reactants, consequently the energy of activation is increased. The solvation of the transition state has a converse effect. According to the theory of absolute reactions rates, the entropy of activation ΔS^*, is related to the parameter A by the formula (13).

$$A = \mathrm{e}(kT/h)\mathrm{e}^{\Delta S^*/R} \qquad (13)$$

Solvation of the reactants tends to increase A as well as E, while solvation of the activated complex has just the opposite effect.

The variation of the reaction rate with the polar effect of *meta*- and *para*-substituents in the alkaline hydrolysis of substituted phenyl benzoates is described by σ° constants (eqn. (5), Tables 3 and 4). In the case of *ortho*-substituents the complementary inductive σ_I and the steric $E_\mathrm{S}{}^\mathrm{B}$ scale were included. In 2.25 M Bu_4NBr solution the polar effect for *ortho*-substituents appeared similar to that for *para*-substituents. In 2.25 M Bu_4NBr solution the additional inductive term appeared not to be essential and the *ortho*-effect *i.e.* (log k_{ortho} − log k_{para}) is caused only by the steric effect of *ortho*-substituents.

In Table 6 are compared the experimental log k values for the alkaline hydrolysis in aqueous Bu_4NBr and those calculated according to the modified Fujita–Nishioka equation (Fig. 5). The difference log (k_obs − log k_calc) for *ortho*-substituents does not exceed that for *meta*- and *para*-substituents (average deviation 0.08 log k units) while the data at 40 °C were processed according to the modified Fujita–Nishioka eqn. (6). The relative contribution of the polar effect of *ortho*-substituents was found to be approximately 92% and the contribution of the steric term 10%, when the data were treated according to the Fujita–Nishioka eqn. (6) (Table 7). The relative contribution of the polar effect and steric effect appeared independent of temperature and had the same magnitude for 2.25 M Bu_4NBr solution and water. In water, the contribution of the additional inductive effect was found to be approximately 6% while the total polar contribution is approximately 92%, similar to pure water.

Table 7 Inductive and steric contributions calculated according to eqn. (6)

		Contributions		
Solvent	T/°C	% Inductive term $(\rho^\circ)_{m,p,ortho}\sigma^\circ$	% Inductive term $(\rho_\mathrm{I})_{ortho}\sigma_\mathrm{I}$	% Steric term $\delta_{ortho}E_\mathrm{s}{}^\mathrm{B}$
2.25 M Bu_4NBR	50	92.8	0	7.2
	40	93.3	0	6.7
	25	93.5	0	6.5
	15	89.8	0	10.2
H_2O	50	79.4	5.0	15.6[a]
		88.5	5.8	5.7
	40	78.2	1.9	19.9[a]
		85.6	1.9	12.5
	25	76.8	4.4	18.3[a]
		86.2	5.8	8.0
	15	81.7	3.1	15.2[a]
		89.0	3.6	7.4
		79.1	6.3	14.6[a]
		89.1	7.2	3.7

[a] Data set includes 2-$N(CH_3)_2$ phenyl benzoate.

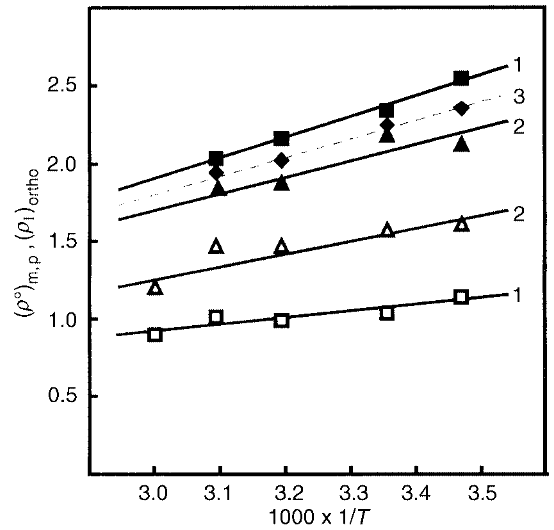


Fig. 6 Dependence of the $(\rho^\circ)_{m,p}$ (plot 1) and $(\rho_\mathrm{I})_{ortho}$ (plot 2) values on ($1/T$) for water and 2.25 M aqueous Bu_4NBr. Light characters denote water, shaded characters 2.25 M aqueous Bu_4NBr. Dependence for $(\rho^\circ)_{m,p,ortho}$ is shown by plot (3).

When going from water to 2.25 M aqueous Bu_4NBr the polar effect of *meta*- and *para*-substituents increased considerably. In 2.25 M aqueous Bu_4NBr we found $(\rho^\circ)_{m,p}$ to be in the range 2.0–2.5 (Table 3) depending on temperature. In water the $(\rho^\circ)_{m,p}$ value for the same reaction appeared in the range 0.8–1.2 (Table 4). The increase in the $(\rho^\circ)_{m,p}$ value is about 1.0 units, depending on temperature, when going from water to 2.25 M Bu_4NBr solution (Figs. 1, 6, Table 7). Previously we have found a similar change in the $(\rho^\circ)_{m,p}$ value when going from water to 2.25 M Bu_4NBr solution for the alkaline hydrolysis of substituted phenyl tosylates[27] and, in the case of the acidic dissociation of substituted benzoic acids and phenols, when going from water to 7.75 M Bu_4NBr solution.[27,69] Correia, Cuccovia, and Chaimovich[56] detected an increase in the ρ° value by nearly 0.8 units in the alkaline hydrolysis of substituted phenyl benzoates and *p*-nitrophenyl benzoates when changing from water to hexadecyltrimethylammonium bromide micelles. The increase in the polar substituent effect, when the medium is changed from water to 2.25 M aqueous Bu_4NBr, is comparable with the variation of ρ° when going from water to 80% aqueous DMSO. This is in accordance with the similar electrophilicity properties of both media considered, which are considerably lower than in water.

The results of the the data processing according to eqns. (5)–(8) for the alkaline hydrolysis of substituted phenyl benzoates in 2.25 M Bu_4NBr solution (Table 3) and in water (Table 4) demonstrate that the modified Fujita–Nishioka and Charton three parameter treatments give the excellent and identical results. The inductive, resonance and steric terms found using the two different approaches, appeared practically identical to each other. The total sensitivity to the inductive effect for *ortho*-substituents, $(c_\mathrm{I})_{ortho} + (\rho^\circ)_{m,p,ortho}$ found from eqn. (6), is equal to the $(\rho_\mathrm{I})_{ortho}$ detected according to eqn. (7). The magnitudes of sensitivity to resonance of *ortho*-substituents obtained from the data treatment according to eqn. (7) for *ortho*-substituents only, demonstrate that the resonance of *ortho*-substituents is practically equal to that for *para*-substituents (or 0.15 units smaller than the resonance for *para*-substituents) in the reaction series studied. Consequently, at our data treatment, the assumption of similarity of resonance effects from *ortho*- and *para*-positions made by Nishioka and Fujita, appears to be valid (except for the 2-$N(CH_3)_2$ substituent).

Earlier[29,36] we found, on the basis of the kinetic data for the

Table 8 The values $(\rho^{o})_{m,p}$ and $(\rho_I)_{ortho}$ for water and 2.25 M aqueous Bu_4NBr for the alkaline hydrolysis of substituted phenyl benzoates (this paper) and tosylates (from ref. 1)

			Benzoates			Tosylates		
T/°C	ρ	Eqn.	H_2O	2.25 M Bu_4NBr	$\Delta\rho$[a]	H_2O	2.25 M Bu_4NBr	$\Delta\rho$[a]
85	$(\rho^{o})_{m,p}$	8				1.54	2.58	1.04
	$(\rho_I)_{ortho}$	10				2.58	2.94	0.36
75	$(\rho^{o})_{m,p}$	8				1.67	2.50	0.83
	$(\rho^{o})_{m,p,o}$	9				1.75	2.71	0.96
	$(\rho_I)_{ortho}$	10				2.78	3.25	0.47
50	$(\rho^{o})_{m,p}$	8	1.01	2.03	1.02	1.84	3.01	1.17
	$(\rho^{o})_{m,p,o}$	9	0.99	1.97	0.98	1.88	3.11	1.23
	$(\rho_I)_{ortho}$	10	1.53	1.84	0.31	2.94	3.59	0.65
			1.40[b]	1.94[c]	0.54			
	$(\rho_I)_{ortho}$		1.47	1.94	0.47			
30	$(\rho^{o})_{m,p}$	8				1.98[d]	3.22	1.24
25	$(\rho^{o})_{m,p}$	8	1.08	2.34	1.26			
	$(\rho^{o})_{m,p,o}$	9	1.07	2.25	1.17			
	$(\rho_I)_{ortho}$	10	1.58	2.19	0.61			
15	$(\rho^{o})_{m,p}$	8	1.18	2.55	1.37			
	$(\rho_I)_{ortho}$	10	1.61	2.12	0.51			

[a] The differences are given by $\Delta(\rho^{o})_{m,p} = [(\rho^{o})_{m,p}]_{2.25\ \mathrm{M\ Bu_4NBr}} - [(\rho^{o})_{m,p}]_{H_2O}$ $\Delta(\rho_I)_{ortho} = [(\rho_I)_{ortho}]_{2.25\ \mathrm{M\ Bu_4NBr}} - [(\rho_I)_{ortho}]_{H_2O}$. [b] The value of $(\rho_I)_{ortho}$ equal to 1.53 is too high and deviates with dependence on $(1/T)$. A more reliable value for $(\rho_I)_{ortho}$ could be considered to be 1.40. [c] For the 2.25 M Bu_4NBr solution $(\rho^{o})_{m,p,ortho}$ used. [d] The value for $(\rho^{o})_{m,p,ortho}$ was calculated from the relationship between the values of $(\rho^{o})_{m,p,ortho}$ and the term $(1/T)$.

alkaline hydrolysis of benzoates and tosylates, that the induction effect in the case of *ortho*-substituents exceeds the effect for *para*- and *meta*-substituents in water solution. The additional inductive effect for *ortho*-substituents was found to be dependent on temperature and on medium parameters.[29,36,43] When going from water to 2.25 M Bu_4NBr solution, for the alkaline hydrolysis of substituted phenyl benzoates, the additional inductive effect of *ortho*-substituents decreases by about 0.4–0.6 units of $(c_I)_{ortho}$ in comparison with water solution, depending on temperature. It is seen in Fig. 1 and in Table 3 that the additional inductive effect from the *ortho* position in 2.25 M Bu_4NBr solution is very little or effectively nil and the points for *ortho*-substituted derivatives in the relationship between the ($\log k - 1.2\, E_S{}^B{}_{(ortho)}$) and σ^{o} fall onto the same straight line with *para*- and *meta*-substituted derivatives. In the case of water, the points for *ortho*-substituted derivatives lie above the straight line for *para*- and *meta*-substituted derivatives because of the additional inductive effect from the *ortho*-position. The point for the 2-CH_3-derivative fall onto the same line with *meta*- and *para*-substituents, while for the CH_3 substituent the σ_I constant was nearly zero (−0.05).

In the alkaline hydrolysis of substituted phenyl benzoates in water solution, the influence of the inductive effect from the *ortho*-position was found to be 1.5-fold stronger than that from the *para*-position when the data at a single temperature were considered. Similarly, in water solution, the *ortho*-inductive effect was found to be 1.5-fold stronger in the alkaline hydrolysis of substituted phenyl tosylates[36] as well. When passing from water to 2.25 M aqueous Bu_4NBr, the influence of the polar effect of *para*-substituents was found to increase about two times more (1.0 units of ρ) than that for the inductive effect of *ortho*-substituents (Fig. 6, Table 8). For that reason, the inductive effect of *para*-substituents reaches the level for the *ortho*-inductive effect and the additional *ortho*-inductive effect disappears or even became negative in the alkaline hydrolysis of substituted phenyl benzoates in 2.25 M Bu_4NBr solution. Because of the difference in variation (two-fold) of the *ortho*-inductive and *para*-inductive terms with solvent, in 2.25 M aqueous Bu_4NBr the *para*-inductive effect not only reaches the level of the *ortho*-inductive effect, and even surpasses the value of the *ortho*-inductive term by 0.15 units. It could be considered that the *ortho*-effect (*i.e.* $\log k_{ortho} - \log k_{para}$) in the alkaline hydrolysis of substituted phenyl benzoates 2.25 M aqueous Bu_4NBr, which is more negative than in water, is caused mainly by steric factors.

We found that steric effects of *ortho*-substituents reduce the rate of the alkaline hydrolysis of substituted benzoates while the substituent constants we used are negative, and the susceptibility to the steric effects were $\delta_{ortho} \approx 1.2$ for 2.25 M Bu_4NBr solution (Table 3). Nearly the same value for δ_{ortho} was earlier found for water[29] (Table 4) and 80% aqueous DMSO.[34] Steric effects of the *ortho*-position in 2.25 M aqueous Bu_4NBr appeared practically independent of temperature, as was found earlier for water and 80% aqueous DMSO.

Dependence on temperature

The dependence of the activation energy, E, on substituent effects in the alkaline hydrolysis of substituted phenyl benzoates, in the case of *meta*- and *para*- as well as *ortho*-substituents, is completely caused by the polar effect of substituents. In basic hydrolysis of esters, electron-withdrawing substituents decrease activation energy, E, and electron repelling substituents increase E. While the steric factor of *ortho*-substituents appeared independent of temperature, it influences only the $\log A$ value, consequently only the entropy of reaction. Similarly Chapman and Shorter[70] have found in the alkaline hydrolysis of methyl benzoates the $\log A$ values for *ortho*-substituted derivatives lower than those for *meta*- and *para*-derivatives. They ascribed this phenomenon to the steric "bulky" effect of *ortho* substituents. Chapman and Shorter concluded that *ortho*-substituents near the reaction centre will reduce the number of energy levels available to the transition state relative to those in the initial state and will make ΔS^* more negative.

The activation energies of the alkaline hydrolysis of substituted benzoates in water for *ortho*-substituted derivatives were found to be lower than those for *para*-substituted derivatives. The same situation was observed in the case of the alkaline hydrolysis of tosylates (Fig. 3). Activation energies increase for both reaction series considered, while the solvent composition changes from water to 2.25 M Bu_4NBr solution. The sensitivity

Table 9 The values of const$_1$ and $\Delta = (\text{const}_1)_{Bu_4NBr} - (\text{const}_1)_{H_2O}$. Values for const$_1$ are determined from eqn. (14) and (15)

H_2O	2.25 M Bu_4NBr	Δ	Notes
For *meta*- and *para*-substituents, $(\rho^o)_{m,p}$			
0.33	1.34	1.01	[a,b]
0.60	1.33	0.73	[b,c]
For *ortho*-substituents, $(\rho_I)_{ortho}$			
0.5–0.7	0.89	~0.3	[a,b]
1.6	1.80	0.4	[b,c]

[a] Alkaline hydrolysis of substituted phenyl benzoates. [b] The values of const$_1$ in the alkaline hydrolysis of substituted phenyl benzoates and tosylates for water and 2.25 M Bu_4NBr solution were determined from the multilinear relationships, see refs. 29 and 36. [c] Alkaline hydrolysis of substituted phenyl tosylates.

of activation energies to the polar substituent effect in the case of *meta*- and *para*-substituents increases considerably, while going from water to 2.25 M Bu_4NBr solution. A similar change in the activation energies for *ortho*-substituted derivatives is notably smaller than for *para*-substituted derivatives. Variations in the activation energies, depending on the substituent effect and solvent composition, are similar for the alkaline hydrolysis of substituted phenyl benzoates and substituted phenyl tosylates (Fig. 3).

In water solution, the log *A* values for *meta*- and *para*-substituted derivatives were found to be nearly constant, being independent of the substituent effect (isoentropic reaction series) both in the case of the alkaline hydrolysis of benzoates[29] and tosylates.[36]

It is seen in Fig. 4, that the variation ranges of the log *A* values dependent on solvent are similar for the two reaction series considered, both for *meta* and *para* substituents as well as for *ortho* substituents. Only in the case of *ortho*-substituted phenyl benzoates the influence of the steric factor in decreasing the log *A* values could be observed.

The alkaline hydrolysis of substituted phenyl benzoates in 2.25 M Bu_4NBr solution in the case of *meta*- and *para*-substituents belong to isokinetic reaction series, as was found earlier for the corresponding reaction series of tosylates in 2.25 M Bu_4NBr solution.[36]

The dependence of the $(\rho^o)_{m,p}$ and $(\rho_I)_{ortho}$ values on the $(1/T)$ term for water and 2.25 M Bu_4NBr solution is shown in Fig. 6. In Table 9 are listed the values of const$_1$ characterising the dependence of the *para*-polar substituent effect and the *ortho*-inductive effect on temperature, and the Δ values characterising the variation of const$_1$ when going from water to 2.25 M Bu_4NBr solution.

The values of const$_1$ and Δ in Table 9 were determined from the following relationship [eqns. (14), (15), and (16)].

$$(\rho^o)_{m,p} = \text{const} + \text{const}_1(1/T) \qquad (14)$$

$$(\rho_I)_{ortho} = \text{const} + \text{const}_1(1/T) \qquad (15)$$

$$\Delta = (\text{const}_1)_{Bu_4NBr} - (\text{const}_1)_{H_2O} \qquad (16)$$

Our data treatment shows that in water the influence of the inductive effect of *ortho*-substitutents appears about 1.5 times stronger than the polar effect of *para*- and *meta*-substituents when the data at a single temperature are considered. In water, we found the dependence of the *ortho*-inductive term on temperature nearly twice as large as the same dependence of the polar influence of *meta*- and *para*-substituents (see const$_1$ values in Table 9). In 2.25 M Bu_4NBr solution the dependence of the polar effect of *para*- and *meta*-substituents on temperature surpasses a little the analogous dependence for the *ortho*-inductive effect. The change in the const$_1$ value (Δ values in Table 9) for the *ortho*-inductive effect appeared twice as small as the similar change for the polar effect of *para*- and *meta*-substituents. Similar change in the const$_1$ value for the inductive effect of *ortho*-substituents and polar effect of *meta*- and *para*-substituents, when going from water to 2.25 M Bu_4NBr aqueous solution, was earlier found in the alkaline hydrolysis of substituted phenyl tosylates. Fig. 7 illustrates the change in the const$_1$ value when going from water to 2.25 M Bu_4NBr solution. In Fig. 7 is shown the dependence of the $\Delta E = (E_{2.25\ M\ Bu_4NBr} - E_{water})$ values on the substituent constants, σ°, for the alkaline hydrolysis of substituted phenyl benzoates and tosylates (it should be mentioned that: $(E^X - E^H)/\sigma^o = 2.3R\text{const}_1$). For comparison, the dependence of $\Delta E = (E_{80\%DMSO} - E_{water})$ on constants σ° for the alkaline hydrolysis of substituted phenyl benzoates and tosylates is shown in Fig. 7 as well. In the relationship between the ΔE and the substituent constants σ°, the points for benzoate reaction series and tosylate reaction series fall onto two parallel straight lines, both in the case of 2.25 M Bu_4NBr solution and in an 80% DMSO solution. This indicates an equal change in the *E* values for both the alkaline hydrolysis of substituted phenyl benzoates and tosylates, when going from water to 2.25 M Bu_4NBr and 80% DMSO. The change in activation energy, *E*, for *ortho*-substituted derivatives is approximately half that for *para*-substituted derivatives when passing from water to another media. In Fig. 7 (where for *ortho* substituents $(\sigma^o)_{ortho} = 1/2\ \sigma_I + \sigma_R^o$) the points for *ortho* derivatives fell nearly on the same straight line as the *meta*- and *para*-derivatives.

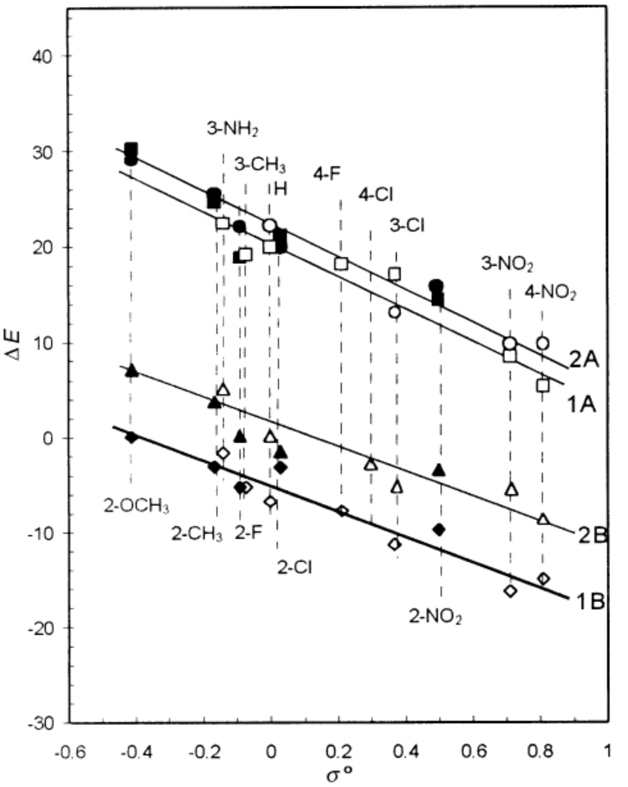


Fig. 7 Dependence of $\Delta E\ (\text{kJ mol}^{-1}) = (E)_{Medium} - (E)_{water}$ on substituent constants σ° in the case of the alkaline hydrolysis of substituted phenyl benzoates (plot 1) and substituted phenyl tosylates (plot 2). $\Delta E = E_{2.25\ M\ Bu_4NBr} - E_{water}$ (plot A); $\Delta E = E_{80\%\ DMSO} - E_{water}$ (plot B). For *ortho* substituents $(\sigma^o)_{ortho} = (1/2\ \sigma_I + \sigma_R^o)$ were used. The values of activation energies *E* from refs. 29, 34 and 36 were used as well.

The dependence of the *ortho*-resonance effect on both temperature and solvent variation appeared equal to, or a little less than, that for *para*-substitents.

In the case of the alkaline hydrolysis of substituted phenyl tosylates in water, the *ortho*-effect was found to be caused only by the higher induction effect from the *ortho*-position (the additional induction effect is nearly 1.0 units of σ_I). In the case of the alkaline hydrolysis of substituted phenyl tosylates the *ortho* effect diminishes considerably (by about 0.5 units of σ_I) but did not disappear when going from water to 2.25 M Bu_4NBr solution. Due to an equal variation in substituent effects when passing from water to another solvent, in the case of the two reaction series considered, the same difference in polar substituent effects (including additional *ortho*-induction effect) having been found for water, will appear in other media.

In two reaction series, alkaline hydrolysis of substituted phenyl benzoates and tosylates, the induction factor from *ortho*-position, 1.5-fold higher than from *para*-position in water, varies nearly two times less than from *para*-position, while temperature or solvent composition is changing. When the inductive effect of *para*-substituents reaches the level of *ortho*-substituents, the *ortho* effect caused by the inductive term will disappear.

Acknowledgements

Financial support in part from grant (ETF3978) by Estonian Science Foundation is gratefully acknowledged.

References

1 V. Nummert, *Org. React.*, 1989, **26**, 98.
2 T. Fujita and T. Nishioka, *Prog. Phys. Org. Chem.*, 1976, **12**, 49.
3 M. Charton, *Prog. Phys. Org. Chem.*, 1971, **8**, 235.
4 M. Charton, *J. Am. Chem. Soc.*, 1969, **91**, 624.
5 L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill Book Co., New York, N.Y., 1940, p. 206.
6 R. W. Taft, Jr., *Steric Effects in Organic Chemistry*, ed. M. S. Newman, Wiley, New York, 1956, p. 556.
7 J. Shorter, *Advances in Linear Free Energy Relationships*, eds. N. B. Chapman and J. Shorter, Plenum Press, London, 1972, p. 71.
8 N. B. Chapman, J. Shorter and J. H. P. Utley, *J. Chem. Soc.* (*B*), 1963, 1291.
9 N. B. Chapman, M. G. Rodgers and J. Shorter, *J. Chem. Soc.* (*B*), 1968, 157.
10 A. C. Farthing and B. Nam, *Steric Effects in Conjugate Systems*, ed. G. W. Gray, Butterworth, London, 1958, p. 131.
11 K. Bowden and G. E. Manser, *Can. J. Chem.*, 1968, **46**, 2941.
12 M. Charton, *J. Am. Chem. Soc.*, 1974, **97**, 3691.
13 M. Charton, *J. Am. Chem. Soc.*, 1977, **42**, 3531.
14 M. Charton, *J. Org. Chem.*, 1968, **33**, 3872.
15 M. Charton, *J. Am. Chem. Soc.*, 1969, **91**, 619.
16 M. Charton, *J. Am. Chem. Soc.*, 1969, **91,** 6649.
17 M. Charton, *J. Am. Chem. Soc.*, 1975, **97**, 3691.
18 M. Hojo, M. Utaka and Z. Yoshida, *Tetrahedron*, 1971, **27**, 5433.
19 S. C. Dash and G. B. Behera, *J. Indian Chem. Soc.*, 1980, **LVII**, 542.
20 T. Fujita, *Prog. Phys. Org. Chem.*, 1983, **14**, 75.
21 P. Segura, *J. Am. Chem. Soc.*, 1985, **50**, 1045.
22 C. N. Robinson, J. L. Horton, D. O. Foshee, J. W. Jones, S. H. Hanissian and C. D. Slater, *J. Org. Chem.*, 1986, **51**, 3535.
23 E. Kutter and C. Hansch, *J. Med. Chem.*, 1969, **12**, 6.
24 C. G. Swain and E. C. Lupton, *J. Am. Chem. Soc.*, 1968, **90**, 4328.
25 L. A. Janovskaja and S. S. Juffit, *Organic Synthesis In Two-Phase Systems*, Moscow, Khimia, 1982 (in Russian).
26 I. A. Koppel, A. Prodel, J. B. Koppel and V. O. Pihl, *Org. React.*, 1990, **27**, 74.
27 J. Steigman and D. Sussman, *J. Am. Chem. Soc.*, 1967, **89**, 6406.
28 V. Nummert and A. Bogdanov, *Org. React.*, 1989, **26**, 231.
29 V. Nummert, M. Piirsalu and V. Palm, *Org. React.*, 1996, **30**, 85.
30 V. Nummert and M. Piirsalu, *Org. React.*, 1975, **11**, 899.
31 V. Nummert and M. Piirsalu, *Org. React.*, 1975, **11**, 921.
32 V. Nummert and M. Piirsalu, *Org. React.*, 1995, **29**, 109.
33 V. Nummert and M. Piirsalu, *Org. React.*, 1996**, 30**, 95.
34 V. Nummert and M. Piirsalu, *Org. React.*, 1997, **31**, 101.
35 V. Nummert, M. Eek and M. Piirsalu, *Org. React.*, 1981, **18**, 363.
36 V. Nummert and V. Palm, *Org. React.*, 1993, **28**, 63.
37 V. Nummert and M. Eek, *Org. React.*, 1984, **21**, 304.
38 V. Nummert, M. Eek and V. Palm, *Org. React.*, 1985, **22**, 263.
39 V. Nummert, M. Piirsalu and V. Palm, *Org. React.*, 1990, **27**, 99.
40 V. Nummert and M. Piirsalu, *Org. React.*, 1990, **27**, 217.
41 V. Nummert, K. Ojassalu and A. Bogdanov, *Org. React.*, 1989, **26**, 92.
42 R. W. Taft, Jr and I. C Lewis, *J. Am. Chem. Soc.*, 1958, **80**, 2436.
43 V. Nummert, M. Piirsalu and V. Palm, *Org. React.*, 1993, **28**, 82.
44 V. Nummert, *Org. React.*, 1981, **18**, 274.
45 V. Nummert and V. Palm, *Org. React.*, 1980, **17**, 292.
46 V. Nummert, R. Pärismaa and M. Piirsalu, *Org. React.*, 1986, **23**, 83.
47 T. O. Püssa, V. M. Nummert and V. A. Palm, *Reakts. Sposobn. Org. Soedin.*, 1972, **9**, 697.
48 A. Uri, A. Tuulmets and V. Palm, *Org. React.*, 1983, **20**, 122.
49 V. Palm, *J. Chem. Inf. Comput. Sci.*, 1990, **30**, 409.
50 *Tables of Rate and Equilibrium Constants of Heterolytic Organic Reactions*, **5(II)**, ed. V. Palm, Publishing House of VINITI, Moscow, 1979.
51 R. W. Taft, Jr, S. Ehrenson, I. C. Lewis and R. E. Glick, *J. Am. Chem. Soc.*, 1959, **81**, 5352.
52 M. L. Bender, *Mechanisms of Catalysis of Nucleophilic Reactions of Carboxylic Acid Derivatives*, *Chemical Reviews*, 1960, vol. 60 (in Russian 1964).
53 J. F. Kirsch, W. Clewell and A. Simon, *J. Org. Chem.*, 1968, **33**, 127.
54 Z. S. Chaw, A. Fischer and D. A. R. Happer, *J. Chem. Soc.* (*B*), 1971, 1818.
55 T. Nishioka, T. Fujita, K. Kitamura and M. Nakajima, *J. Org. Chem.*, 1975, **40**, 2520.
56 V. R. Correia, I. M. Cuccovia and H. Chaimovich, *J. Phys. Org. Chem.*, 1991, **4**, 13.
57 I. A. Koppel and J. B. Koppel, *Org. React.*, 1984, **21**, 98.
58 *Water. A Comprehensive Treatise*, vol. 3, ed. F. Franks, Plenum Press, New York, London, 1973.
59 P. S. Jastremitski, G. V. Kokovina, A. K. Ljastsenko, O. J. Somoilov and J. A. Mirgorod, *Zh. Fiz. Khim.*, 1979, **20,** 612 (in Russian).
60 I. A. Koppel and J. B. Koppel, *Org. React.*, 1983, **20**, 513.
61 R. Bates, L. Johnson and R. A. Robinson, *Chem. Anal.* (*Warsaw*), 1972, **17**, 479.
62 E. S. Amis, *Solvent Effects on Reaction Rates and Mechanisms*, Academic Press, New York, 1966.
63 E. Tommila and L. Palenius, *Acta Chem. Scand.*, 1963, **17**, 1980.
64 E. Tommila, *Suom. Kemistil.*, B 1964, **37**, 117.
65 M. Hojo, M. Utaka and Z. Yoshida, *Tetrahedron Lett.*, 1966, **1**, 25.
66 J. Steigman, D. Sussman, *J. Am. Chem. Soc.*, 1967, **89**, 6400.
67 J. E. Dersnoyers, G. E. Pelletier and C. Jolicoeur, *Can. J. Chem.*, 1965, **43**, 3233.
68 E. Tommila and A. Hella, *Ann. Acad. Sci. Fenn., Chem.*, 1954, **53**, 1954.
69 V. Nummert, *Org. React.*, 1978, **15**, 412.
70 N. B. Chapman, J. Shorter and J. H. P. Utley, *J. Chem. Soc.*, 1963, 1291.

Paper a904741g