KINETIC STUDY OF HYDROLYSIS OF BENZOATES. PART XXVI. VARIATION OF THE SUBSTITUENT EFFECT WITH SOLVENT IN ALKALINE HYDROLYSIS OF SUBSTITUTED ALKYL BENZOATES

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The second-order rate constants k_2 ($dm^3 mol^{-1} s^{-1}$) for the alkaline hydrolysis of substituted alkyl benzoates $C_6H_5CO_2R$ have been measured spectrophotometrically in aqueous 0.5 M Bu_4NBr at 50 and 25 °C (R = CH_3, CH_2Cl, CH_2CN, $CH_2C{\equiv}CH$, $CH_2C_6H_5$, CH_2CH_2Cl, $CH_2CH_2OCH_3$, CH_2CH_3) and in aqueous 5.3 M $NaClO_4$ at 25 °C (R = CH_3, CH_2Cl, CH_2CN, $CH_2C{\equiv}CH$). The dependence of the alkyl substituent effects on different solvent parameters was studied using the following equations:

$$\Delta \log k = c_0 + c_1\sigma_I + c_2E_s^B + c_3\Delta E + c_4\Delta Y + c_5\Delta P + c_6\Delta E\sigma_I + c_7\Delta Y\sigma_I + c_8\Delta P\sigma_I$$
$$\Delta \log k = c_0 + c_1\sigma^* + c_2E_s^B + c_3\Delta E + c_4\Delta Y + c_5\Delta P + c_6\Delta E\sigma^* + c_7\Delta Y\sigma^* + c_8\Delta P\sigma^* .$$

$\Delta \log k = \log k^R - \log k^{CH_3}$. σ_I and σ^* are the Taft inductive and polar substituent constants. E, Y and P are the solvent electrophilicity, polarity and polarizability parameters, respectively. In the data treatment $\Delta E = E_S - E_{H_2O}$, $\Delta Y = Y_S - Y_{H_2O}$, $\Delta P = P_S - P_{H_2O}$ were used. The solvent electrophilicity, E, was found to be the main factor responsible for changes in alkyl substituent effects with medium. When σ_I constants were used, variation of the polar term of alkyl substituents with the solvent electrophilicity E was found to be similar to that observed earlier for *meta* and *para* substituents, but twice less when σ^* constants were used. The steric term for alkyl substituents was approximately independent of the solvent parameters.

Keywords: Esters; Alkyl benzoates; Alkaline hydrolysis; Substituent effects; Solvent effects; Kinetics.

Recently[1,2] the importance of different solvent parameters for substituent effects in alkaline hydrolysis of *ortho*-, *meta*- and *para*-substituted phenyl benzoates and tosylates including various media (pure water, aqueous 0.5 M Bu_4NBr, 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 and 80% EtOH) have been analyzed at 50 °C using Eq. (*1*):

$$\Delta \log k_{m,p,ortho} = a_0 + a_{1(m,p)}\sigma^\circ + a_{2(ortho)}\sigma_I + a_{3(ortho)}\sigma^\circ_R + a_{4(ortho)}E_s^B +$$
$$a_5\Delta E + a_6\Delta Y + a_7\Delta P + a_{8(m,p)}\Delta E\sigma^\circ + a_{9(m,p)}\Delta Y\sigma^\circ + a_{10(m,p)}\Delta P\sigma^\circ +$$
$$+ a_{11(ortho)}\Delta E\sigma_I + a_{12(ortho)}\Delta Y\sigma_I + a_{13(ortho)}\Delta P\sigma_I + a_{14(ortho)}\Delta E\sigma^\circ_R +$$
$$+ a_{15(ortho)}\sigma^\circ_R + a_{16(ortho)}\Delta P\sigma^\circ_R . \tag{1}$$

In Eq. (*1*), $\Delta \log k = \log k^X - \log k^H$. $\sigma°$, σ_I and $\sigma°_R$ are the Taft polar, inductive and resonance substituent constants; $\Delta E = E_S - E_{H_2O}$, $\Delta Y = Y_S - Y_{H_2O}$, $\Delta P = P_S - P_{H_2O}$. *E*, *Y* and *P* are the solvent electrophilicity, polarity and polarizability parameters of the Koppel–Palm equation[3,4]. In Eq. (*1*) reaction constants a_1, a_2, a_3 and a_4 are the characteristics of substituent effects in the standard medium (pure water). In alkaline hydrolysis of substituted phenyl benzoates[1] and tosylates[2] the solvent electrophilicity was found to be the main factor responsible for the changes in the *ortho*, *para* and *meta* polar substituent effects with medium. In the alkaline hydrolysis of substituted benzoates and tosylates the variation of the *ortho*-inductive term with solvent electrophilicity, E_S, was found to be approximately three times smaller than that for *meta* and *para* substituents (for benzoates in Eq. (*1*) $a_{8(m,p)} = -0.0645$). The steric term of *ortho* substitutents $a_{4(ortho)}E_s^B$ in alkaline hydrolysis of substituted phenyl benzoates was approximately independent of solvent parameters. The solvent terms for pure water, $a_5\Delta E$, $a_6\Delta Y$ and $a_7\Delta P$ were excluded as indistinguishable from zero.

The alkyl substituent effects in alkaline hydrolysis of alkyl-substituted benzoates, $C_6H_5CO_2R$, were studied previously by us[5–8] in water, aqueous 2.25 M Bu$_4$NBr, 80% (v/v) DMSO at 15, 25, 35 and 50 °C, and in 5.3 M NaClO$_4$ and 4.8 M NaCl at 50 °C. One purpose of the present work was to extend our study of alkyl substituent effects to aqueous 0.5 M Bu$_4$NBr at 25 and 50 °C and to 5.3 M NaClO$_4$ at 25 °C. The electrophilic solvating power of aqueous 0.5 M Bu$_4$NBr is reduced compared with pure water and still it is higher than that of aqueous 2.25 M Bu$_4$NBr and 80% (v/v) DMSO. The electrophilic solvating power of aqueous 5.3 M NaClO$_4$ is higher than that of water.

In the earlier papers[5–7], the variation of the reaction rate with substituent in alkaline hydrolysis of alkyl benzoates, $C_6H_5CO_2R$, in pure water, aqueous 2.25 M Bu$_4$NBr and 80% (v/v) DMSO was precisely described by a linear combination of polar and steric terms. Dual parameter analysis of the log *k* values with σ^* (or σ_I) and E_s^B constants gave an excellent correlation with correlation coefficient $R = 0.997$. On going from pure water to aqueous 2.25 M Bu$_4$NBr and 80% (v/v) DMSO, the change in the ρ_I value in alkaline hydrolysis of alkyl benzoates, $C_6H_5CO_2R$, ranged from 1.0 to 1.3. A similar change in the $\rho°_{m,p}$ value on going from water to aqueous 2.25 M Bu$_4$NBr and 80% (v/v) DMSO has been found for alkaline hydrolysis of *meta*- and *para*-substituted phenyl benzoates and phenyl tosylates.

The susceptibility of substituents to the steric effect, δ, in alkaline hydrolysis of alkyl benzoates, $C_6H_5CO_2R$, was found to be in the range 0.9–1.3, approximately independent of the solvent and temperature[5–7].

It was interesting to check up the significance of different solvent parameters for the alkyl substituent effects in the alkaline hydrolysis of substituted alkyl benzoates, $C_6H_5CO_2R$, using a multilinear relationship[9,10] similar to Eq. (*1*):

$$\Delta \log k = \log k^R - \log k^{CH_3} = c_1\sigma^* + c_2E_s^B + c_3\Delta E\sigma^* + c_4\Delta Y\sigma^* + c_5\Delta P\sigma^* \quad (2)$$

$$\Delta \log k = \log k^R - \log k^{CH_3} = c_1\sigma_I + c_2E_s^B + c_3\Delta E\sigma_I + c_4\Delta Y\sigma_I + c_5\Delta P\sigma_I \quad (3)$$

including the kinetic data determined in this work for aqueous 0.5 M Bu_4NBr and those reported earlier[5–8,11,12] (pure water, aqueous 2.25 M Bu_4NBr, 80% (v/v) DMSO, 5.3 M $NaClO_4$, 4.8 M NaCl, and 50% CH_3CN).

In Eqs (*2*) and (*3*) reaction constants c_3, c_4 and c_5 are the same that characterize the dependence of ρ^* and ρ_I values on the ΔE, ΔY and ΔP parameters.

EXPERIMENTAL

The preparation and characteristics of substituted phenyl benzoates, $C_6H_5CO_2R$, and the technique of kinetic measurements have been described previously[5–8]. As a reagent in aqueous 0.5 M Bu_4NBr 0.0184 M and 0.0374 M tetrabutylammonium hydroxide and in aqueous 5.3 M $NaClO_4$ 0.0386 M NaOH were used. The purification of Bu_4NOH, Bu_4NBr and NaOH was described earlier[5]. The kinetics was measured spectrophotometrically as described previously[5–7]. The pseudo-first-order rate constants k_1 (s^{-1}) were determined using the least-squares computer program. The second-order rate constants k ($dm^3 mol^{-1} s^{-1}$) were calculated by dividing the pseudo-first-order rate constants k_1 (s^{-1}) by alkali concentration. The kinetic measurements were repeated 3–5 times for each derivative and the average values of the second-order rate constants k ($dm^3 mol^{-1} s^{-1}$) were calculated. The k values for substituted alkyl benzoates $C_6H_5CO_2R$ in aqueous 0.5 M Bu_4NBr and 5.3 M $NaClO_4$, the number of measurements and the wavelength, λ, used in spectrophotometric kinetic measurements are given in Table I.

DATA PROCESSING

The log k_2 values for the alkaline hydrolysis of substituted alkyl benzoates in aqueous 0.5 M Bu_4NBr at 50 and 25 °C (Table I) were treated using the following equations:

$$\log k_R = \log k_o + \rho^*\sigma^* + \delta E_s^B \quad (4)$$

$$\log k_{CH_2X} = \log k_o + \rho_I\sigma_I^X + \delta E_s^B . \quad (5)$$

TABLE I
The second-order rate constants k for alkaline hydrolysis of substituted alkyl benzoates, $C_6H_5CO_2R$, in aqueous 0.5 M Bu_4NBr and 5.3 M $NaClO_4$ and the substituent constants used in correlations[a]

R = CH₂X	λ[b] nm	k[c] dm³ mol⁻¹ s⁻¹ 0.5 M Bu₄NBr 50 °C	n[d]	k[c] dm³ mol⁻¹ s⁻¹ 0.5 M Bu₄NBr 25 °C	n[d]	k[c] dm³ mol⁻¹ s⁻¹ 5.3 M NaClO₄ 25 °C	n[d]	σ* for R[e]	σ_I for X[f]	−E_s^B for R[g]
CH_3	240	0.158 ± 0.002	3	0.0339 ± 0.0002	5	0.0140 ± 0.0007	4		0	0
CH_2CN	240	5.36 ± 0.25	4	1.58 ± 0.11	3	0.399 ± 0.012	5	1.30	0.58	0.55
CH_2Cl	240	4.79 ± 0.24	5	1.27 ± 0.09	3	0.463 ± 0.007	4	1.05	0.47	0.17
$CH_2C{\equiv}CH$	240	0.554 ± 0.003	5	0.134 ± 0.019	5	0.0531 ± 0.0014	4	0.61	0.27	0.41
$(CH_2)_2Cl$	240	0.276 ± 0.001	4	0.0549 ± 0.0004	4			0.385	0.17	0.23
$CH_2C_6H_5$	240	0.110 ± 0.003	4	0.0233 ± 0.0008	4			0.215	0.11	0.24
$(CH_2)_2COCH_3$	240	0.143 ± 0.002	3	0.0325 ± 0.0017	3			0.187	0.07	0.20
CH_2CH_3	238	0.064 ± 0.0010	4	0.0130 ± 0.0004	4			−0.10	−0.05	0.04[h]

[a] In 0.5 M aqueous Bu_4NBr 0.0187 M or 0.0374 M Bu_4NOH, in 5.3 M $NaClO_4$ 0.0386 M NaOH were used. [b] The wavelength used in kinetic measurements. [c] The arithmetic mean value of the second-order rate constants with value of standard deviation of arithmetic mean. [d] The number of remaining k values after exclusion of significantly deviating rate constants in the calculation of the arithmetic mean values. [e] Refs[13,14]. [f] Refs[13,14]. [g] Refs[5,11,16]. [h] Calculated from $E_s^B = E_s/1.52$[5].

As polar substituent parameters, both the Taft σ^* [13,14] and the inductive σ_I [14,15] constants were used. The σ_I scale was chosen to compare the influence of the induction effect of aliphatic substituents $-CH_2X$ and that of *meta*- and *para*-substituted phenyls $-C_6H_4X$. The steric constants for the variable substituent in the alcohol component of ester, E_s^B, were calculated as follows: $E_s^B = (\log k_{H^+}^R - \log k_{H^+}^{CH_3})$, where $k_{H^+}^R$ and $k_{H^+}^{CH_3}$ are the rate constants for acid hydrolysis of R-substituted and CH_3-substituted alkyl benzoate, $C_6H_5CO_2R$, or acetate, CH_3CO_2R, in water[11,16].

In order to check whether Eqs (*2*) and (*3*) could be applied to describe the dependence of the alkyl substituent effects on different solvent parameters, the $\Delta \log k = \log k^R - \log k^{CH_3}$ values for the alkaline hydrolysis of substituted alkyl benzoates at 50 and 25 °C in various media were correlated with Eqs (*6*) and (*7*):

$$\Delta \log k = c_0 + c_1\sigma^* + c_2E_s^B + c_3\Delta E + c_4\Delta Y + c_5\Delta P + c_6\Delta E\sigma^* + c_7\Delta Y\sigma^* + c_8\Delta P\sigma^* \quad (6)$$

$$\Delta \log k = c_0 + c_1\sigma_I + c_2E_s^B + c_3\Delta E + c_4\Delta Y + c_5\Delta P + c_6\Delta E\sigma_I + c_7\Delta Y\sigma_I + c_8\Delta P\sigma_I . \quad (7)$$

The steric term of *ortho* substituents in alkaline hydrolysis of substituted alkyl benzoates was considered to be independent of solvent[1,5] and the corresponding cross-terms with the solvent parameters were omitted. In Eqs (*6*) and (*7*) 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 R = CH_3. The values of electrophilicity, E, of Koppel and Palm[10,17–19], polarity, Y, calculated as the function of dielectric permittivity $(\varepsilon - 1)/(\varepsilon + 2)$ and the polarizability, P, as the function of refractive index $(n^2 - 1)/(n^2 + 2)$ were used. The data processing was carried out using a multiple-parameter linear least-squares (LLSQ) procedure[20]. Significantly deviating points were excluded using a Student criterion. The exclusion of the significantly deviating points was performed on different confidence levels of the *t*-test. Results of the data treatment in the present work are given mainly at the confidence level 0.99.

The results of the data treatment with Eqs (*4*)–(*7*) are presented in Tables II and III. The values of σ^*, σ_I, and E_s^B used for alkyl substituents are listed in Table I. The solvent characteristics for solvents used (water, aqueous 0.5 M

TABLE II
Correlation of the log k values for alkaline hydrolysis of substituted alkyl benzoates, $C_6H_5CO_2R$, in various media at 25 and 50 °C with Eqs (4) and (5)

Medium	n	Eq. (4)			Eq. (5)		
		$\log k_0$	ρ^*	δ	$\log k_0$	ρ_I	δ
Water[a]	8[b,c]	-0.640 ± 0.075	1.52 ± 0.09	1.04 ± 0.20	-0.634 ± 0.085	3.38 ± 0.19	1.05 ± 0.23
	8[d,c]	-1.292 ± 0.064	1.64 ± 0.07	0.94 ± 0.18	-1.272 ± 0.075	3.64 ± 0.15	0.98 ± 0.19
0.5 M Bu$_4$NBr	8[b,c]	-0.934 ± 0.116	1.76 ± 0.11	1.16 ± 0.31	-0.927 ± 0.117	3.93 ± 0.26	1.17 ± 0.32
	8[d,c]	-1.621 ± 0.134	1.87 ± 0.13	1.16 ± 0.36	-1.613 ± 0.136	4.17 ± 0.30	1.17 ± 0.37
2.25 M Bu$_4$NBr[a]	7[b,e]	-1.217 ± 0.074	1.85 ± 0.07	1.09 ± 0.19	-1.216 ± 0.076	4.15 ± 0.18	1.09 ± 0.22
	7[d,e]	-1.922 ± 0.092	2.07 ± 0.08	1.24 ± 0.23	-1.921 ± 0.090	4.64 ± 0.19	1.24 ± 0.24
80% DMSO[a]	6[b,f]	0.067 ± 0.096	1.94 ± 0.11	0.97 ± 0.31	0.072 ± 0.085	4.37 ± 0.22	0.99 ± 0.27
	6[d,f]	-0.538 ± 0.092	2.21 ± 0.11	1.29 ± 0.32	-0.532 ± 0.082	4.94 ± 0.21	1.32 ± 0.18
5.3 M NaClO$_4$[g]	5[b,h]	-1.047 ± 0.079	1.33 ± 0.09	0.98 ± 0.41	-1.041 ± 0.071	2.95 ± 0.18	0.94 ± 0.37
	4[d,i]	-1.828 ± 0.115	1.57 ± 0.10	1.05 ± 0.22	-1.831 ± 0.103	3.52 ± 0.19	1.05 ± 0.20
4.8 M NaCl[g]	5[b,h]	-0.636 ± 0.100	1.30 ± 0.11	1.03 ± 0.51	-0.630 ± 0.092	2.87 ± 0.24	1.00 ± 0.48

[a] Ref.[5]. [b] Correlation at 50 °C. [c] Esters, $C_6H_5CO_2R$, with R = CH_3, CH_2CH_3, CH_2Cl, CH_2CN, $CH_2C_6H_5$, $CH_2C{\equiv}CH$, CH_2CH_2Cl, $CH_2CH_2OCH_3$ included. [d] Correlation at 25 °C. [e] Alkyl substituents R = CH_3, CH_2Cl, CH_2CN, $CH_2C_6H_5$, $CH_2C{\equiv}CH$, CH_2CH_2Cl, $CH_2CH_2OCH_3$ were included. [f] Alkyl substitents R = CH_3, CH_2Cl, $CH_2C_6H_5$, $CH_2C{\equiv}CH$, CH_2CH_2Cl, $CH_2CH_2OCH_3$ were included. [g] Ref.[8]. [h] Alkyl substituents R = CH_3, CH_2CH_3, CH_2Cl, CH_2CH_2Cl, $CH_2CH_2OCH_3$ included. [i] R = CH_3, CH_2Cl, CH_2CN, $CH_2C{\equiv}CH$ included.

Bu$_4$NBr, 2.25 M Bu$_4$NBr, 80% (v/v) DMSO, 5.3 M NaClO$_4$, 4.8 M NaCl, and 50% CH$_3$CN) are collected in Table IV.

DISCUSSION

In alkaline hydrolysis of substituted alkyl benzoates, C$_6$H$_5$CO$_2$R, in aqueous 0.5 M Bu$_4$NBr at 50 °C the dependence of the reaction rates on the substituent effects is nicely described by Eqs (4) and (5) (Table II):

TABLE III
Correlation of the $\Delta \log k$ values for alkaline hydrolysis of substituted alkyl benzoates, C$_6$H$_5$CO$_2$R, in various media at 50 and 25 °C with Eqs (6) and (7)[a]

Reaction constants	Eq. (6)		Eq. (7)	
	σ*	weight	σ$_I$	weight
	Solvent electrophilicity, ΔE, and polarity, ΔY, parameters included[b]			
c_0	–0.086 ± 0.044[c]		–0.080 ± 0.043[c]	
	–0.087 ± 0.054[d]		–0.082 ± 0.053[d]	
c_1	1.463 ± 0.043[c]	0.98	3.263 ± 0.094[c]	0.98
	1.744 ± 0.052[d]	1.07	3.896 ± 0.113[d]	1.07
c_2	1.016 ± 0.118[c]	–0.16	1.107 ± 0.117[c]	–0.13
	1.16 ± 0.135[d]	–0.16	1.117 ± 0.130[d]	–0.16
c_6	–0.0320 ± 0.0034[c]	0.15	–0.0714 ± 0.0074[c]	0.15
	–0.0241 ± 0.0035[d]	0.09	–0.0536 ± 0.0076[d]	0.09
n/n_o	39/39[c]		39/39[c]	
	36/36[d]		36/36[d]	
R	0.992[c]		0.992[c]	
	0.992[d]		0.993[d]	
s	0.082[c]		0.080[d]	
	0.093[d]		0.0989[d]	
s_0	0.127[c]		0.124[c]	
	0.127[d]		0.122[d]	
t	0.99[c]		0.99[c]	
	0.99[d]		0.99[d]	

Reaction constants	Eq. (*6*)		Eq. (*7*)	
	σ^*	weight	σ_I	weight
Solvent electrophilicity, ΔE, polarity, ΔY, and polarizability, ΔP, parameters included[b]				
c_0	-0.078 ± 0.041[c]		-0.071 ± 0.039[c]	
	-0.085 ± 0.084[d]		-0.078 ± 0.081[d]	
c_1	1.493 ± 0.042[c]	1.00	3.329 ± 0.088[c]	1.00
	1.696 ± 0.053[d]	1.04	3.790 ± 0.115[d]	1.04
c_2	1.047 ± 0.108[c]	-0.15	1.051 ± 0.102[c]	-0.15
	1.152 ± 0.119[d]	-0.16	1.161 ± 0.115[d]	-0.16
c_3	0.015 ± 0.005[d]	0.002	0.014 ± 0.052[d]	0.002
c_5	3.46 ± 1.04[d]	0.02	3.31 ± 1.00[d]	0.02
c_6	-0.0299 ± 0.0030[c]	0.15	-0.0667 ± 0.0065[c]	0.15
	-0.0277 ± 0.0049[d]	0.10	-0.0617 ± 0.0011[d]	0.10
n/n_0	37/39[c]		37/39[c]	
	36/36[d]		36/36[d]	
R	0.994[c]		0.994[c]	
	0.993[d]		0.993[d]	
s	0.072[c]		0.068[c]	
	0.082[d]		0.080[d]	
s_0	0.111[c]		0.105[c]	
	0.112[d]		0.108[d]	
t	0.97[c]		0.97[c]	
	0.99[d]		0.99[d]	

[a] If the scale is not shown in the table, the corresponding argument scale is excluded as insignificant in data processing ($c = 0$). [b] In Eqs (*6*) and (*7*) terms $c_5\Delta P$, $c_8\Delta P\sigma^*$ and $c_8\Delta P\sigma_I$ were omitted before data processing. [c] The log k values for pure water, aqueous 0.5 M Bu$_4$NBr (Table I), 2.25 M Bu$_4$NBr, 80% DMSO, 5.3 M NaClO$_4$, 4.8 M NaCl at 50 °C were included[5–8]. The two methods of calculation, exclusion of insignificant argument scales before excluding considerably deviating points and exclusion of significantly deviating points before excluding insignificant argument scales, gave the same results. Cross terms are formed from non-centered basic argument scales. [d] The log k values for pure water, aqueous 0.5 M Bu$_4$NBr (Table I), 2.25 M Bu$_4$NBr, 80% DMSO, 50% CH$_3$CN and 5.3 M NaClO$_4$ (Table I)[5–8,11,12] at 25 °C embraced. Exclusion of insignificant argument scales before excluding considerably deviating points and exclusion of significantly deviating points before excluding insignificant argument scales, gave the same results.

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

Medium	E [10,17–19]	n_D [17–19]	ε	P	Y	ΔE	ΔP	ΔY
Water	21.74	1.333	78.39 [21]	0.2057	0.9627	0	0	0
0.5 M Bu$_4$NBr	16.83	1.358	61.2 [22]	0.2196	0.9545	–4.91	0.0139	–0.0082
2.25 M Bu$_4$NBr	8.11	1.447	60.29 [23]	0.2672	0.9518	–13.63	0.0615	–0.0109
5.3 M NaClO$_4$	25.53[a]	1.3719 [24]	32.4 [25]	0.2272	0.9128	3.79	0.0215	–0.0499
80% DMSO	7.93	1.455 [26]	63.8 [27]	0.2713	0.9544	–13.81	0.0656	–0.0083
4.8 M NaCl	22.34	1.3757 [28]	43.33 [29]	0.2293	0.9339	0.60	0.0236	–0.0289
50% MeCN	15.16	1.3448	58.4 [30]	0.2123	0.9503	–6.58	0.0075	–0.0124

[a] Determined for methanolic 5.3 M NaClO$_4$ solution.

$$\log k = (-0.934 \pm 0.116) + (1.76 \pm 0.11)\sigma^* + (1.16 \pm 0.30)E_s^B \qquad (8)$$

$$\log k = (-0.927 \pm 0.117) + (3.93 \pm 0.26)\sigma_I + (1.17 \pm 0.32)E_s^B . \qquad (9)$$

The rate was increased by the polar effect of the electron-withdrawing electronegative substituents but retarded by the steric effect (Fig. 1). This is in accord with the $B_{Ac}2$ mechanism[31,32] via a tetrahedral intermediate [RCO(OH)OR′]$^-$, proposed for the alkaline hydrolysis of substituted alkyl benzoates. The electron-withdrawing groups stabilize the intermediate by delocalization of the fractional negative charge in the activated complex and thus lead to an increase in the rate constant. On going from water to aqueous 0.5 M Bu$_4$NBr the decrease in the log k value for the non-substituted derivative, i.e. methyl benzoate, was about 0.3 units compared with the corresponding value in pure water.

In transition from water to aqueous 0.5 M Bu$_4$NBr the polar effect of alkyl substituents increased at 50 °C by 0.24 units of ρ^* or 0.55 units of ρ_I. The change in the susceptibility to the polar effect of alkyl substituents, ρ_I, in transition from pure water to aqueous 0.5 M Bu$_4$NBr is similar to the increase in $\rho°$ value observed earlier for alkaline hydrolysis of *meta*- and *para*-substituted phenyl benzoates, $C_6H_5CO_2C_6H_4$–X ($\Delta\rho° = 0.39$)[1]. The corresponding values of $\rho°$ for the alkaline hydrolysis of phenyl benzoates in pure water and aqueous 0.5 M Bu$_4$NBr at 50 °C were 0.96 [33] and 1.35 [5].

The susceptibility to the steric effect of substituents, δ, in aqueous 0.5 M Bu$_4$NBr appeared to be approximately of the same magnitude as found for pure water, 2.25 M Bu$_4$NBr, 80% (v/v) DMSO, 5.3 M NaClO$_4$ and 4.8 M NaCl (Table II).

To study the influence of the solvent parameters on the substituent effects in alkaline hydrolysis of substituted alkyl benzoates, the $\Delta \log k = \log k^R - \log k^{CH_3}$ values at 50 and 25 °C for various media were subjected to the multi-linear regression analysis according to Eqs (*6*) and (*7*) in two different ways: (i) both the solvent electrophilicity, ΔE, and the solvent polarity, ΔY, were included or (ii) all the three solvent parameters, solvent electrophilicity, ΔE, solvent polarity, ΔY, and solvent polarizability, ΔP, were included. For comparison, the data treatment is shown separately using σ* and σ$_I$ scales (Table III). If the scale is not shown in the Table III, the corresponding argument scale is excluded during the data processing as insignificant.

The correlation of the $\Delta \log k$ values of alkaline hydrolysis of substituted alkyl benzoates at 50 °C in various media (water, aqueous 0.5 M Bu$_4$NBr, 25 M Bu$_4$NBr, 80% (v/v) DMSO, 5.3 M NaClO$_4$ and 4.8 M NaCl) using Eqs (*6*) and (*7*) showed that solvent electrophilicity parameter, ΔE, is the main factor responsible for the changes of the polar substituent effects with medium (Table III):
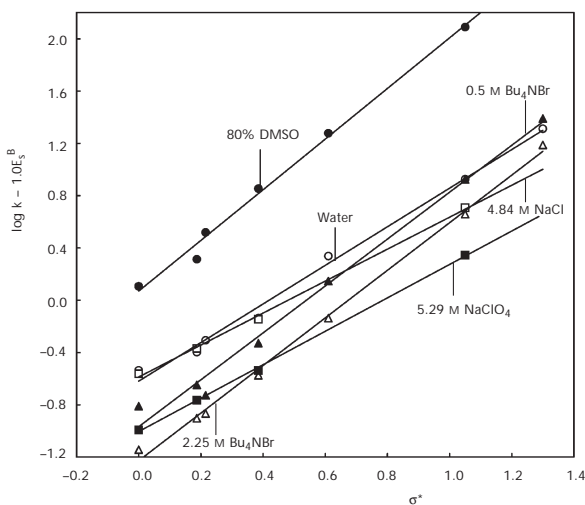

FIG. 1

Dependence of $\log k - 1.0 E_s^B$ on σ* for the alkaline hydrolysis of substituted alkyl benzoates, C$_6$H$_5$CO$_2$R, for pure water (○), aqueous 0.5 M Bu$_4$NBr (▲), 2.25 M Bu$_4$NBr (△), 80% (v/v) DMSO (●), 5.3 M NaClO$_4$ (■), and 4.8 M NaCl (□) (refs[5–8])

$$\Delta \log k = \log k^{\mathrm{R}} - \log k^{\mathrm{CH_3}} = (-0.086 \pm 0.044) + (1.463 \pm 0.042)\sigma^* +$$

$$+ (1.016 \pm 0.118)E_{\mathrm{s}}^{\mathrm{B}} - (0.0320 \pm 0.0003)\Delta E\sigma^* \qquad (10)$$

$$R = 0.992, \; s = 0.082, \; s_{\mathrm{o}} = 0.127, \; n_{\mathrm{o}} = 39/39$$

$$\Delta \log k = \log k^{\mathrm{R}} - \log k^{\mathrm{CH_3}} = (-0.080 \pm 0.043) + (3.263 \pm 0.094)\sigma_{\mathrm{I}} +$$

$$+ (1.021 \pm 0.116)E_{\mathrm{s}}^{\mathrm{B}} - (0.0714 \pm 0.0074)\Delta E\sigma_{\mathrm{I}} \qquad (11)$$

$$R = 0.992, \; s = 0.080, \; s_{\mathrm{o}} = 0.124, \; n_{\mathrm{o}} = 39/39 \; .$$

In correlations with Eqs (*6*) and (*7*) the contribution of cross terms containing the solvent electrophilicity parameter $c_6\Delta E\sigma^*$ and $c_6\Delta E\sigma_{\mathrm{I}}$ was found to be significant independently on the way used for the data treatment (Table III). The cross terms with solvent polarity ($c_7\Delta Y\sigma^*$, $c_7\Delta Y\sigma_{\mathrm{I}}$) and polarizability ($c_8\Delta P\sigma^*$, $c_8\Delta P\sigma_{\mathrm{I}}$) were indistinguishable from zero ($c = 0$) and the corresponding argument scale was excluded as insignificant during the data processing.

The variation of the alkyl polar effect with the solvent electrophilicity was about twice lower in the case the σ^* scale was used as the measure of the polar effect of alkyl substituents. The magnitude of the c_6 value calculated according to Eq. (*6*) proved to range from –0.0299 to –0.032. In the case the σ_{I} scale was used, the corresponding reaction constant c_6 calculated using Eq. (*7*) was found to range from –0.0667 to –0.0714. Previously[1,2] nearly the same magnitude for the reaction constants ($c_{6(\mathrm{m,p})} = -0.0645$)[1] has been found in alkaline hydrolysis of *meta*- and *para*-substituted phenyl benzoates at 50 °C and in alkaline hydrolysis of *meta*- and *para*-substituted phenyl tosylates at 75 °C ($c_{6(\mathrm{m,p})} = -0.0856$)[2]. The value of reaction constant c_6 calculated in alkaline hydrolysis of substituted alkyl benzoates using the σ^* scale was found to be comparable with the susceptibility of the *ortho*-inductive effect to variation of the solvent electrophilicity[1,2].

Consequently, in alkaline hydrolysis of substituted alkyl benzoates, the same extent of variation of the alkyl polar effect with the solvent electrophilicity was found as found earlier[1,2] in alkaline hydrolysis of *meta*- and *para*-substituted phenyl benzoates and *meta*- and *para*-substituted phenyl tosylates though the susceptibilities to polar effect of substituents in

water differed 3.4-fold $((\rho_I)_{Alk}/(\rho°_{m,p})_{Benz} = 3.4)$ and twice $((\rho_I)_{Alk}/(\rho°_{m,p})_{Tos} \approx 2)$ [34], respectively.

The reaction constant c_0 and terms $c_3\Delta E$, $c_4\Delta Y$, $c_5\Delta P$ were indistinguishable from zero ($c \approx 0$) or the corresponding scale is excluded as insignificant during the data processing. In case $c_0 = c_3\Delta E = c_4\Delta Y = c_5\Delta P = 0$ Eqs (*6*) and (*7*) turn to Eqs (*2*) and (*3*), respectively.

The reaction constant $c_1 = 1.463$ (Eq. (*10*)) and $c_1 = 3.263$ (Eq. (*11*)) is the susceptibility to the polar effect of alkyl substituents in standard solution, in water at 50 °C (Table III). Earlier[5] it was found that for alkaline hydrolysis of substituted alkyl benzoates in water at 50 °C $\rho^* = 1.52$ and $\rho_I = 3.38$ (Table II).

The values of c_2 as the susceptibilities to the alkyl steric effect in the alkaline hydrolysis of alkyl benzoates calculated according to Eqs (*6*) and (*7*) ranged from 1.02 to 1.16. The values of δ calculated for alkaline hydrolysis of alkyl benzoates at 50 °C from Eqs (*4*) and (*5*) in various media range from 0.94 to 1.32. The results of data treatment in Tables II and III confirm that the steric effect of alkyl substituents could be really considered to be independent of solvent parameters as assumed in Eqs (*6*) and (*7*).

The excellent fit between the experimental $\Delta \log k$ values at 50 °C (Table I, refs[5–8]) and predicted $\log k$ values calculated with Eqs (*10*) and (*11*) was found:

$$\Delta \log k_{obs} = (0.004 \pm 0.014) + (1.008 \pm 0.019) \, \Delta \log k_{calc} \qquad (12)$$

$$R = 0.994, \; s = 0.071, \; s_o = 0.110, \; n_o = 37/39$$

$$\Delta \log k_{obs} = (0.010 \pm 0.014) + (1.004 \pm 0.019) \, \Delta \log k_{calc} \qquad (13)$$

$$R = 0.994, \; s = 0.071, \; s_o = 0.110, \; n_o = 37/39 \; .$$

Excluded $R = CH_2C_6H_5$ in 0.5 M Bu_4NBr and $R = CH_2Cl$ in 4.8 M NaCl.

Correlation of the $\Delta \log k$ values for alkaline hydrolysis of substituted alkyl benzoates at 25 °C obtained with Eqs (*6*) and (*7*), was similar to correlation obtained at 50 °C (Eqs (*10*) and (*11*)). The solvent electrophilicity only was significant when both the solvent electrophilicity and the solvent polarity or all the three solvent parameters, solvent electrophilicity, ΔE, solvent polarity, ΔY, and solvent polarizability, ΔP, were included (Table III).

From the dependence of the (log k^R – log k^{CH_3}) values on the solvent electrophilicity ΔE (Eqs (*10*) and (*11*)) the value of solvent electrophilicity could be calculated at which the polar effect of alkyl substituents ρ^* and ρ_I becomes zero:

$$-1.463\sigma^* = -0.0320\Delta E\sigma^*, \quad \Delta E(\rho^* = 0) = 45.7 \tag{14}$$

$$-3.263\sigma_I = -0.0714\Delta E\sigma_I, \quad \Delta E(\rho_I = 0) = 45.7 . \tag{15}$$

The polar substituent effect in the hydrolysis of substituted alkyl benzoates becomes zero, i.e. $\rho^* = 0$ and $\rho_I = 0$ in solvent with the electrophilicity parameter $\Delta E = 45.7$ which corresponds to ca. neat solution of H_2SO_4 [34]. This supports the assumption made by Taft[9] that in strongly acidic solutions the polar effect of alkyl substituents in the hydrolysis reaction becomes nearly zero and the substituent effect is determined mainly by the steric effect.

The present work shows that in alkaline hydrolysis of substituted alkyl benzoates, $C_6H_5CO_2R$, similarly to the previously found behavior in alkaline hydrolysis of phenyl benzoates[1] and phenyl tosylates[2], the variation of the alkyl polar substituent effect with solvent occurs mainly due to change in electrophilicity of medium considered. The polar effect of alkyl substituents increases in transition from pure water to aqueous solutions of organic salts (0.5 M Bu$_4$NBr, 2.25 M Bu$_4$NBr) and aqueous 80% DMSO, the electrophilic solvating power of which being reduced compared with water. On the other hand, the polar effect of alkyl substituents decreased on going from water to aqueous inorganic salt solutions (5.3 M NaClO$_4$, 4.8 M NaCl) whose electrophilic solvating power is higher than that of pure water. In organic salt solutions and 80% DMSO the transition state of the ester hydrolysis involving minus charge could be considered as rather weakly electrophilically solvated which leads to essentially increased ρ values compared with pure water. In inorganic salt solutions the complexation of the little M$^+$ cations to negatively charged transition state should decrease the polar effect of substituents (ρ) in contrast with water.

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