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# Influence of solvent on the *ortho* substituent effect in the alkaline hydrolysis of phenyl esters of substituted benzoic acids

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The second-order rate constants  $k (dm^3 mol^{-1} s^{-1})$  for the alkaline hydrolysis of phenyl esters of *meta-*, *para-* and *ortho*-substituted benzoic acids in aqueous 5.3 M NaClO<sub>4</sub> and 1.0 M Bu<sub>4</sub>NBr were measured by UV/Vis spectrophotometry at 25 °C. The variations in the *ortho* inductive, *ortho* resonance, as well as *meta* and *para* polar effects with solvent parameters were studied using data for the alkaline hydrolysis of phenyl esters of substituted benzoic acids in various media. The dependence of the *ortho* substituent effect on solvent can be precisely described with the following equation:  $\Delta \log k_{ortho} = \log k_{ortho} - \log k_{H} = 0.059 + 2.19\sigma_1 + 0.304\sigma_R^{\circ} + 2.79E_s^{B} - 0.016\Delta E\sigma_1 - 0.085\Delta E\sigma_{R'}^{\circ}$ , where  $\Delta E$  is the solvent electrophilicity,  $\Delta E = E_S - E_{H2O}$ , characterizing the hydrogen-bond donating power of the solvent. The increase in the *meta* and *para* polar substituent effects with decrease in the solvent hydrogen-bond donor capacity (electrophilicity) was approximately to the same extent ( $-0.068\Delta E\sigma_{m,p}^{\circ}$ ) as the resonance term for the *ortho* inductive, *ortho* resonance, as well as *meta* and *para* polar substituents effects with the solvent parameters. The variations in the *ortho* inductive, *ortho* resonance, as well as *meta* and *para* polar substituent effects with the solvent electrophilicity were to the same extent as in phenyl benzoates containing the substituents in the phenyl part. The substituent effects in the alkaline hydrolysis of ethyl benzoates appeared to vary with the solvent electrophilicity nearly to the same extent as in the alkaline hydrolysis of substituted phenyl esters of benzoic acids. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: ortho effect; phenyl esters of benzoic acids; solvent electrophilicity; substituent effects

## INTRODUCTION

In our previous works,<sup>[1-6]</sup> we investigated the ortho, meta, para and alkyl substituent effects dependent on the solvent parameters and temperature for the alkaline hydrolysis of substituted phenyl benzoates, C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-X, phenyl tosylates, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>OC<sub>6</sub>H<sub>4</sub>-X and alkyl benzoates, C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>R, containing substituents at the phenyl or alkyl moiety. The significance of different solvent parameters (i.e. the solvent electrophilicity, polarity and polarizability) for the ortho, meta, para and alkyl substituent effects was studied on the basis of kinetic data for the alkaline hydrolysis of substituted phenyl benzoates, phenyl tosylates and alkyl benzoates, determined in water, aqueous 80% DMSO, aqueous 2.25 M Bu<sub>4</sub>NBr, 1.0 M Bu<sub>4</sub>NBr, 0.5 M Bu<sub>4</sub>NBr, 5.3 M NaClO<sub>4</sub> and 4.8 M NaCl (References<sup>[1-6]</sup> and the references cited therein). The ortho, para and meta polar as well as the alkyl polar substituent effects were found to be mainly dependent on the solvent electrophilicity,  $\Delta E_{s_i}^{[7-13]}$  which characterizes the hydrogen-bond donating power of the solvent. The variation in the ortho inductive term with the solvent electrophilicity,  $E_{S_1}$  was found to be ca. 3-2.5-fold smaller than that for the para substituents, while the ortho resonance term appeared to vary with the solvent electrophilicity nearly similarly to that for the para substituents.<sup>[3,5,6]</sup> The steric term in the alkaline hydrolysis of ortho-substituted phenyl benzoates and alkyl benzoates was approximately independent of temperature and solvent.<sup>[1,3-5]</sup> The variation in the meta and para polar, ortho inductive and resonance substituent effects with the solvent electrophilicity,  $\Delta E_{\rm S}$ , was nearly the same in both, the alkaline hydrolysis of substituted phenyl benzoates and the alkaline hydrolysis of substituted phenyl tosylates, though the susceptibilities to the polar effect of substituents in these two reactions series in water differed 2-fold,  $^{[1,3,6]}$  i.e.  $[(\rho^{\circ})_{m,p}]_{\rm Tos}/[(\rho^{\circ})_{ortho}]_{\rm Tos}/[(\rho_{\rm I})_{ortho}]_{\rm Benz}\approx 2:$ 

$$\begin{split} (\Delta \log k_{\text{ortho}})_{\text{Benz}} &= \log k^{\text{X}} - \log k^{\text{H}} = 0.014 + 1.428\sigma_{\text{I}} + 0.838\sigma_{\text{R}}^{\circ} \\ &+ 1.228E_{\text{s}}^{\text{B}} - 0.0212\Delta F\sigma_{\text{I}} - 0.0685\Delta F\sigma_{\text{R}}^{\circ} \qquad (1) \\ (R &= 0.988, s = 0.081, s_{0} = 0.153, n/n_{0} = 41/46) \\ (\Delta \log k_{\text{ortho}})_{\text{Tos}} &= \log k_{\text{X}} - \log k_{\text{H}} = 0.015 + 2.77\sigma_{\text{I}} + 1.82\sigma_{\text{R}}^{\circ} \\ &- 0.0298\Delta F\sigma_{\text{I}} - 0.0887\Delta F\sigma_{\text{R}}^{\circ} \\ (R &= 0.996, s = 0.096, s_{0} = 0.094, n/n_{0} = 42/47) \end{split}$$

The purpose of the present work was to study the significance of the solvent electrophilicity<sup>[7–9]</sup> and polarity<sup>[7–9]</sup> parameters on the *ortho* inductive, *ortho* resonance, as well as *meta* and *para* polar substituent effects in the alkaline hydrolysis of substituted

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phenyl benzoates containing the substituents at the benzoyl moiety. It was interesting to check whether the variation in the substituent polar effects with solvent parameters in the alkaline hydrolysis of esters depends on the magnitude of the  $\rho$  value for a reaction series considered. The susceptibility for the meta and para polar substituent effects,  $\rho$ , for the alkaline hydrolysis of phenyl esters of substituted benzoic acids in water was 1.6 times higher than that for the meta and para polar effects for the same reaction series containing substituents at the phenyl moiety.<sup>[14]</sup> Previously, the ortho, meta and para substituent effects in the alkaline hydrolysis of phenyl esters of substituted benzoic acids,  $X-C_6H_4CO_2C_6H_5$ , in pure water,<sup>[14]</sup> in aqueous 0.5 M Bu<sub>4</sub>NBr, 2.25 M Bu<sub>4</sub>NBr,<sup>[15]</sup> and 50% DMSO<sup>[16,17]</sup> at 25  $^{\circ}$ C were studied. In order to extend the study of the solvent-dependent ortho, meta and para substituent effects, in the present work the second-order rate constants k for the base-catalysed hydrolysis of phenyl esters of meta-, para- and ortho-substituted benzoic acids, X-C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>C<sub>6</sub>H<sub>5</sub> (X = H, 3-Cl, 3-NO<sub>2</sub>, 3-CH<sub>3</sub>, 4-NO<sub>2</sub>, 4-Cl, 4-F, 4-CH<sub>3</sub>, 4-OCH<sub>3</sub>, 2-NO<sub>2</sub>, 2-CN, 2-F, 2-Cl, 2-Br, 2-I, 2-CF<sub>3</sub>, 2-CH<sub>3</sub>, 2-OCH<sub>3</sub>, 2-NH<sub>2</sub>), were determined in aqueous 1.0 M Bu<sub>4</sub>NBr and aqueous 5.3 M NaClO<sub>4</sub>. For comparison, the dependence of the substituent effects on the solvent electrophilicity and polarity parameters in the alkaline hydrolysis of ethyl esters of substituted benzoic acids, X-C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>, was studied as well. For this purpose, additional rate constants for the alkaline hydrolysis of ethyl esters of substituted benzoic acids (X = H, 2-NO<sub>2</sub>, 2-CN, 2-Cl) in aqueous 0.5 M Bu<sub>4</sub>NBr and 5.3 M NaClO<sub>4</sub> were measured at 25 °C. In the previous works,<sup>[2,3,6]</sup> the ortho inductive, ortho resonance, as well as meta and para polar substituent effects in the alkaline hydrolysis of substituted phenyl benzoates and tosylates, containing substituents in the phenyl moiety, were found to become weaker in aqueous 5.3 M NaClO<sub>4</sub> solution and to grow in aqueous Bu<sub>4</sub>NBr solutions as compared to the same effects in pure water. The polar substituent effects were found to grow with decrease in the electrophilic properties of the solvent, and to decrease in solvents in which the electrophilic solvating power is stronger as compared to that of pure water.<sup>[2-6]</sup> In aqueous organic salt solutions of Bu<sub>4</sub>NBr, the electrophilic solvating power is considered to be reduced, whereas in inorganic salt solutions, it is considered to be increased, as compared to the hydrogenbond donating power of pure water.

### **EXPERIMENTAL**

The syntheses of phenyl and ethyl esters of substituted benzoic acids, X-C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>C<sub>6</sub>H<sub>5</sub> and X-C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>, the technique of kinetic measurements, as well as the purification of reagents were described earlier.<sup>[14–20]</sup> Ethyl benzoates were obtained commercially (Aldrich). The preparation of *ortho*-substituted ethyl benzoates and ethyl 4-nitrobenzoate had been described earlier.<sup>[21,22]</sup> For kinetic measurements with phenyl esters of substituted benzoic acids, aqueous 0.0187 M Bu<sub>4</sub>NOH in aqueous 1.0 M Bu<sub>4</sub>NBr and 0.0386 M NaOH in aqueous 5.3 M NaClO<sub>4</sub> were used. To estimate the rate constants for ethyl esters of substituted benzoic acids in pure water and aqueous 0.5 M Bu<sub>4</sub>NBr, 0.0936 M Bu<sub>4</sub>NOH was applied. In aqueous 5.3 M NaClO<sub>4</sub>, 0.10 M NaOH was used. For kinetic measurements, the UV/Vis spectrophotometric method was applied.<sup>[19]</sup>

The second-order rate constants,  $k \, (dm^3 \, mol^{-1} \, s^{-1})$ , for the alkaline hydrolysis of phenyl esters of substituted benzoic acids, X-C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, in aqueous 5.3 M NaClO<sub>4</sub> and aqueous 1.0 M

Bu<sub>4</sub>NBr at 25 °C are given in Table 1. For the alkaline hydrolysis of ethyl esters of benzoic acids, X-C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>, the second-order rate constants, k (dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>), measured in water, in aqueous 0.5 M Bu<sub>4</sub>NBr, and in aqueous 5.3 M NaClO<sub>4</sub> at 25 °C are listed in Table 2.

## DATA PROCESSING AND RESULTS

To study the influence of the *ortho* inductive, *ortho* resonance, as well as *meta* and *para* polar substituent effects in the alkaline hydrolysis of phenyl esters of substituted benzoic acids,  $X-C_6H_4CO_2C_6H_5$ , in aqueous 5.3 M NaClO<sub>4</sub> and 1.0 M Bu<sub>4</sub>NBr at 25°C, the corresponding log *k* values determined in the present work (Table 1) were treated according to the equations of Hammett [Eqn (3)]<sup>[23]</sup> and Charton [Eqn (4)]:<sup>[24]</sup>

$$\log k_{\rm m,p} = \log k_0 + \rho_{\rm m,p}\sigma \tag{3}$$

$$\log k_{\text{ortho}} = \log k_0 + (\rho_{\text{I}})_{\text{ortho}} \sigma_{\text{I}} + (\rho_{\text{R}}^{\circ})_{\text{ortho}} \sigma_{\text{R}}^{\circ} + \delta_{\text{ortho}} E_{\text{s}}^{\text{B}}$$
(4)

To check the significance of the solvent electrophilicity and polarity parameters for the *meta* and *para* as well as the *ortho* substituent effects, the corresponding values of  $\Delta \log k_{m,p} = \log k^X - \log k^H$  and  $\Delta \log k_{ortho} = \log k^X - \log k^H$  for the alkaline hydrolysis of phenyl and ethyl esters of substituted benzoic acids, X-C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>C<sub>6</sub>H<sub>5</sub> and X-C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>, at 25 °C in various media were correlated with Eqn (5):

$$\Delta \log k_{m,p,ortho} = c_{o} + c_{1(m,p)}\sigma + c_{2(ortho)}\sigma_{I} + c_{3(ortho)}\sigma_{R}^{\circ}$$

$$+ c_{4(ortho)}E_{s}^{B} + c_{5}\Delta E + c_{6}\Delta Y + c_{7(m,p)}\Delta E\sigma$$

$$+ c_{8(ortho)}\Delta E\sigma_{I} + c_{9(ortho)}\Delta E\sigma_{R}^{\circ} + c_{10(m,p)}\Delta Y\sigma$$

$$+ c_{11(ortho)}\Delta Y\sigma_{I} + c_{12(ortho)}\Delta Y\sigma_{R}^{\circ}$$
(5)

The steric term of ortho substituents was considered to be independent of the solvent parameters<sup>[3,5]</sup> and, therefore, the corresponding cross-terms with the solvent parameters were omitted. In the data processing including ortho-substituted derivatives, the log k value for the unsubstituted derivative (X = H) as standard was included besides the *ortho*-substituted derivatives. The values of the Hammett polar substituent constants,  $\sigma$ , reviewed by Hansch, Leo and Taft,<sup>[25]</sup> the Taft inductive  $\sigma_l^{[26]}$  and resonance  $\sigma_R^\circ$  constants<sup>[27]</sup>  $[\sigma_R^\circ = (\sigma^\circ)_{para} - \sigma_l]$ were used in the data processing. As steric constants for the ortho substituents,  $E_s^B$  constants<sup>[14]</sup> ( $E_s^B = \log k_H + X^X - \log k_H + H^H$ , where  $k_H + X^X$  and  $k_H + H^H$  are the rate constants for the acidic hydrolysis of ortho-substituted and unsubstitued phenyl benzoates in water at 50 °C<sup>[28]</sup>) were used. For comparison, Charton's steric v-scale,<sup>[14,24,29]</sup> calculated on the basis of the van der Waals radii,  $r_{\rm vr}$  was used as well. In the data processing according to Eqn (5), the log k values for the alkaline hydrolysis of phenyl esters of ortho-, meta- and para-substituted benzoic acids determined at 25 °C in aqueous 1 M Bu<sub>4</sub>NBr and 5.3 M NaClO<sub>4</sub> (the present work), as well as in pure water, aqueous 0.5 M Bu₄NBr, 2.25 M Bu₄NBr and 50% (v/v) DMSO given in papers<sup>[14–17]</sup> were included. When the log k values for ethyl esters of substituted benzoic acids were correlated with Eqn (5), log k values from the literature<sup>[30,31]</sup> and, also shown in Table 2 were used. In Eqn (5) the values of  $\Delta E$ and  $\Delta Y$  are the differences in electrophilicities and polarities on going from pure water to the corresponding aqueous binary solution,  $\Delta E = E_S - E_{H2O}$ ,  $\Delta Y = Y_S - Y_{H2O}$ , respectively. The standard medium, where  $\Delta E$  and  $\Delta Y$  are equal to zero, is pure water **Table 1.** The second-order rate constants k (dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>) for the alkaline hydrolysis of phenyl esters of substituted benzoic acids, X-C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, in aqueous 5.3 M NaClO<sub>4</sub> and 1.0 M Bu<sub>4</sub>NBr at 25 °C

х	$\lambda$ (nm) <sup>a</sup>	$k  (\mathrm{dm^3  mol^{-1}  s^{-1}})^\mathrm{b}$	n <sup>c</sup>	$k  (dm^3  mol^{-1}  s^{-1})^{b}$	n <sup>c</sup>	$\lambda$ (nm) <sup>d</sup>
		5.3 M NaClO <sub>4</sub> e		1.0 M Bu₄NBr <sup>f</sup>		
н	250	$0.0897 \pm 0.0086$	3	$0.0743 \pm 0.0083$	3	292
2-NO <sub>2</sub>	240	$\textbf{0.231} \pm \textbf{0.011}$	3	$\textbf{0.360} \pm \textbf{0.038}$	3	240
2-CN	250	$1.25\pm0.05$	3	$3.14\pm0.09$	3	285
2-F	250	$\textbf{0.384} \pm \textbf{0.031}$	5	$\textbf{0.224}\pm\textbf{0.002}$	3	240
2-Cl	250	$\textbf{0.236} \pm \textbf{0.039}$	3	$0.0976 \pm 0.0043$	4	285
2-Br	250	$\textbf{0.231} \pm \textbf{0.010}$	6	$0.0677 \pm 0.0036$	4	290
2-l	250	$\textbf{0.110} \pm \textbf{0.010}$	3	$0.0496 \pm 0.0026$	3	235
$2-CF_3$	250	$\textbf{0.0178} \pm \textbf{0.005}$	3	$0.0256 \pm 0.0015$	3	240
2-OCH₃	250	$0.0503 \pm 0.0010$	3	$0.0220 \pm 0.0030$	3	240
2-CH₃	250	$0.0171 \pm 0.0009$	3	$0.00936 \pm 0.00102$	3	250
2-NH <sub>2</sub>	250	$0.0115 \pm 0.0003$	3	_	_	_
4-NO <sub>2</sub>	240	$1.46\pm0.10$	3	$\textbf{8.51} \pm \textbf{0.18}$	3	292
3-NO <sub>2</sub>	240	$1.11\pm0.18$	3	$\textbf{4.03} \pm \textbf{0.10}$	3	292
3-Cl	250	$\textbf{0.320} \pm \textbf{0.034}$	3	$\textbf{0.536} \pm \textbf{0.082}$	3	250, 290
4-Cl	255	$\textbf{0.294} \pm \textbf{0.020}$	3	$\textbf{0.227} \pm \textbf{0.022}$	3	235, 292
4-F	245	$0.0912 \pm 0.0038$	3	$\textbf{0.141} \pm \textbf{0.012}$	3	245, 290
3-CH₃	250	$0.0684 \pm 0.0008$	3	$0.0424 \pm 0.0010$	3	290
4-CH₃	250	$0.0433 \pm 0.0013$	3	$0.0215 \pm 0.0007$	3	290
4-OCH <sub>3</sub>	260	$0.0219 \pm 0.0017$	3	_	—	—

 $^{\rm a}\lambda$  is the wavelength used in the kinetic measurements in 5.3 M NaClO<sub>4</sub>.

<sup>b</sup> The mean values of the second-order rate constants and their standard deviations.

<sup>c</sup> *n* is the number of remaining *k* values after exclusion of significantly deviating rate constants in the calculation of mean values.

 $^{d}\lambda$  is the wavelength used in the kinetic measurements in 1.0 M Bu<sub>4</sub>NBr.

<sup>e</sup> Aqueous 0.0386 M NaOH was used.

<sup>†</sup>Aqueous 0.0187 M Bu<sub>4</sub>NOH was used.

and the standard substituent is X = H. The electrophilicity values of Koppel and Palm,<sup>[7–13]</sup> *E*, and the polarity parameters, *Y*, calculated as a function of the dielectric constant  $\varepsilon$  in the form  $(\varepsilon - 1)/(\varepsilon + 2)$  were used. The dependence of zero-order partial

correlation coefficients of the independent variables on each other for the substituent constants,  $\sigma_{I_c} \sigma^{\circ}_{R}$ ,  $E_s^B$ , v and solvent parameters,  $\Delta E$ ,  $\Delta Y$ , were calculated. No collinearity was detected between the independent variables (very low values of  $R^2$ ). The

**Table 2.** The second-order rate constants k (dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>) for the alkaline hydrolysis of ethyl esters of benzoic acids, X-C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>, in water, in aqueous 0.5 M Bu<sub>4</sub>NBr and 5.3 M NaClO<sub>4</sub> at 25 °C

Х	$\lambda$ (nm) <sup>a</sup>	$k  (dm^3  mol^{-1}  s^{-1})^{b}$	nc	$k  (dm^3  mol^{-1}  s^{-1})^{b}$	nc	$k  (dm^3  mol^{-1}  s^{-1})^{b}$	nc
		Water <sup>d</sup>		0.5 M Bu₄NBr <sup>e</sup>		5.3 M NaClO <sub>4</sub> <sup>f</sup>	
Н	244	$0.0319 \pm 0.0002$	3	$0.0131 \pm 0.0004^{g}$	3	$0.00828 \pm 0.00083$	4
$2-NO_2$	240, 274	$0.0950 \pm 0.0122$	3	$\textbf{0.0605} \pm \textbf{0.086}$	3	$\textbf{0.0183} \pm \textbf{0.0007}$	3
2-CN	250	$0.530\pm0.020$	3	$\textbf{0.374} \pm \textbf{0.015}$	3	$0.0926 \pm 0.0042$	4
2-Cl	250	$0.0417 \pm 0.0021$	3	$0.0157 \pm 0.0004$	3	$0.0118 \pm 0.0001$	3
4-NO <sub>2</sub>	240	_	_	_	_	$0.113\pm0.007$	3

<sup>a</sup>  $\lambda$  is the wavelength used in the kinetic measurements.

<sup>b</sup> The mean values of the second-order rate constants and their standard deviations.

 $c^{r}$  *n* is the number of the remaining *k* values after exclusion of the significantly deviating rate constants in the calculation of mean values.

 $^{\rm d}$  Aqueous 0.037 M and 0.0936 M  $\rm Bu_4NOH$  was used.

<sup>e</sup> Aqueous 0.0936 M Bu<sub>4</sub>NOH was used.

<sup>f</sup>Aqueous 0.10 M NaOH was used.

<sup>g</sup> Reference [4].

**Table 3.** Correlation with Eqns (3) and (4) for the alkaline hydrolysis of phenyl esters of substituted benzoic acids,  $X-C_6H_4CO_2C_6H_5$ , in aqueous 5.3 M NaClO<sub>4</sub> and 1.0 M Bu<sub>4</sub>NBr 25 °C<sup>a</sup>

Eqn	log k <sub>o</sub>	$ ho_{\rm m,p}$ or $( ho_{\rm l})_{\rm ortho}$	$( ho_{R})_{ortho}$	$\delta_{ m ortho}$	R <sup>b</sup>	sc	n <sup>d</sup>
			5.3 M NaClO₄				
3	$-1.091 \pm 0.035$	$1.63\pm0.09$	_	_	0.989	0.093	9
4	$-1.022 \pm 0.054$	$\textbf{2.11} \pm \textbf{0.09}$	0	$\textbf{2.58} \pm \textbf{0.13}$	0.994	0.067	11
4	$-1.101\pm0.120$	$\textbf{2.19} \pm \textbf{0.21}$	0	$-1.16\pm0.13$	0.972	0.150	11 <sup>e</sup>
			1.0 M Bu₄NBr				
3	$-1.166 \pm 0.036$	$\textbf{2.54} \pm \textbf{0.09}$	—	—	0.996	0.084	8
4	$-1.073\pm0.146$	$\textbf{2.35} \pm \textbf{0.23}$	$\textbf{1.18} \pm \textbf{0.26}$	$\textbf{2.84} \pm \textbf{0.31}$	0.977	0.154	10
4	$-1.095 \pm 0.068$	$\textbf{2.36} \pm \textbf{0.11}$	$1.19\pm0.12$	$-1.32\pm0.07$	0.995	0.073	10 <sup>e</sup>

<sup>a</sup> Data analysis was performed at confidence level t = 0.99.

 $^{b}R$  is the correlation coefficient.

<sup>c</sup>s is the the standard deviation.

dn is the number of points remaining after exclusion of the significantly deviating points.

<sup>e</sup> The Charton steric constants,  $v_{i}^{[29]}$  were used.

data processing was carried out using a multiple parameter linear least-squares (LLSQ) procedure.<sup>[32]</sup> Significantly deviating points were excluded using a Student criterion. The exclusion of the significantly deviating points was performed on the different confidence levels of the *t*-test. The results of the data treatment with Eqns (3)–(5) are presented in Tables 3 and 4.

# DISCUSSION

# Influence of substituents in aqueous 5.3 M NaClO<sub>4</sub> and 1.0 M $Bu_4 NBr$

On moving from water to aqueous 5.3 M NaClO<sub>4</sub>, and aqueous 1.0 M Bu<sub>4</sub>NBr, for all phenyl esters of substituted benzoic acids, X-C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, a decrease in the rate constants of the alkaline hydrolysis was observed. For the unsubstituted derivative (X = H), approximately the same retardation (0.60 units of log *k* at 25 °C) was detected in the transition from water to aqueous 5.3 M NaClO<sub>4</sub> as in going from water to aqueous 1.0 M Bu<sub>4</sub>NBr. On moving from water to aqueous 5.3 M NaClO<sub>4</sub>, the decrease in the rates was higher for esters with electron-withdrawing substituents than that for the esters with electron-donating substituents. In the transition from water to aqueous 1.0 M Bu<sub>4</sub>NBr, the decrease was higher for esters with electron-donating substituents.

The log *k* values for the alkaline hydrolysis of phenyl esters of *meta* and *para*-substituted benzoic acids,  $X-C_6H_4CO_2C_6H_5$ , in aqueous 5.3 M NaClO<sub>4</sub> and 1.0 M Bu<sub>4</sub>NBr show excellent correlations with the Hammett equation (Eqn (3)). The log *k* values for *ortho*-substituted esters correlate well with the Charton equation (Eqn (4)) (Table 3). For the alkaline hydrolysis in aqueous 5.3 M NaClO<sub>4</sub>, we obtained:

$$\log k_{\rm m,p} = (-1.091 \pm 0.035) + (1.63 \pm 0.09)\sigma$$
(6)  
(R = 0.989, s = 0.093, n = 9)

(7)

$$\begin{array}{l} \log k_{\rm ortho} = (-1.022 \pm 0.054) + (2.11 \pm 0.09)\sigma_{\rm I} + (2.58 \pm 0.13)E_{\rm s}^{\rm B} \\ R = 0.994, \, s = 0.067, \, n = 11) \end{array}$$

In aqueous 1.0 M Bu<sub>4</sub>NBr we found:

$$\log k_{\rm m,p} = (-1.166 \pm 0.036) + (2.54 \pm 0.09)\sigma$$
(*R* = 0.996, s = 0.084, n = 8) (8)

$$\begin{split} \log \, k_{\rm ortho} &= (-1.073 \pm 0.146) + (2.35 \pm 0.23) \sigma_{\rm I} + (1.18 \pm 0.26) \sigma_{\rm R}^\circ \\ &+ (2.84 \pm 0.31) E_{\rm s}^{\rm B} \, ({\it R} = 0.977, \, {\it s} = 0.154, \, {\it n} = 10) \end{split} \tag{9}$$

In aqueous 5.3 M NaClO<sub>4</sub> the polar effect of meta and para substituents was 0.1 units of  $\rho$  lower, but in aqueous 1.0 M Bu<sub>4</sub>NBr 0.8 units of  $\rho$  higher as compared to pure water ( $\rho = 1.72$  in water at 25 °C<sup>[14]</sup>). The susceptibility to the ortho inductive and the resonance effects diminished by *ca.* 0.1 and 0.3 units of  $\rho$  on moving from pure water to aqueous 5.3 M NaClO<sub>4</sub> and increased by 0.2 and 0.9 units of  $\rho$  in the transition from water to aqueous 1.0 M Bu<sub>4</sub>NBr (( $\rho_l$ )<sub>ortho</sub> = 2.13 and ( $\rho_R$ )<sub>ortho</sub> = 0.31 in water at  $25 \,{}^{\circ}C^{[14]}$ ). The observed variation in the susceptibility to inductive effect from the ortho position with solvent was less than three times smaller as compared to that for the meta and para polar effects, as well as the ortho resonance effect. In the alkaline hydrolysis of phenyl esters of substituted benzoic acids,  $X-C_6H_4CO_2C_6H_5$ , containing substituents in the acyl part, we found that the variation in the substituent effects in a transition from water to aqueous 1.0 M Bu<sub>4</sub>NBr and 5.3 M NaClO<sub>4</sub> is approximately equal to the variation in the substituent effects with solvent in the alkaline hydrolysis of benzoates containing substituents in the phenyl part. In the alkaline hydrolysis of ortho-substituted phenyl benzoates with substituents in the phenyl part, C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-X, the susceptibility to the ortho inductive effect and resonance increased by 0.1 and 0.7 units of  $\rho$ on moving from water to aqueous 1.0 M Bu<sub>4</sub>NBr,<sup>[20]</sup> and diminished by 0.1 and 0.3 units of  $\rho$  on moving from water to aqueous 5.3 M NaClO<sub>4</sub>.<sup>[2]</sup> Recently,<sup>[15]</sup> in the alkaline hydrolysis of substituted phenyl benzoates, on moving from water to aqueous 0.5 M and 2.25 Bu<sub>4</sub>NBr, the  $\rho$  values for the *meta* and *para* polar, the *ortho* inductive and resonance effects in the acyl part were found to vary with the solvent to the same extent as compared to the variation in the  $\rho$  values for the corresponding substituent effects in the phenyl part.

<b>Table 4.</b> Results (X-C <sub>6</sub> H <sub>5</sub> , )	of the correlation of th X-C <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ) in vari	e kinetic data, ous media at 2	$\Delta \log k_{m,p,ortho} = \log k^{X} - \log (5).$	$k^{H}$ , for the alka	line hydrolysis of phe	inyl and ethyl es	sters of substituted benzoic ac	ids
React. constant	Ortho derivatives	Weight	<i>Meta</i> and <i>para</i> derivatives	Weight	Ortho derivatives	Weight	<i>Meta</i> and <i>para</i> derivatives	Weight
	Su	bstituted phenyl b	en zoates <sup>a</sup>			Substituted ethyl be	enzoates <sup>b</sup>	
c <sub>0</sub>	$\textbf{0.059}\pm\textbf{0.055}$		$-0.005\pm0.032$	I	$-0.019\pm 0.078$	I	$\textbf{0.018}\pm\textbf{0.024}$	
	$0.026\pm0.054^{\rm c}$	Ι	$-0.001\pm0.023^{d}$	I	$-0.013 \pm 0.058^{c}$	Ι	$0.021\pm0.022^{d}$	
C1(m,p)	Ι		$1.67\pm0.05$	0.778	Ι	Ι	$1.45\pm0.03$	0.660
	I		$1.77\pm0.04^{ m d}$	0.826	I	I	$1.50\pm0.04^{ m d}$	0.687
C2(ortho)	$2.19\pm0.07$	0.516	1	I	$\textbf{1.98}\pm\textbf{0.09}$	0.613	1	
	$2.23\pm\mathbf{0.08^{c}}$	0.525		I	$2.00 \pm \mathbf{0.06^c}$	0.611	I	
C3(ortho)	$0.304 \pm 0.089$	0.037	I		$0.383 \pm 0.158$	0.068	I	I
	$0.431\pm0.089^{\rm c}$	0.052	I	I	$0.401 \pm 0.117^{c}$	0.070	I	I
C4(ortho)	$2.79 \pm 0.09$	0.370	1	I	$\textbf{2.23}\pm\textbf{0.14}$	0.154	1	
	$-1.31\pm0.04^{\circ}$	0.348	I		$-1.16\pm0.05^{\circ}$	0.135	I	
c <sub>5</sub>	0	I	0	I	0	I	0	
	0 0	I	0	I	0 0	I	0	
C <sub>6</sub>	0 0		0		0 0		0	
C <sub>7(m,p)</sub>	•	Ι	$-0.0764 \pm 0.0060$	0.194	•	I	$-0.0836\pm0.0047$	0.273
	Ι	Ι	$-0.0683 \pm 0.0055^{ m d}$	0.174	Ι	Ι	$-0.0953 \pm 0.0049^{ m d}$	0.313
C8(ortho)	$-0.0164\pm0.0064$	0.020	I	I	$-0.0412\pm0.0086$	0.075	I	I
	$-0.0180\pm0.0064^{c}$	0.022	Ι	I	$-0.0460 \pm 0.0063^{\circ}$	0.082	Ι	
C9(ortho)	$-0.0854\pm0.0114$	0.057	I	I	$-0.0653 \pm 0.0180$	060.0	Ι	
	$-0.0789 \pm 0.0114^{\circ}$	0.053	1	I	$-0.0743 \pm 0.0133^{\circ}$	0.102	Ι	
C10(m.p)	I	I	-4 96 $+ 1$ 84	0.078			$-518\pm0.03$	0.067
n/n <sup>e</sup>	63/63		-4:20 ± 1:24 55/55	07070	50/50	I	62.0 ± 01.0-	10000
0	62/63 <sup>c</sup>	I	55/55 <sup>d</sup>	I	50/50 <sup>c</sup>	Ι	94/96 <sup>d</sup>	
Ŗ	0.986	I	0.995	I	0.984	I	266.0	
	0.986	Ι	0.995 <sup>d</sup>	Ι	0.991	Ι	0.995ª	I
S <sup>4</sup>	0.114	I	0.082	I	0.124	I	0.070	
h,	0.114		0.00/		0.091		0.000	
0c	0.166		0.102		0.133 <sup>c</sup>		0.096 <sup>d</sup>	
ť	0:99 0.05	Ι	0.09	I	0.99	Ι	0:99	
	0.99		0.99	I	0.99	I	n66 <sup>0</sup>	I
The solvent electr	ophilicity, $\Delta E$ and pola	rity, $\Delta Y$ , param	eters were involved.		-			
<sup>b</sup> Kinetic data for p	oure water, aqueous 0.	5 M, 1.0 M and M% othenol 10	2.25 M Bu4NBr, 5.3 M NaClO4, 3 11 7 15 1 20 0 and 28 3 M%	, 50% DMSO at	25°C were included. I 59 M% DMSO 0 5 M F	Del M E 3 M NaC	10 . and nurse water at 25 $^\circ$ C wer	hevlovini e
<sup>c</sup> The Charton ster	ic constants, <sup>[29]</sup> wer	e used.	ייו ו יה או היטב או וש ייטב יו ירו י <i>י</i> יו ו ירי	מרבוחווב' זע מוור		שאו ואו כיכ יומאוקטי	יוסל מווח לחוב אמובו מו בט כ אבו	
<sup>d</sup> Only the solvent	electrophilicity param	eters, <i>ΔE</i> , were	included.					
$e^{n}$ is the number	of points remaining af	fter exclusion c	if significantly deviating point	ts and $n_0$ is the	total number of poi	nts subjected to	the data analysis.	
<sup>t</sup> R is the correlation	on coefficient.							
<sup>9</sup> s is the standard	deviation.							
$\int_{0}^{n} s_0$ is the scaled s	standard deviation.							
<sup>1</sup> t is the confidence	ce level.							

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#### Influence of solvent on substituent effects

The variation in the susceptibilities to *meta* and *para* polar, *ortho* inductive, *ortho* resonance and *ortho* steric effects with the solvent parameters in the alkaline hydrolysis of phenyl and ethyl esters of substituted benzoic acids, X-C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>C<sub>6</sub>H<sub>5</sub> and X-C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>, was studied in two different ways: (i) by correlating the  $\Delta \log k_{m,p,ortho} = \log k_X - \log k_H$ , values in various media at 25 °C with Eqn (5), only the solvent electrophilicity,  $\Delta E$ , or (ii) by including parameters such as the solvent electrophilicity,  $\Delta E$  and the solvent polarity,  $\Delta Y$ . The data treatment was performed separately for *meta*- and *para*-substituted derivatives and for *ortho*-substituted derivatives (Table 4). If the scale is not shown in Table 4, the corresponding argument scale was excluded during the data treatment as insignificant ( $c_{11(ortho)}\Delta Y\sigma_{\rm R}$ ).

When the  $\Delta \log k$  values for the alkaline hydrolysis of phenyl and ethyl esters of substituted benzoic acids were treated according to Eqn (5), the calculated values of reaction constants  $c_{1(m,p)}$ ,  $c_{2(ortho)}$ ,  $c_{3(ortho)}$  and  $c_{4(ortho)}$  as the susceptibilities to the meta and para polar effect, ortho inductive, ortho resonance and ortho steric effects, in the standard solution (pure water) were approximately the same as found earlier for pure water with Eqns (3) and (4), respectively (Table 4). Earlier<sup>[14,15]</sup> the corresponding values of  $c_{1(m,p)}$ ,  $c_{2(ortho)}$ ,  $c_{3(ortho)}$  and  $c_{4(ortho)}$  for the alkaline hydrolysis of phenyl and ethyl esters of substituted benzoic acids for pure water at 25 °C were found to be 1.72, 2.13, 0.31 and 2.67, as well as 1.44, 1.95, 0.33 and 2.73, respectively.

We found the contribution of the cross-terms containing the solvent electrophilicity parameter to be significant for the meta and para polar effects as well as for ortho inductive and ortho resonance effects (i.e.  $c_{7(m,p)}\Delta E\sigma \neq 0$ ,  $c_{8(ortho)}\Delta E\sigma_{l} \neq 0$ ,  $c_{9(ortho)}$  $\Delta E \sigma^{\circ}_{R} \neq 0$  in both the alkaline hydrolysis of phenyl esters as well as ethyl esters of substituted benzoic acids. The cross-term containing the solvent polarity was different from zero for the meta and para polar effects in the alkaline hydrolysis of both phenyl and ethyl esters of substituted benzoic acids  $(c_{10(m,p)}\Delta Y\sigma \neq 0$ , Table 4). However, the contribution of the solvent polarity to the polar effect of *meta* and *para* substituents can be considered almost insignificant due to its extremely low relative weight (Table 4). In the case of ortho derivatives the cross-terms containing the solvent polarity are insignificant for both the inductive and resonance effects. The corresponding cross-terms ( $c_{11(ortho)}\Delta Y\sigma_{I}$  and  $c_{12(ortho)}\Delta Y\sigma_{R}^{\circ}$ ) were excluded as insignificant during the data processing.

Consequently, in the alkaline hydrolysis of phenyl and ethyl esters of substituted benzoic acids,  $X-C_6H_4CO_2C_6H_5$  and  $X-C_6H_4CO_2C_2H_5$ , the solvent electrophilicity parameter,  $\Delta E$ , can be considered as the main factor responsible for the solvent-dependent variation in the *meta* and *para* polar, as well as *ortho* inductive and *ortho* resonance effects.

In the medium considered, the *meta*, *para* and *ortho* substituent effects in the alkaline hydrolysis of phenyl esters of substituted benzoic acids can be expressed by Eqns (10)–(12) (Table 4)

$$\begin{split} \Delta \log k_{\rm m,p} &= \log k_{\rm X} - \log k_{\rm H} = (-0.010 \pm 0.023) \\ &+ (1.77 \pm 0.04)\sigma - (0.0683 \pm 0.0055)\Delta E\sigma \\ &(R = 0.995, \, s = 0.087, \, s_0 = 0.108, \, n/n_0 = 55/55) \end{split}$$

$$\begin{split} \Delta \log k_{\text{ortho}} &= \log k_{\text{X}} - \log k_{\text{H}} = (0.059 \pm 0.055) \\ &+ (2.19 \pm 0.07)\sigma_{\text{I}} + (0.304 \pm 0.089)\sigma_{\text{R}}^{\circ} \\ &+ (2.79 \pm 0.09)E_{\text{s}}^{\text{B}} - (0.0164 \pm 0.0064)\Delta E\sigma_{\text{I}} \\ &- (0.0854 \pm 0.0114)\Delta E\sigma_{\text{R}}^{\circ} \\ (R = 0.986, s = 0.114, s_0 = 0.167, n/n_0 = 63/63) \end{split}$$

Almost the same results as shown by Eqn (11) were obtained when the Charton steric v scale,<sup>[29]</sup> based on van der Waals radii, was used for the *ortho* substituents. Only on using the Charton steric v scale, the susceptibility to the steric influence of *ortho* substituents was twice lower and has the opposite sign

$$\begin{split} \Delta \log \, k_{\rm ortho} &= \log \, k_{\rm X} - \log \, k_{\rm H} = (0.026 \pm 0.054) \\ &+ (2.23 \pm 0.08) \sigma_{\rm I} + (0.431 \pm 0.089) \sigma_{\rm R}^{\circ} \\ &- (1.31 \pm 0.04) \upsilon - (0.0180 \pm 0.0064) \Delta E \sigma_{\rm I} \quad (12) \\ &- (0.0789 \pm 0.0114) \Delta E \sigma_{\rm R}^{\circ} \\ (R &= 0.986, \, s = 0.114, \, s_0 = 0.166, \, n/n_0 = 62/63) \end{split}$$

In the alkaline hydrolysis of phenyl esters of substituted benzoic acids, the meta and para polar effect was found to vary with the solvent electrophilicity,  $\Delta E$ , nearly three times higher  $(c_{7(m,p)} = -0.0683 \pm 0.0055)$  than that for the ortho inductive effect ( $c_{8(ortho)} = -0.0164 \pm 0.0064$ ). In the case of ethyl esters of ortho-substituted benzoic acids, the susceptibility of the ortho inductive effect to the solvent electrophilicity was approximately twice lower ( $c_{8(\text{ortho})} = -0.0412 \pm 0.0086$ ) than that for the meta and para polar effects ( $c_{7(m,p)} = -0.0953 \pm 0.0049$ ). The ortho resonance effect was found to vary with the solvent electrophilicity to nearly the same extent as the resonance effect from the para position, though in pure water the role of the resonance from the ortho position was negligible. When moving from water to media in which the electrophilic solvating power, i.e. the hydrogen-bond donor power, is reduced ( $\Delta E < 0$ ), the resonance effect from the ortho position increases essentially. In the transition from pure water to aqueous 1.0 M Bu<sub>4</sub>NBr solution  $(\Delta E = -7.97)$  the  $(\rho_{\rm R})_{\rm ortho}$  value increased by 0.87 units of  $\rho_{\rm R}$ (Table 3).

The present study proved that in the alkaline hydrolysis of substituted phenyl benzoates, the meta, para polar effect, as well as ortho inductive and ortho resonance effect for substituents in the acyl moiety  $(X-C_6H_4CO_2C_6H_5)$  vary with the solvent electrophilicity,  $\Delta E$ , nearly to the same extent as was found earlier for the substituents in the phenyl moiety (C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-X). The corresponding values of the reaction constants were:  $c_{7(m,p)} = -0.0646$ ,  $c_{8(ortho)} = -0.0212$  and  $c_{9(ortho)} = -0.0685$ .<sup>[3]</sup> Approximately the same values for the reaction constants  $c_{7(m,p)}$ ,  $c_{8(ortho)}$  and  $c_{9(ortho)}$ , characterizing the variation in the meta, para polar effect, ortho inductive and ortho resonance effects with the solvent electrophilicity, were found in the alkaline hydrolysis of substituted phenyl tosylates ( $c_{7(m,p)} = -0.0656$ ,  $c_{8(ortho)} =$ -0.0298 and  $c_{9(ortho)} = -0.0887$ .<sup>[6]</sup> Consequently, in the alkaline hydrolysis of the phenyl and ethyl esters of substituted benzoic acids, phenyl tosylates and phenyl esters of benzoic acid, the same variation in the substituent effects with the solvent electrophilicity was found, though the ratio of the susceptibilities to polar effect of substituents in pure water differed by more than 1.7 times. The influence of the steric factor of ortho substituents on the alkaline hydrolysis of both phenyl and ethyl esters of substituted benzoic acids was found to be independent of the solvent parameters as assumed in Eqn (5) (constants  $c_{4(ortho)}$  in Table 4).

The combined influence of the substituent effects and the solvent electrophilicity, i.e. the H-bond donation power on the alkaline hydrolysis of esters can be explained by the contribution of the corresponding structure factors and the solvent to stabilize the transition-state and the ground state in the alkaline hydrolysis.<sup>[33]</sup> The alkaline hydrolysis of aryl benzoates is accepted to follow the stepwise  $B_{Ac}2$  mechanism<sup>[34–37]</sup> by forming a negatively charged tetrahedral intermediate  $R_1CO^-(OH)OR_2$ :



The negative charge localized on oxygen in the transition state is a good hydrogen-bond acceptor.<sup>[38]</sup> In all the used solvents, the polar effects of electron-withdrawing substituents were found to enhance the rates in the alkaline hydrolysis of esters. The polar effects of the electron-withdrawing substituents in the alkaline hydrolysis are considered to stabilize the transition state by the delocalization of the negative charge in the transition state and destabilize the resonance forms in the esters' ground state.<sup>[34–39]</sup> According to Buncel,<sup>[40]</sup> in the hydrolysis of esters the transition-state structure varies with the solvent composition. In media in which the hydrogen-bond donating ability is reduced as compared to pure water ( $\Delta E < 0$  for aqueous DMSO and Bu<sub>4</sub>NBr solutions), the negative charge of the transition state is enhanced. Due to reduced solvation of the transition state, the contribution of the electron-withdrawing substituents to delocalize and electron-donating substituents to localize the negative charge in the transition state is increased as compared to pure water.

In aqueous 5.3 M NaClO<sub>4</sub> solution in which the electrophilic solvating power (H-bond donating capability) is increased in comparison to pure water ( $\Delta E$ >0), the transition state becomes less negative due to complexation of Na<sup>+</sup> to the negatively charged transition state<sup>[41]</sup> and due to the increased H-bond donating capability of water in inorganic salt solutions. In inorganic salt solutions with stronger electrophilic power compared to water ( $\Delta E$ >0) the role of the solvent is increased and the polar substituent effects are reduced during stabilization of the transition state. In solutions with stronger electrophilic solvating power ( $\Delta E$ >0), electron-withdrawing substituents do not favour the complexation of Na<sup>+</sup> or water molecules by H-bond to the negatively charged transition state.

# CONCLUSIONS

In the present paper the second-order rate constants, k (dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>), for the alkaline hydrolysis of phenyl esters of *meta-*, *para-* and *ortho-*substituted benzoic acids, X-C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, in aqueous 5.3 M NaClO<sub>4</sub> and aqueous 1.0 M Bu<sub>4</sub>NBr were determined. The variation of the *meta* and *para* polar, *ortho* inductive and resonance substituent effects with the solvent

parameters in the alkaline hydrolysis of phenyl and ethyl esters of *meta-, para-* and *ortho*-substituted benzoic acids was studied. The solvent electrophilicity, i.e. the hydrogen-bond donor power of the solvent, was found to be the main solvent property responsible for the changes in the *ortho, meta* and *para* polar substituent effects with the solvent. The variation in the *ortho* inductive, *ortho* resonance as well as *meta* and *para* polar substituent effects with the solvent electrophilicity appeared to be to the same extent as found previously in phenyl benzoates,  $C_6H_5CO_2C_6H_4$ -X, containing substituents in the phenyl part and in the alkaline hydrolysis of substituted phenyl tosylates,  $CH_3C_6H_4SO_2OC_6H_4$ -X, though the  $\rho$  values for *meta* and *para* derivatives in water for the reaction series considered differ *ca*. twice. The steric factor for the *ortho* derivatives was independent of the solvent used.

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