

**KINETIC STUDY OF HYDROLYSIS OF BENZOATES.
PART XXVII. *ortho* SUBSTITUENT EFFECT IN ALKALINE
HYDROLYSIS OF PHENYL ESTERS OF SUBSTITUTED
BENZOIC ACIDS IN AQUEOUS Bu₄NBr**

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The second-order rate constants k (in $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) for alkaline hydrolysis of phenyl esters of *meta*-, *para*- and *ortho*-substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, have been measured spectrophotometrically in aqueous 0.5 and 2.25 M Bu₄NBr at 25 °C. The substituent effects for *para* and *meta* derivatives were described using the Hammett relationship. For the *ortho* derivatives the Charton equation was used. For *ortho*-substituted esters two steric scales were involved: the E_s^B and the Charton steric (ν) constants. When going from pure water to aqueous 0.5 and 2.25 M Bu₄NBr, the *meta* and *para* polar effects, the *ortho* inductive and resonance effects in alkaline hydrolysis of phenyl esters of substituted benzoic acids, became stronger nearly to the same extent as found for alkaline hydrolysis of $\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4\text{-X}$. The steric term of *ortho*-substituted esters was almost independent of the media considered. The rate constants of alkaline hydrolysis of *ortho*-, *meta*- and *para*-substituted phenyl benzoates ($\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, $\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4\text{-X}$) and alkyl benzoates, $\text{C}_6\text{H}_5\text{CO}_2\text{R}$, in water, 0.5 and 2.25 M Bu₄NBr were correlated with the corresponding IR stretching frequencies of carbonyl group, $(\Delta\nu_{\text{CO}})_\text{X}$.

Keywords: Esters; Phenyl benzoates; Alkaline hydrolysis; Kinetics; *ortho*-Effect; Substituent effects; Hammett equation; IR stretching frequencies of carbonyl group.

Recently¹⁻³ we studied the significance of different solvent parameters for the substituent effects in alkaline hydrolysis of *ortho*-, *meta*- and *para*-substituted phenyl benzoates, $\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4\text{-X}$, phenyl tosylates, $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{OC}_6\text{H}_4\text{-X}$, and for substituted alkyl benzoates, $\text{C}_6\text{H}_5\text{CO}_2\text{R}$, including the $\log k$ values in water, aqueous 80% DMSO, 2.25 M Bu₄NBr, 1.0 M Bu₄NBr, 0.5 M Bu₄NBr, 5.3 M NaClO₄ and 4.8 M NaCl. The solvent electrophilicity⁴⁻⁸, ΔE_s^F , which characterizes the hydrogen-bond donating

power of the solvent, was found to be the main factor responsible for the changes in the *ortho*, *para* and *meta* polar, as well as the alkyl polar substituent effects with the medium. The variation of the *ortho* inductive term with the solvent electrophilicity, E_s , was found to be ca. 2.5-fold smaller than that for *para* substituents, while the *ortho* resonance term appeared to vary with the solvent almost similarly to that for *para* substituents. In alkaline hydrolysis of substituted phenyl benzoates, the variation of the polar effect of *meta* and *para* substituents, as well as of the *ortho* inductive and resonance effect with the solvent electrophilicity appeared by the same extent as in alkaline hydrolysis of substituted phenyl tosylates, though the ratio of the susceptibilities to the polar effect of substituents in water differed two-fold^{3,9}. The steric term in alkaline hydrolysis of *ortho*-substituted phenyl benzoates and alkyl benzoates was almost independent of the solvent parameters^{1,3}.

To extend the study of the *ortho* substituent effects dependent on the solvent to the acyl part of substituted phenyl benzoates, we recently¹⁰ determined the second-order rate constants k in the base-catalyzed hydrolysis of phenyl esters of *meta*-, *para*- and *ortho*-substituted benzoic acids, $X-C_6H_4CO_2C_6H_5$, in pure water at 25 °C. The kinetics of alkaline hydrolysis of phenyl esters of *para*- and *ortho*-substituted benzoic acid in aqueous 50% (v/v) dimethyl sulfoxide at 25 °C was measured by Bauerová and Ludwig^{11,12}. To our knowledge, there are no other systematic kinetic data on alkaline hydrolysis of phenyl esters of benzoic acids containing *ortho* substituents together with *meta*- and *para*-substituted derivatives available in the literature.

The $\log k$ values for alkaline hydrolysis of phenyl esters of *para*-substituted benzoic acids in both water¹⁰ and 50% aqueous DMSO¹¹ were found to be well correlated with the Hammett relationship¹³. In water at 25 °C, the main factors responsible for changes in the *ortho* substituent effect in alkaline hydrolysis of phenyl esters of *ortho*-substituted benzoic acids were the inductive and steric factors while the role of the resonance term was negligible.

In the present paper we determined the second-order rate constants k for alkaline hydrolysis of phenyl esters of substituted benzoic acid, $X-C_6H_4CO_2C_6H_5$ ($X = H, 3-Cl, 3-NO_2, 3-CH_3, 4-NO_2, 4-Cl, 4-F, 4-CH_3, 4-OCH_3, 2-NO_2, 2-CN, 2-F, 2-Cl, 2-Br, 2-I, 2-CH_3, 2-OCH_3, 2-CF_3, 2-NH_2$) in aqueous 0.5 and 2.25 M Bu_4NBr at 25 °C. The main purpose of the present work was to check how the structural factors, the polar influence of *meta* and *para* substituents, the inductive, resonance and steric factors of *ortho* substituents in acyl part of phenyl benzoates vary when going from

water to aqueous 0.5 and 2.25 M Bu_4NBr , whose electrophilic solvating power⁸ is significantly lower compared with water. It is interesting to compare the variation of substituent effects with the solvent in alkaline hydrolysis of phenyl benzoates containing substituents in the acyl part with similar variation of substituent effects in the phenyl part of benzoates. Earlier we found¹⁰ that the *meta* and *para* polar effects, as well as the *ortho* inductive effect in alkaline hydrolysis of substituted benzoates containing substituents in the acyl part in the pure water were 1.6 times and steric influence 2.7 times higher than the corresponding influences from the phenyl part of benzoates. It was also of interest to check up how the *ortho* resonance effect, which in water was negligible¹⁰, varies with the solvent.

The second purpose of the present work was to compare the substituent effects on the rates of the alkaline hydrolysis of phenyl esters of substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, substituted phenyl esters of benzoic acid, $\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4\text{-X}$, and alkyl benzoates, $\text{C}_6\text{H}_5\text{CO}_2\text{R}$, in water, aqueous 0.5 and 2.25 M Bu_4NBr at 25 °C with the corresponding substituent effects in the IR stretching frequencies of the carbonyl group, $\Delta\nu_{\text{CO}}$.

Recently¹⁴ we determined the IR stretching frequencies of carbonyl group, ν_{CO} , for 25 substituted phenyl esters of benzoic acid, $\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4\text{-X}$, 8 alkyl benzoates, $\text{C}_6\text{H}_5\text{CO}_2\text{R}$, and 22 phenyl esters of substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, in tetrachloromethane. The IR stretching frequencies of the carbonyl group, ν_{CO} , of *cis* and *trans* conformers of *ortho* derivatives in the benzoyl part of esters showed good correlations when dual-parameter equations were used: $(\nu_{\text{CO}})_{\text{cis}} = (\nu_{\text{CO}})_0 + 22.0\sigma_{\text{I}} - 21.5E_{\text{s}}^{\text{B}}$ and $(\nu_{\text{CO}})_{\text{trans}} = (\nu_{\text{CO}})_0 + 12.6\sigma_{\text{p}}^+ - 11.9E_{\text{s}}^{\text{B}}$ ($R = 0.99$). The carbonyl stretching frequencies of *ortho* derivatives, ν_{CO} , in the phenoxy part of esters were shown to depend on the inductive substituent constants, σ_{I} , only. In the case of alkyl benzoates the substituent effects in $(\nu_{\text{CO}})_{\text{Alk}}$ were well described by both the Taft σ^* and the steric E_{s}^{B} constants¹⁴.

EXPERIMENTAL

The preparation and characteristics of phenyl esters of substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, the reagent purification as well as technique of kinetic measurements were described earlier^{10,15,16}. As the reagent, aqueous 0.0187 M Bu_4NOH was used for kinetic measurements in aqueous 0.5 and 2.25 M Bu_4NBr .

The second-order rate constants k (in $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) for alkaline hydrolysis of phenyl esters of substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, in aqueous 0.5 and 2.25 M Bu_4NBr at 25 °C, the wavelength, λ , used in the kinetic measurements and the number of measurements, n , are given in Table I.

DATA PROCESSING

For the study of the substituent effects in alkaline hydrolysis of phenyl esters of substituted benzoic acids in aqueous 0.5 and 2.25 M Bu₄NBr at 25 °C, the corresponding log *k* values measured in the present work (Table I) were treated using the Hammett¹³ (1) and the Charton¹⁷ (2) equations.

$$\log k_{m,p} = \log k_0 + \rho_{m,p} \sigma \quad (1)$$

$$\log k_{ortho} = \log k_0 + (\rho_I)_{ortho} \sigma_I + (\rho^o_R)_{ortho} \sigma^o_R + \delta_{ortho} E_S^B \quad (2)$$

TABLE I

The second-order rate constants *k* for alkaline hydrolysis of phenyl esters of substituted benzoic acids, X-C₆H₄CO₂C₆H₅, in aqueous 0.5 and 2.25 M Bu₄NBr at 25 °C

X	λ^a nm	k^b dm ³ /mol s	n^c	log <i>k</i>	λ^a nm	k^b dm ³ /mol s	n^c	log <i>k</i>	
		0.5 M Bu ₄ NBr				2.25 M Bu ₄ NBr			
4-NO ₂	240	10.8±0.1	3	1.033					
3-NO ₂	292	6.63±0.11	3	0.822	290	6.76±1.30	3	0.830	
3-Cl	292	1.36±0.15	3	0.134	290	0.708±0.080	3	-0.150	
4-Cl	240, 292	0.592±0.057	4	-0.228	255, 292	0.396±0.046	3	-0.402	
4-F	245	0.275±0.030	3	-0.561	260, 290	0.180±0.003	3	-0.745	
H	292	0.199±0.017	3	-0.701	292	0.0818±0.0048	3	-1.087	
3-CH ₃	292	0.163±0.026	4	-0.788	290	0.0435±0.0034	3	-1.362	
4-CH ₃	292	0.104±0.015	3	-0.983	290	0.0338±0.0017	3	-1.471	
4-OCH ₃	292	0.0706±0.0015	3	-1.151	260, 290	0.0127±0.0001	3	-1.896	
2-NO ₂	240	0.650±0.047	3	-0.187	240	0.610±0.018	4	-0.215	
2-CN	250	4.45±0.07	3	0.648	290	3.69±0.57	3	0.567	
2-F	250	0.630±0.056	4	-0.201	250	0.292±0.011	3	-0.535	
2-Cl	235, 250	0.248±0.017	4	-0.606	250	0.163±0.009	3	-0.788	
2-Br	235, 250	0.204±0.019	4	-0.690	250	0.0993±0.0084	3	-1.003	
2-I	235, 250	0.111±0.010	5	-0.955	240, 290	0.0659±0.0081	5	-1.181	
2-CF ₃	232	0.0355±0.0068	3	-1.450	240	0.0225±0.0010	3	-1.648	
2-OCH ₃	250	0.0376±0.0027	3	-1.425	240	0.0114±0.0003	3	-1.943	
2-CH ₃	250	0.0237±0.0015	3	-1.625	250	0.0122±0.0004	3	-1.914	
2-NH ₂	240	0.00952±0.00077	3	-2.021					

^a λ is the wavelength used in the kinetic measurements; ^b the mean value of the second-order rate constants and standard deviation; ^c *n* is equal to the number of the remaining *k* values after exclusion of significantly deviating rate constants in calculation of mean values.

The log k values for *meta*- and *para*-substituted derivatives were correlated with Eq. (1) and the log k values for *ortho*-substituted derivatives with the Charton equation, Eq. (2). In the data processing, using Eq. (2), the log k value for the unsubstituted derivative ($X = H$) as a standard was included besides the *ortho*-substituted derivatives. The values of the Hammett polar substituent constants, σ , reviewed by Hansch, Leo and Taft¹⁸, the Taft inductive σ_I ¹⁹ and resonance σ_R^o constants²⁰ ($\sigma_R^o = \sigma^o - \sigma_I$) were used in the data processing. As the steric constants for *ortho* substituents we employed the values of E_s^B obtained from the acid hydrolysis of *ortho*-substituted phenyl benzoates, $C_6H_5CO_2C_6H_4-X$, with *ortho* substituents in the phenyl part^{1,9} ($E_s^B = \log k_{H+X} - \log k_{H+H}$, where k_{H+X} and k_{H+H} are the rate constants for the acid hydrolysis of *ortho*-substituted and unsubstituted phenyl benzoates in water at 50 °C²¹). For comparison, the calculations were performed using the Charton steric constants, ν , as well^{10,22}.

The results of the data treatment with Eqs (1) and (2) for alkaline hydrolysis of phenyl esters of substituted benzoic acids, $X-C_6H_4CO_2C_6H_5$, in aqueous 0.5 and 2.25 M Bu_4NBr at 25 °C (Table I) are shown in Table II. The values of σ_I , σ_R^o , E_s^B and ν used are given in the previous work¹⁰.

To compare the *meta* and *para* polar substituent effects in alkaline hydrolysis of substituted phenyl benzoates, $X-C_6H_4CO_2C_6H_5$, and $C_6H_5CO_2C_6H_4-X$ with those in the IR stretching frequencies of carbonyl group, $(\Delta\nu_{CO})_X$, the following relationships were used:

$$\log k_m = \log k_H + a(\Delta\nu_{CO})_m \quad (3)$$

$$\log k_{m,p} = \log k_H + a(\Delta\nu_{CO})_{m,p} \quad (4)$$

where $(\Delta\nu_{CO})_X = (\nu_{CO})_X - (\nu_{CO})_H$.

In the case of phenyl esters of *ortho*-substituted benzoic acids, $X-C_6H_4CO_2C_6H_5$, *ortho*-substituted phenyl esters of benzoic acid, $C_6H_5CO_2C_6H_4-X$, and substituted alkyl benzoates, $C_6H_5CO_2R$, the log k values of alkaline hydrolysis were correlated with the IR stretching frequencies of carbonyl group, $\Delta\nu_{CO}$, using the following equations:

$$\log k_{ortho} = \log k_H + a_{1(ortho)} \Delta\nu_{CO} + a_{2(ortho)} \sigma_R^o + a_{3(ortho)} E_s^B \quad (5)$$

$$\log k_{Alk} = \log k_{CH_3} + a_{1(Alk)} \Delta\nu_{CO} + a_{3(Alk)} \Delta E_s^B. \quad (6)$$

TABLE II

Correlation with Eqs (1) and (2) of kinetic data for alkaline hydrolysis of phenyl esters of substituted benzoic acids, X-C₆H₄CO₂C₆H₅, in water¹⁰, aqueous 0.5 M Bu₄NBr, 2.25 M Bu₄NBr, and 50% DMSO¹⁰⁻¹² at 25 °C

Reaction constants	Water	0.5 M Bu ₄ NBr	2.25 M Bu ₄ NBr	50% DMSO
<i>meta and para substituents</i>				
log <i>k</i> ₀	-0.451±0.011	-0.651±0.015	-1.073±0.037	-0.018±0.028
ρ	1.72±0.03	2.06±0.04	2.71±0.12	2.32±0.06
<i>R</i> ^a	0.999	0.999	0.993	0.994
<i>s</i> ^b	0.033	0.039	0.099	0.114
<i>s</i> ₀ ^c	0.044	0.050	0.114	0.105
<i>n/n</i> ₀ ^d	10/10	9/9	8/8	9/9
<i>t</i> ^e	0.99	0.99	0.99	0.99
<i>ortho substituents</i>				
log <i>k</i> ₀	-0.333±0.078 -0.356±0.102 ^f	-0.683±0.080 -0.718±0.062 ^f	-0.993±0.098 -1.035±0.111 ^f	0.047±0.104 0.063±0.089 ^f
ρ _I	2.13±0.12 2.12±0.16 ^f	2.20±0.13 2.27±0.13 ^f	2.56±0.15 2.57±0.18 ^f	2.31±0.16 2.45±0.13 ^f
ρ _R	0.31±0.13 0.44±0.17 ^f	0.82±0.13 0.94±0.10 ^f	1.42±0.18 1.42±0.20 ^f	0.78±0.17 0.96±0.14 ^f
δ	2.67±0.16 -1.26±0.10 ^f	2.96±0.16 -1.39±0.06 ^f	3.07±0.21 -1.39±0.11 ^f	2.69±0.23 -1.35±0.09 ^f
<i>R</i> ^a	0.992 0.987 ^f	0.993 0.996 ^f	0.991 0.989 ^f	0.987 0.991 ^f
<i>s</i> ^b	0.085 0.113 ^f	0.087 0.069 ^f	0.104 0.118 ^f	0.106 0.085 ^f
<i>s</i> ₀ ^c	0.126 0.160 ^f	0.114 0.090 ^f	0.133 0.151 ^f	0.167 0.135 ^f
<i>n/n</i> ₀ ^d	11/11 10/11 ^f	11/11 11/11 ^f	10/10 10/10 ^f	10/10 10/10 ^f
<i>t</i> ^e	0.99 0.99 ^f	0.99 0.99 ^f	0.99 0.99 ^f	0.99 0.99 ^f

^a *R*, correlation coefficient; ^b *s*, the standard deviation; ^c *s*₀, the scaled standard deviation; ^d *n/n*₀, a numerator reflects the total number of data (points) subjected to the regression analysis, and a denominator is equal to a number of points remained after excluding of significantly deviating points; ^e *t*, confidence level. ^f Charton's steric constants^{10,22}, *v*, were used.

Earlier¹⁴ the substituent effects on the IR frequencies of the carbonyl group, $\Delta\nu_{\text{CO}}$, for phenyl esters of *ortho*-substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, and alkyl benzoates, $\text{C}_6\text{H}_5\text{CO}_2\text{R}$ ($\text{R} = \text{CH}_3, \text{CH}_2\text{CH}_3, \text{CH}_2\text{Cl}, \text{CH}_2\text{CN}, \text{CH}_2\text{C}\equiv\text{CH}, \text{CH}_2\text{CH}_2\text{Cl}, \text{CH}_2\text{CH}_2\text{OCH}_3, \text{CH}_2\text{C}_6\text{H}_5$), were found to be described as the sum of the inductive and the steric terms. In the case of *ortho*-substituted phenyl esters of benzoic acid, $\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4\text{-X}$, the IR stretching frequencies of carbonyl group, $\Delta\nu_{\text{CO}}$ were shown to depend on the inductive substituent constants, only. Consequently, in Eqs (5) and (6) the a_1 value is the ratio of the inductive effects in alkaline hydrolysis (AH) and IR frequencies of the carbonyl group, $a_1 = \rho_1(\text{AH})/\rho_1(\text{IR})$, the $a_{2(\text{ortho})} \sigma_{\text{R}}^{\text{o}}$ term is the resonance in alkaline hydrolysis and the a_3 is the sum of the susceptibilities to the steric effects in alkaline hydrolysis and IR frequencies of the carbonyl group, $\Delta\nu_{\text{CO}}$: $a_3 = \delta(\text{AH}) + a_1\delta(\text{IR})$.

To correlate the carbonyl stretching frequencies of *cis* conformer in the phenyl esters of *ortho*-substituted benzoic acids, $(\nu_{\text{CO}})_{\text{ortho-cis}}$, in the present work the following equation was found:

$$(\nu_{\text{CO}})_{\text{ortho-cis}} = (1742.7 \pm 0.8) + (16.4 \pm 1.4)\sigma_1 - (22.6 \pm 1.8)E_s^{\text{B}} \quad (7)$$

$R = 0.993$, $s_0 = 0.117$; $\text{X} = \text{H}, 2\text{-NO}_2, 2\text{-CN}, 2\text{-F}, 2\text{-Cl}, 2\text{-Br}, 2\text{-CH}_3, 2\text{-OCH}_3, 2\text{-CF}_3$.

For the 2- CH_3 substituent, the value of the steric constant $E_s^{\text{B}} = 0$ was used instead of $E_s^{\text{B}} = -0.264$ to correlate the $\log k$ values.

To correlate the rates of alkaline hydrolysis with the corresponding IR stretching frequencies of the carbonyl group, $\Delta\nu_{\text{CO}}$, the $\log k$ values for phenyl esters of substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, substituted phenyl esters of benzoic acid, $\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4\text{-X}$, and substituted alkyl benzoates, $\text{C}_6\text{H}_5\text{CO}_2\text{R}$, in water, aqueous 0.5 and 2.25 M Bu_4NBr reported in Table I and in the previous works^{1,3,9,10,15,16,23,24} were used. The IR stretching frequencies of the carbonyl group, $\Delta\nu_{\text{CO}}$, in tetrachloromethane, used in correlations with Eqs (3)–(6), were determined earlier¹⁴. As the $\Delta\nu_{\text{CO}}$ values for phenyl esters of *ortho*-substituted benzoic acids, the $\Delta\nu_{\text{CO}}$ values for *cis* conformers estimated by the carbonyl stretching frequencies deconvolution were used¹⁴. The steric substituent constants, E_s^{B} , for the variable alkyl substituent in the alkyl component of esters, $\text{C}_6\text{H}_5\text{CO}_2\text{R}$, (Eq. (6)) were calculated as follows: $E_s^{\text{B}} = (\log k_{\text{H}^{\text{R}}} - \log k_{\text{H}^{\text{CH}_3}})$, where $k_{\text{H}^{\text{R}}}$ and $k_{\text{H}^{\text{CH}_3}}$ are the rate constants for acid hydrolysis of R-substituted alkyl benzoates, $\text{C}_6\text{H}_5\text{CO}_2\text{R}$, in water^{3,24,25}. The results of correlations with Eqs (3)–(6) are listed in Table III. Correlations of that type could be helpful in practical

rough estimation of the $\log k$ values on the bases of knowing the easily measurable $\Delta\nu_{\text{CO}}$ values of the respective phenyl or alkyl benzoates.

The data processing was carried out using a multiple-parameter linear least-squares (LLSQ) procedure²⁶.

TABLE III

Correlation of the $\log k$ values for alkaline hydrolysis of phenyl esters of *ortho*-, *meta*- and *para*-substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, substituted phenyl esters of benzoic acid, $\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4\text{-X}$, and substituted alkyl benzoates, $\text{C}_6\text{H}_5\text{CO}_2\text{R}$, in water, aqueous 0.5 and 2.25 M Bu_4NBr at 25 °C with the IR stretching frequencies of carbonyl group, $(\Delta\nu_{\text{CO}})_{\text{X}} = (\nu_{\text{CO}})_{\text{X}} - (\nu_{\text{CO}})_{\text{H}}$ ¹⁴ using Eqs (3)–(6)

Line	Medium	$\log k_{\text{H}}$	a_1	a_2	a_3	R^2	s_0^a	n/n_0^a
Phenyl esters of <i>meta</i> -substituted benzoic acids, Eq. (3)								
1	Water ^b	-0.385±0.041	0.157±0.010	-	-	0.994	0.113	4/4
2	0.5 M Bu_4NBr	-0.610±0.056	0.201±0.014	-	-	0.993	0.118	4/4
3	2.25 M Bu_4NBr	-1.068±0.049	0.263±0.012	-	-	0.997	0.080	4/4
Phenyl esters of <i>meta</i> - and <i>para</i> -substituted benzoic acids, Eq. (4)								
4	Water ^b	-0.259±0.066	0.143±0.014	-	-	0.961	0.276	10/10
5		-0.316±0.044	0.131±0.009			0.981	0.192	9/10 ^c
6	0.5 M Bu_4NBr	-0.449±0.106	0.186±0.028	-	-	0.941	0.394	9/9
7		-0.594±0.062	0.197±0.019	-	-	0.972	0.236	7/9 ^{c,d}
8	2.25 M Bu_4NBr	-0.884±0.084	0.219±0.023	-	-	0.963	0.271	8/8
Phenyl esters of <i>ortho</i> -substituted benzoic acids, Eq. (5)								
9	Water ^b	-0.360±0.325	0.127±0.019	-	5.60±0.63	0.958	0.288	8/9 ^{e,f}
10	0.5 M Bu_4NBr	-0.644±0.314	0.130±0.012	0.74±0.20	5.97±0.40	0.987	0.163	8/8 ^{e,g}
11	2.25 M Bu_4NBr	-1.022±0.244	0.157±0.023	1.19±0.22	6.66±0.46	0.987	0.160	8/9 ^{e,f}
<i>meta</i> - and <i>para</i> -substituted phenyl esters of benzoic acid ^{h,j,k} , Eq. (4)								
12	Water ^b	-0.434±0.034	0.118±0.008	-	-	0.974	0.227	12/12
13		-0.465±0.031	0.124±0.007			0.983	0.181	11/12 ^c
14	0.5 M Bu_4NBr	-0.789±0.044	0.150±0.011	-	-	0.973	0.231	12/12
15		-0.793±0.032	0.139±0.009	-	-	0.982	0.191	11/12 ^c
16	2.25 M Bu_4NBr	-1.073±0.089	0.247±0.022	-	-	0.977	0.213	7/7

TABLE III
(Continued)

Line	Medium	$\log k_H$	a_1	a_2	a_3	R^a	s_0^a	n/n_0^a
<i>ortho</i> -Substituted phenyl esters of benzoic acid ^{h,j,k} , Eq. (5)								
17	Water ^b	-0.394±0.061	0.083±0.005	1.01±0.11	0.99±0.12	0.992	0.122	11/11 ⁱ
18	0.5 M Bu ₄ NBr	-0.777±0.088	0.089±0.007	1.36±0.15	1.20±0.17	0.989	0.150	11/11 ⁱ
19	2.25 M Bu ₄ NBr	-1.062±0.172	0.120±0.013	1.88±0.26	1.62±0.50	0.984	0.179	6/6 ⁱ
Alkyl benzoates ^m , Eq. (6)								
20	Water ^b	-1.181±0.035	0.062±0.002	-	-1.16±0.11	0.998	0.064	8/8 ⁿ
21	0.5 M Bu ₄ NBr	-1.500±0.067	0.072±0.004	-	-1.20±0.22	0.994	0.106	8/8 ⁿ
22	2.25 M Bu ₄ NBr	-1.854±0.032	0.077±0.002	-	-1.67±0.10	0.999	0.044	7/7 ^o

^a See notes ^{a,c,d} in Table II. ^b Ref.¹⁰ ^c The 4-NO₂ derivative was excluded. ^d The 4-OCH₃ derivative was excluded. ^e The 2-NO₂, 2-CN, 2-F, 2-Cl, 2-Br, 2-I, 2-CF₃, 2-OCH₃ and unsubstituted derivatives were included. The Δv_{CO} values for *cis* isomers were used. ^f The 2-I derivative was excluded. ^g The 2-I derivative was omitted before data analysis. ^h Refs^{10,23}. ⁱ The 2-NO₂, 2-CN, 2-F, 2-Cl, 2-I, 2-CF₃, 2-OCH₃, 2-N(CH₃)₂, 2-C(CH₃)₃ and unsubstituted derivatives were included. ^j Ref.¹ ^k Ref.⁹. ^l The 2-NO₂, 2-F, 2-Cl, 2-CH₃, 2-OCH₃ and unsubstituted derivatives were included. ^m Refs^{3,24}. ⁿ R = CH₃, CH₂CH₃, CH₂Cl, CH₂CN, CH₂C≡CH, CH₂CH₂Cl, CH₂CH₂OCH₃, CH₂C₆H₅. ^o The CH₂CH₃ derivative was not included.

DISCUSSION

The $\log k$ values for alkaline hydrolysis of phenyl esters of *meta*- and *para*-substituted benzoic acids, X-C₆H₄CO₂C₆H₅, in aqueous 0.5 and 2.25 M Bu₄NBr at 25 °C, determined in the present work, gave excellent correlation with the Hammett σ constants ($R > 0.993$, Table II). The values of $\rho_{m,p}$ in aqueous 0.5 and 2.25 M Bu₄NBr at 25 °C were 2.06 and 2.71, respectively. The $\log k$ values for alkaline hydrolysis of phenyl esters of *ortho*-substituted benzoic acids, were well correlated using the Charton equation, Eq. (2) ($R > 0.987$, Table II). The data treatment of *ortho* derivatives according to Eq. (2) showed almost the identical correlation using two alternative steric scales: the E_s^B constants and the Charton steric parameter²², ν . The values of $(\rho_I)_{ortho}$, $(\rho^o_R)_{ortho}$ and δ_{ortho} in aqueous 0.5 and 2.25 M Bu₄NBr at 25 °C were 2.20 (2.27), 0.82 (0.94), 2.96 (-1.39) and 2.56 (2.57), 1.42 (1.42), 3.07 (-1.39), respectively (Table II). In brackets are shown the values of $(\rho_I)_{ortho}$, $(\rho^o_R)_{ortho}$ and δ_{ortho} obtained using the Charton steric scale, ν .

In alkaline hydrolysis of phenyl esters of substituted benzoic acids, the increase in the susceptibility to the polar effect of *meta* and *para* substituents, ρ , is 0.34 and 0.99 units of ρ , when going from water to aqueous 0.5 and 2.25 M Bu₄NBr. The susceptibility to the inductive effect of *ortho* substituents became larger by 0.07 and 0.43 units of ρ_I in the same change of the solvent. Earlier²⁷, in alkaline hydrolysis of substituted phenyl benzoates, C₆H₅CO₂C₆H₄-X, the *meta* and *para* polar effects were found to grow by 0.40 and 1.16 units of ρ° and the *ortho* inductive effect increased by 0.03 and 0.61 units of ρ_I , respectively, when going from water to aqueous 0.5 and 2.25 M Bu₄NBr. Consequently, in alkaline hydrolysis of phenyl esters of substituted benzoic acids, X-C₆H₄CO₂C₆H₅, and in alkaline hydrolysis of substituted phenyl esters of benzoic acid, C₆H₅CO₂C₆H₄-X ($\rho^\circ_{m,p} = 1.05$ and $(\rho_I)_{ortho} = 1.54$ in pure water at 25 °C) approximately the same variations of the *meta* and *para* polar substituent effect and *ortho* inductive effects with that solvent were observed though the polar effect of *meta* and *para* substituents in water for the two reaction series considered differs ca. 1.6 times.

Although the contribution of the resonance term for *ortho* substituents in the benzoyl part of esters in water was negligible ($(\rho^\circ_R)_{ortho} = (0.31 \pm 0.13)$, Table II) the resonance from the *ortho* position ($(\rho^\circ_R)_{ortho}$ value) increases approximately by the same extent as from the *para* position when going from water to aqueous 0.5 and 2.25 M Bu₄NBr (by 0.51 and 1.11 units of ρ°_R , respectively).

When going from pure water to aqueous 0.5 M Bu₄NBr, 50% DMSO and 2.25 M Bu₄NBr the solvent electrophilicity⁴⁻⁸, ΔE_S , which characterizes the hydrogen-bond donor power of the solvent, decreases as follows: $\Delta E_S = E_S - E_{H_2O} = 0$ for pure water, -4.9 for aqueous 0.5 M Bu₄NBr, -8.0 for 50% DMSO, -13.6 for 2.25 M Bu₄NBr. Therefore, in alkaline hydrolysis of phenyl esters of substituted benzoic acids, X-C₆H₄CO₂C₆H₅, we found the polar substituent effects to grow with decreasing the electrophilic properties of the solvent^{7,8}, ΔE_S , similarly to what we have earlier found for alkaline hydrolysis of substituted phenyl benzoates, C₆H₅CO₂C₆H₄-X^{1,27}. In aqueous Bu₄NBr and DMSO solutions the transition state in the ester hydrolysis involving negative charge, could be considered as weakly electrophilically solvated, which leads to essentially increased ρ values compared with pure water^{2,28}. In concentrated aqueous Bu₄NBr salt solutions, similarly to those in aqueous DMSO, only few water molecules are assumed to be able to form hydrogen bonds. At the same time the bulky Bu₄N⁺ ions are not able to complex with the partially negatively charged phenolic oxygen in the ester hydrolysis transition state.

The contribution of the steric term in alkaline hydrolysis of phenyl esters of *ortho*-substituted benzoic acids was approximately the same in the four media considered, and independent of the steric scale used. In the case of steric constants E_s^B and the Charton ν values the magnitudes of δ and $\delta(\nu)$ were 2.67, 2.96, 3.07, 2.69 and -1.26 , -1.39 , -1.39 , -1.39 .

Correlation of the Rates of Alkaline Hydrolysis with the IR Carbonyl Stretching Frequencies ν_{CO}

The substituent effects on the rates of alkaline hydrolysis of phenyl esters of *meta*-, *para*- and *ortho*-substituted benzoic acids, $X-C_6H_4CO_2C_6H_5$, *meta*-, *para*- and *ortho*-substituted phenyl esters of benzoic acid, $C_6H_5CO_2C_6H_4-X$, and substituted alkyl benzoates, $C_6H_5CO_2R$, in pure water, aqueous 0.5 and 2.25 M Bu_4NBr at 25 °C were compared with those in the IR stretching frequencies of the carbonyl group, $\Delta\nu_{CO}$, using Eqs (3)–(6) (Table III). The log k values of alkaline hydrolysis of phenyl esters of *meta*-substituted benzoic acids, $X-C_6H_4CO_2C_6H_5$, and *meta*- and *para*-substituted phenyl esters of benzoic acid, $C_6H_5CO_2C_6H_4-X$, in aqueous 2.25 M Bu_4NBr , 0.5 M Bu_4NBr and pure water show a good correlation with the corresponding IR carbonyl stretching frequencies, $\Delta\nu_{CO}$ ($0.997 > R > 0.972$, Table III).

The correlation of the log k values versus $\Delta\nu_{CO}$ was not so good for phenyl esters of *para*-substituted benzoic acids due to the additional contribution of the through-resonance to the $\Delta\nu_{CO}$ values in the case of $+R$ *para* substituents in the benzoyl part of esters¹⁴.

The log k values for *ortho*-substituted benzoates ($X-C_6H_4CO_2C_6H_5$, $C_6H_5CO_2C_6H_4-X$) correlated well with the IR stretching frequencies of the carbonyl group, $(\Delta\nu_{CO})_{ortho}$, in case the additional resonance and steric terms were included (Eq. (5), $0.958 \leq R \leq 0.992$, Table III). In the case of alkyl benzoates, $C_6H_5CO_2R$, the dependence of the log k values on $(\Delta\nu_{CO})_{Alk}$ showed an excellent correlation when an additional steric influence was taken into consideration ((Eq. (6), $0.998 \leq R \leq 0.998$, Table III).

The slope a in Eqs (3) and (4) for *meta* and *para* derivatives represents the ratio of the polar effects in alkaline hydrolysis and in the corresponding IR stretching frequencies, $(\Delta\nu_{CO})$. In the case of *ortho* and alkyl derivatives the parameter a_1 in Eqs (5) and (6) is the ratio of the corresponding inductive effects. The slope a in Eqs (3) and (4) found for *meta* and *para* derivatives in all media studied (pure water, aqueous 0.5 and 2.25 M Bu_4NBr) are higher as compared to the slope a_1 for *ortho* and alkyl derivatives (Table III). Therefore, in the case of *meta* and *para* substituents, the ratio of the polar effects in alkaline hydrolysis and in the corresponding IR stretching frequencies,

($\Delta\nu_{\text{CO}}$), is higher compared with the ratio of the inductive effects in alkaline hydrolysis and in the corresponding IR stretching frequencies, ($\Delta\nu_{\text{CO}}$), for *ortho* and alkyl derivatives. The slope a for *meta* and *para* derivatives varied with media considerably, more compared with *ortho* and alkyl derivatives (Table III). When going from water to aqueous 2.25 M Bu_4NBr , the a parameter for phenyl esters of *meta*-substituted benzoic acids become larger ca. 0.11 units of a (Table III, lines 1–3). In the same change of the solvent, the increase in the a_1 value for phenyl esters of *ortho*-substituted benzoic acids was 0.03 units of a_1 only (Table III, lines 9–11). The variation of the slope with media characterizes the variation of the substituent effects with the electrophilic solvating power of the solvent. Earlier¹ the *ortho* inductive effect was found to vary with solvent electrophilicity ca. three times less than the *meta* and *para* polar effect.

The magnitudes of the parameters a_1 (or a) found with Eqs (3)–(6) (Table III) coincide quite well with the corresponding ratios of the polar or inductive effects in alkaline hydrolysis (AH) and in the IR frequencies of the carbonyl group, $\Delta\nu_{\text{CO}}$: $a = \rho_{\text{m,p}}(\text{AH})/\rho_{\text{m,p}}(\text{IR})$, $a_1 = \rho_{\text{I(ortho)}}(\text{AH})/\rho_{\text{I(ortho)}}(\text{IR})$, $a_1 = \rho_{\text{I(Alk)}}(\text{AH})/\rho_{\text{I(Alk)}}(\text{IR})$ (Table II, Eq. (7)). In the case of phenyl esters of *ortho*-substituted benzoic acids the susceptibility to the resonance effect, $a_{2(\text{ortho})}$, determined according to Eq. (5) (Table III, lines 9–11) is almost the same as found with Eq. (3) for a solvent considered (Table II).

In the case of phenyl esters of *ortho*-substituted benzoic acids and alkyl benzoates the sensibility to the steric effect, $a_{3(\text{ortho})}$, and $a_{3(\text{Alk})}$ in Table III show the dependence on solvent: $a_{3(\text{ortho})} = \delta(\text{AH}) + a_1\delta(\text{IR})$, $a_{3(\text{Alk})} = \delta(\text{AH}) - a_1\delta(\text{IR})$ ¹⁴. The steric terms, $a_{3(\text{ortho})}E_s^{\text{B}}$, for *ortho*-substituted phenyl benzoates calculated with Eq. (5) (Table III, lines 17–19) are equal to the corresponding values for alkaline hydrolysis (Table III, lines 17–19).

Comparison of the substituent effects on the $\log k$ values and $\Delta\nu_{\text{CO}}$ shows that, in general, the same structural factors affect the reaction rates of alkaline hydrolysis of esters, as well as the esters IR carbonyl stretching wavenumbers, $\Delta\nu_{\text{CO}}$. The positive value of the slope a_1 (or a) in Eqs (3)–(6) (Table III) indicate, that both the rates of alkaline hydrolysis of esters and the IR carbonyl stretching wavenumbers, $\Delta\nu_{\text{CO}}$, increase with increasing σ values of the corresponding substituent. The rate increase and the higher values of IR carbonyl stretching wavenumbers, $\Delta\nu_{\text{CO}}$ due to electron-withdrawing substituents is attributed to the decrease in the ester ground state resonance stabilization caused by the diminished contributions of resonance forms^{14,29}.

The steric term in alkaline hydrolysis of *ortho*-substituted and alkyl esters decreases the rate while the *ortho* and alkyl substituents disfavour the formation of the tetrahedral intermediate considered as rate limiting^{30,31}. In

the case of phenyl esters of *ortho*-substituted benzoic acids, the IR stretching frequencies of the carbonyl group, $(\nu_{\text{CO}})_{\text{ortho}}$, due to the steric influence of *ortho* substituents, are shifted to the higher values. The positive steric term found for $(\Delta\nu_{\text{CO}})_{\text{ortho}}$ in the case of the *cis* conformers of phenyl esters of *ortho*-substituted benzoic acids was considered as a measure of the steric inhibition of resonance between of benzene ring in the benzoyl part and the carbonyl group caused by bulky *ortho* substituents¹⁴.

Conclusions

In alkaline hydrolysis of phenyl esters of *meta*- and *para*-substituted benzoic acids in aqueous 0.5 and 2.25 M Bu₄NBr, the dependence of the reaction rates on the substituent effects was found to be well correlated with the Hammett equation. The log *k* values for *ortho*-substituted derivatives correlated with the Charton equation, Eq. (2). In alkaline hydrolysis of phenyl esters of substituted benzoic acids, X-C₆H₄CO₂C₆H₅, the polar substituent effects grow with decreasing electrophilicity^{7,8}, ΔE_s , of the solvent. In alkaline hydrolysis of phenyl esters of substituted benzoic acids, X-C₆H₄CO₂C₆H₅, variations of the *meta* and *para* polar substituent effects as well as the *ortho* inductive effects with the solvent were observed approximately to the same extent as found earlier in alkaline hydrolysis of substituted phenyl esters of benzoic acid, C₆H₅CO₂C₆H₄-X. The log *k* values of alkaline hydrolysis for *ortho* derivatives showed good correlation with the IR carbonyl stretching frequencies, $(\Delta\nu_{\text{CO}})_{\text{ortho}}$, in case the additional resonance and the steric terms were included. The relationships obtained between the log *k* values and $\Delta\nu_{\text{CO}}$ might have the practical value because they enable to predict the reaction rates for alkaline hydrolysis in case the corresponding ν_{CO} values are available.

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