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Prediction of ortho substituent effect in alkaline hydrolysis of phenyl esters of substituted benzoic acids in aqueous acetonitrile

Research Article

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Abstract: The second-order rate constants k for the alkaline hydrolysis of phenyl esters of *meta*-, *para*- and *ortho*-substituted benzoic acids, X-$C_6H_4CO_2C_6H_5$, in aqueous 50.9% acetonitrile have been measured spectrophotometrically at 25°C. The log k values for *meta* and *para* derivatives correlated well with the Hammett $\sigma_{m,p}$ substituent constants. The log k values for *ortho*-substituted phenyl benzoates showed good correlations with the Charton equation, containing the inductive, σ_I, resonance, σ°_R, and steric, E_s^B, and Charton υ substituent constants. For *ortho* derivatives the predicted $(\log k_X)_{calc}$ values were calculated with equation $(\log k_{ortho})_{calc} = (\log k^H_{AN})_{exp} + 0.059 + 2.19\sigma_I + 0.304\sigma^\circ_R + 2.79E_s^B - 0.0164\Delta E\sigma_I - 0.0854\Delta E\sigma^\circ_R$, where ΔE is the solvent electrophilicity, $\Delta E = E_{AN} - E_{H2O} = -5.84$ for aqueous 50.9% acetonitrile. The predicted $(\log k_X)_{calc}$ values for phenyl *ortho*-, *meta*- and *para*-substituted benzoates in aqueous 50.9% acetonitrile at 25°C precisely coincided with the experimental log k values determined in the present work.

The substituent effects from the benzoyl moiety and aryl moiety were compared by correlating the log k values for the alkaline hydrolysis of phenyl esters of substituted benzoic acids, X-$C_6H_4CO_2C_6H_5$, in various media with the corresponding log k values for substituted phenyl benzoates, $C_6H_5CO_2C_6H_4$-X.

Keywords: *Ortho effect • Phenyl esters of benzoic acids • Correlation equations • Solvent effect • Substituent effects*

1. Introduction

Earlier we investigated the dependence of the *ortho, meta,* and *para* substituent effects on the solvent electrophilicity (ΔE), polarity (ΔY) and polarizability (ΔP) parameters in the alkaline hydrolysis of substituted phenyl benzoates [1,2] containing substituents in acyl and aryl moiety, $C_6H_5CO_2C_6H_4$-X, X-$C_6H_4CO_2C_6H_5$, as well as in phenyl tosylates [3] $CH_3C_6H_4SO_2OC_6H_4$-X, and alkyl benzoates [4], $C_6H_5CO_2$-R, including log k values for various aqueous media (water, aqueous 80% DMSO, 2.25 M Bu_4NBr, 1.0 M Bu_4NBr, 0.5 M Bu_4NBr, 5.3 M $NaClO_4$ and 4.8 M NaCl).

The variation of the *ortho* inductive, *ortho* resonance, *meta* and *para* polar substituent effects with solvent were found to be mainly dependent on the solvent electrophilicity parameter [5-11], ΔE, characterizing the hydrogen-bond donating power of the solvent. The *meta* and *para* polar, *ortho* inductive and resonance substituent effects were found to vary with the solvent electrophilicity, ΔE_S, nearly to the same extent in the alkaline hydrolysis of substituted phenyl benzoates containing substituents at the phenyl and benzoyl moiety [1,2], as in the alkaline hydrolysis of substituted phenyl tosylates, $CH_3C_6H_4SO_2OC_6H_4$-X [3].

In the alkaline hydrolysis of phenyl esters of substituted benzoic acids, X-$C_6H_4CO_2C_6H_5$, at 25°C the dependence of the *meta*, *para* polar, *ortho* inductive and resonance substituent effects on the solvent electrophilicity, ΔE, calculated using log k values for various solvents (water, aqueous 50% DMSO, 2.25 M Bu_4NBr, 1.0 M Bu_4NBr, 0.5 M Bu_4NBr, 5.3 M $NaClO_4$) was found to be expressed as follows [2]:

$$\Delta\log k_{m,p} = \log k^X - \log k^H = (0.010 \pm 0.023) + (1.77 \pm 0.04)\sigma - (0.0683 \pm 0.0055)\Delta E\sigma \quad (1)$$

$R = 0.995$, $s = 0.087$, $s_0 = 0.108$, $n/n_0 = 55/55$

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$$\Delta\log k_{ortho} = \log k^X - \log k^H = (0.059 \pm 0.055) + (2.19 \pm 0.07)\sigma_I + (0.304 \pm 0.089)\sigma^\circ_R + (2.79 \pm 0.09)E_s^B - (0.0164 \pm 0.0064)\Delta E\sigma_I - (0.0854 \pm 0.0114)\Delta E\sigma^\circ_R \quad (2)$$

$R = 0.986$, $s = 0.114$, $s_0 = 0.167$, $n/n_0 = 63/63$

In Eqs. 1 and 2 ΔE is the solvent electrophilicity parameter, $\Delta E = E_S - E_{H2O}$ [5-11], characterizing the hydrogen-bond donating power of the solvent, E_s^B is the steric substituent constant of *ortho* substituents.

In the alkaline hydrolysis of substituted phenyl benzoates [1,2] and tosylates [3] the variation of the *ortho* inductive term with the solvent electrophilicity, E_S, was found to be approximately 2-3 fold smaller than that for *para* and *meta* substituents, while the *ortho* resonance term appeared to vary with the solvent electrophilicity nearly similarly to that for *para* substituents. The steric term of *ortho* substituents in the alkaline hydrolysis of substituted phenyl benzoates was approximately independent of solvent parameters [1,2].

In our previous work [12] we compared the predicted rate constants, k_{calc}, with the experimental rate constants, k_{exp}, in the alkaline hydrolysis of *ortho-, para-* and *meta*-substituted phenyl benzoates containing substituents in aryl moiety, $C_6H_5CO_2C_6H_4$-X, in aqueous 50.9% (v/v) acetonitrile at 25°C. The predicted rates, k_{calc}, in the alkaline hydrolysis of substituted phenyl benzoates, $C_6H_5CO_2C_6H_4$-X, in aqueous 50.9% (v/v) CH_3CN (AN) at 25°C were calculated as sum (Eq. 3) that consisted of the experimental log k_{exp} value for un-substituted derivative (X = H) in aqueous 50.9% (v/v) CH_3CN (AN) at 25°C and the substituent effect component $(\Delta\log k^X)_{calc}$ calculated for the corresponding *ortho*, *meta* and *para* substituted derivatives with Eqs. 4 and 5 describing the variation of the substituent effect with the solvent electrophilicity parameter at 25°C using for aqueous 50.9% CH_3CN the solvent electrophilicity parameter, $\Delta E = -5.84$:

$$(\log k^X)_{calc} = (\log k^H{}_{AN})_{exp} + (\Delta\log k^X)_{calc} \quad (3)$$

$$\Delta\log k_{m,p} = \log k^X - \log k^H = (0.024 \pm 0.023) + (1.136 \pm 0.042)\sigma^\circ - (0.0741 \pm 0.0054)\Delta E\sigma^\circ \quad (4)$$

$R = 0.988$, $s = 0.088$, $s_0 = 0.162$, $n/n_0 = 44/44$

$$(\Delta\log k_{ortho})^X = \log k^X - \log k^H = (0.017 \pm 0.070) + (1.569 \pm 0.089)\sigma_I + (0.934 \pm 0.117)\sigma^\circ_R + (1.076 \pm 0.125)\Delta E_s^B - (0.0299 \pm 0.0082)\Delta E\sigma_I - (0.0691 \pm 0.0132)\Delta E\sigma^\circ_R \quad (5)$$

$R = 0.976$, $s = 0.122$, $s_0 = 0.217$, $n/n_0 = 39/39$

It was interesting to check up whether also in substituted phenyl benzoates containing *ortho*, *meta* and *para* substituents in the benzoyl moiety, X-$C_6H_4CO_2C_6H_5$, the experimental rate constants, k, for the alkaline hydrolysis in aqueous 50.9% CH_3CN at 25°C coincide with the predicted rate constants, k_{calc}, when the solvent dependent substituent effect was calculated with equations 1 and 2 characterizing the variation of the substituent effect with the solvent electrophilicity parameter ΔE at 25°C. It was also interesting to compare how the *ortho* inductive effect and *para* and *meta* polar effect vary in going from pure water to aqueous 50.9% CH_3CN in acyl-substituted phenyl benzoates, X-$C_6H_4CO_2C_6H_5$, and in substituted phenyl benzoates, $C_6H_5CO_2C_6H_4$-X, containing substituents in the aryl part.

For that aim in the present work the additional rates for the alkaline hydrolysis of *ortho*-, *para*- and *meta*-substituted phenyl benzoates, X-$C_6H_4CO_2C_6H_5$, containing substituents in benzoyl part (X = H, 4-NO_2, 3-NO_2, 3-Cl, 4-Cl, 4-F, 4-CH_3, 4-OCH_3, 2-NO_2, 2-CN, 2-F, 2-Cl, 2-I, 2-Br, 2-CF_3, 2-OCH_3, 2-CH_3) were measured in aqueous 50.9% (v/v) acetonitrile at 25°C. For the alkaline hydrolysis of *ortho*-substituted phenyl benzoates containing substituents in benzoyl moiety, the kinetic data in aqueous acetonitrile solutions are not available in the literature. For *para*- and *meta*-substituted phenyl benzoates the rates of the alkaline hydrolysis has been previously determined in aqueous 10% [13], 31% [14], 33% [15] and 50% CH_3CN [16]. Earlier the rates of the alkaline hydrolysis of *para*-substituted phenyl benzoates in aqueous 50% (v/v) CH_3CN have been determined in 0.02 M phosphate buffer at 25°C [16].

To compare the influence of substituent effects from the benzoyl moiety with that from aryl moiety the log k values for the alkaline hydrolysis of phenyl esters of substituted benzoic acids, X-$C_6H_4CO_2C_6H_5$, in various media were correlated with the corresponding log k values for substituted phenyl benzoates, $C_6H_5CO_2C_6H_4$-X.

2. Experimental procedure

The preparation procedure and characteristics of phenyl esters of substituted benzoic acids, X-$C_6H_4CO_2C_6H_5$, the technique of kinetic measurements and the purification of reagents are described earlier [17,18]. More detailed description of synthesis of phenyl esters of substituted benzoic acids was given in [17] and references cited therein. For kinetic mesurements in aqueous 50.9% (v/v) acetonitrile, 0.10 M NaOH solutions were used. Kinetics was measured spectrophotometrically as described earlier [18]. The measurements were repeated and the arithmetic means of the corresponding second-order rate constants ($dm^3\ mol^{-1}\ s^{-1}$) were calculated. The second-

Tabel 1. The second-order rate constants k ($dm^3\ mol^{-1}\ s^{-1}$) for alkaline hydrolysis of phenyl esters of *ortho*-, *meta*-, and *para*-substituted benzoic acids, X-$C_6H_4CO_2C_6H_5$, in aqueous 50.9% (v/v) CH_3CN at 25°C[a].

X	λ (nm)[b]	k ($dm^3\ mol^{-1}\ s^{-1}$)[c]	X	λ (nm)[b]	k ($dm^3\ mol^{-1}\ s^{-1}$)[c]
2-NO_2	274	0.105 ± 0.007	H	290	0.0261 ± 0.0013
2-CN	255	0.728 ± 0.022	4-NO_2	290	1.08 ± 0.06
2-F	250	0.117 ± 0.011	3-NO_2	290	0.777 ± 0.047
2-Cl	255	0.0471 ± 0.0048	3-Cl	290	0.110 ± 0.003
2-Br	255	0.0447 ± 0.0035	4-Cl	290	0.0863 ± 0.0020
2-I	255	0.0289 ± 0.0042	4-F	290	0.0442 ± 0.0036
2-CF_3	240	0.00542 ± 0.00048	4-CH_3	290	0.0118 ± 0.0012
2-OCH_3	280	0.00966 ± 0.00020	4-OCH_3	290	0.00482 ± 0.00014
2-CH_3	255	0.00340 ± 0.00013			

[a]*Aqueous 0.10 (mol dm^{-3}) sodium hydroxide was used.*
[b]*λ is the wavelength used in the kinetic measurements.*
[c]*The mean values of the second-order rate constants and their standard deviations.*

order rate constants, k ($dm^3\ mol^{-1}\ s^{-1}$) for the alkaline hydrolysis of phenyl esters of *ortho*-, *meta*- and *para*-substituted benzoic acids, X-$C_6H_4CO_2C_6H_5$, in aqueous 50.9% (v/v) acetonitrile at 25°C and the wavelength λ used in the spectrophotometric kinetic measurements are listed in Table 1.

3. Calculation details

The log k values for the alkaline hydrolysis of phenyl esters of substituted benzoic acids, X-$C_6H_4CO_2C_6H_5$, in aqueous 50.9% (v/v) acetonitrile at 25°C (Table 1) were treated according to the Hammett [19,20] and the Charton [21] equations, (Eqs. 6 and 7) using the Hammett σ [20], the Taft inductive σ_I [22,23], resonance σ°_R ($\sigma^\circ_R = \sigma^\circ_p - \sigma_I$) [22,24], and steric E_s^B [17,25-27] substituent constants

$$\log k_{m,p} = \log k_o + \rho_{m,p}\sigma \qquad (6)$$

$$\log k_{ortho} = \log k_o + (\rho_I)_{ortho}\sigma_I + (\rho^\circ_R)_{ortho}\sigma^\circ_R + \delta_{ortho}E_s^B \qquad (7)$$

As the steric constants for *ortho* substituents E_s^B constants ($E_s^B = \log k_H{}^X - \log k_H{}^H$, where $k_H{}^X$ and $k_H{}^H$ are the rate constants for the acidic hydrolysis of *ortho*-substituted and unsubstituted phenyl benzoates in water at 50 °C, $E_s^B < 0$) [17,25-27] were used. For comparison, in the case of *ortho* derivatives the Charton steric scale of υ [26,28,29] calculated on the basis of the van der Waals radii, r_v, was used as well.

As the measure of electrophilicity of solvents, the E_S values of Koppel and Palm [4-11] were used. The values of ΔE are the differences in electrophilicities on going from pure water to the corresponding aqueous binary solution, $\Delta E = E_S - E_{H2O}$ (E_{H2O} = 21.74 [4-11]). For 50.9% (v/v) aqueous acetonitrile $\Delta E = E_{50.9\%\ CH3CN} - E_{H2O}$ = 15.9 – 21.74 = –5.84 was used [12].

The log k values of the alkaline hydrolysis of phenyl esters of substituted benzoic acids, X-$C_6H_4CO_2C_6H_5$, in 50.9% aqueous acetonitrile at 25°C (Table 1) were correlated with the corresponding carbonyl IR stretching frequencies, $\Delta\nu_{CO}$ [30], the carbonyl carbon ^{13}C NMR chemical shifts, $\Delta\delta_{CO}$ [26], and the carbonyl oxygen ^{17}O NMR chemical shifts, $\Delta\delta(^{17}O)$ [31], using the following relationships:

$$\log k_{para} = \log k_H + a_{1(para)}(\Delta\nu_{CO})_X + a_{2(para)}\Delta\sigma^+_R(\sigma^+_R) \qquad (8)$$

$$\log k_{para} = \log k_H + a_{1(para)}(\Delta\delta_{CO})_X + a_{2(para)}\Delta\sigma^+_R(\sigma^+_R) \qquad (9)$$

$$\log k_{para} = \log k_H + a_{1(para)}\Delta\delta(^{17}O)_X + a_{2(para)}\Delta\sigma^+_R(\sigma^+_R) \qquad (10)$$

$$\log k_{ortho} = \log k_H + a_{1(ortho)}(\Delta\nu_{CO})_X + a_{2(ortho)}\sigma^\circ_R + a_{3(ortho)}E_s^B \qquad (11)$$

$$\log k_{ortho} = \log k_H + a_{1(ortho)}(\Delta\delta_{CO})_X + a_{2(ortho)}\sigma^\circ_R + a_{3(ortho)}E_s^B \qquad (12)$$

$$\log k_{ortho} = \log k_H + a_{1(ortho)}\Delta\delta(^{17}O)_X + a_{2(ortho)}\sigma_R(\sigma^+_R) + a_{3(ortho)}E_s^B \qquad (13)$$

In Eqs. 8-13 $(\Delta\nu_{CO})_X = (\nu_{CO})_X - (\nu_{CO})_H$, $(\Delta\delta_{CO})_X = (\delta_{CO})_X - (\delta_{CO})_H$ and $\Delta\delta(^{17}O)_X = \delta(^{17}O)_X - \delta(^{17}O)_H$, $\Delta\sigma^+_R = \sigma^+_{para} - \sigma^\circ$, $\sigma^+_R = \sigma^+_{para} - \sigma_I$, $\sigma_R = \sigma_{para} - \sigma_I$, where σ^+_{para} are the Brown and Okamoto substituent constants σ^+ for *para* substituents [20,32,33]. The substituent constants $\Delta\sigma^+_R$, σ^+_R and σ_R are the characteristics of direct conjugation between the reaction centre and the electron-donating substituent.

Table 2. Correlation of the log *k* values for the alkaline hydrolysis of phenyl esters of *ortho*-, *meta*-, and *para*-substituted benzoic acids, X-$C_6H_4CO_2C_6H_5$, in aqueous 50.9% (v/v) CH_3CN (Table 1) and pure water [17] at 25°C with Eqs. 6 and 7.

Eq.	log k_0	$\rho_{m,p}$	$(\rho_I)_{ortho}$	$(\rho_R)_{ortho}$	δ_{ortho}	R[a]	s[b]	n[c]
				In aqueous 50.9% (v/v) CH_3CN				
6	–1.620 ± 0.042	2.09 ± 0.10	–	–	–	0.992	0.101	8
7	–1.549 ± 0.051	–	2.42 ± 0.08	0.55 ± 0.09	2.93 ± 0.11	0.997	0.054	10
	–1.594 ± 0.101	–	2.43 ± 0.16	0.54 ± 0.19	–1.31 ± 0.10	0.988	0.108	10[d]
				In water[e]				
6	–0.451 ± 0.011	1.72 ± 0.03	–	–	–	0.999	0.033	10
	–0.433 ± 0.045	1.71 ± 0.05	2.24 ± 0.08	0.24 ± 0.10	2.54 ± 0.12	0.995	0.072	20[f]
7	–0.333 ± 0.078	–	2.13 ± 0.12	0.31 ± 0.13	2.67 ± 0.16	0.992	0.085	11
	–0.356 ± 0.102	–	2.12 ± 0.10	0.44 ± 0.10	–1.26 ± 0.10	0.987	0.113	10[d]

[a]*R is correlation coefficient.*
[b]*s is the standard deviation.*
[c]*n is the number of points remaining after exclusion of significantly deviating points.* [d]*Charton steric constants scale of* υ *was used. For 2-CF_3 substituent steric constant* υ = 1.24 *was used.*
[e]*Reference [17].*
[f]*Data were treated with the Hammett-Charton combined equation [17].*

The data processing was carried out using a multiple parameter linear least-squares (LLSQ) procedure [34]. The results of the data treatment with Eqs. 6-13 are presented in Tables 2 and 5.

4. Results and discussion

4.1. Influence of substituents in acyl moiety

In going from pure water to aqueous 50.9% (v/v) acetonitrile the rates of the alkaline hydrolysis for all phenyl esters of *meta*-, *para*- and *ortho*-substituted benzoic acids, X-$C_6H_4CO_2C_6H_5$, measured in the present work at 25ºC were retarded more than 10-fold (Table 1). The retardation of the rates was larger for esters with electron-donating substituents than that for esters with electron-withdrawing substituents what is similar to the corresponding rates of substituted phenyl benzoates containing substituents in phenyl moiety, $C_6H_5CO_2C_6H_4$-X [12].

Similar to previous works carried out earlier in water [17], aqueous 50% DMSO [35-37], 2.25M Bu_4NBr [37], 1.0 M Bu_4NBr [2], 0.5 M Bu_4NBr [37] and 5.3 M $NaClO_4$ [2], the contribution of the *meta* and *para* polar effects to the rates in the alkaline hydrolysis of phenyl esters of substituted benzoic acids, X-$C_6H_4CO_2C_6H_5$, in aqueous 50.9% (v/v) CH_3CN at 25°C (Table 1) was described precisely with the Hammett equation (Eq. 14, Table 2):

$$\log k_{m,p} = (-1.620 \pm 0.042) + (2.09 \pm 0.10)\sigma \quad (14)$$
$$R = 0.992,\ s = 0.101,\ n = 8$$

The log k values for phenyl esters of *ortho*-substituted benzoic acids, X-$C_6H_4CO_2C_6H_5$, in aqueous 50.9% CH_3CN at 25°C (Table 1) showed good correlation with the Charton equation [Eq. 15, Table 2]:

$$\log k_{ortho} = (-1.549 \pm 0.051) + (2.42 \pm 0.08)\sigma_I + (0.55 \pm 0.09)\sigma^\circ_R + (2.93 \pm 0.11)E_s^B \quad (15)$$
$$R = 0.997,\ s = 0.054,\ n = 10$$

When the Charton steric scale of υ (υ > 0) was used in Eq. 7, we obtained the susceptibility to the *ortho* steric effects ca. twice lower than in Eq. 15 (δ_{ortho} = -1.31, Table 2).

Earlier the substituent polar effects were found to grow on moving from water to solutions with the reduced electrophilic solvating power as compared to water and substituent polar effects diminished in going from water to solutions with the stronger electrophilic solvating power [1-4,12,30,37,40]. In the previous work for aqueous 50.9% (v/v) CH_3CN the value of the calculated solvent electrophilicity, $\Delta E_S = E_S - E_{H2O}$, as characteristic of the hydrogen-bond donating power of the solvent, ΔE_S = –5.84, was proposed [12]. Thus, in transition from pure water to aqueous 50.9% (v/v) CH_3CN the electrophilic solvating power was reduced as compared to neat water.

The magnitudes of the *meta* and *para* polar effect and *ortho* inductive effect determined in the present work for the alkaline hydrolysis of phenyl esters of substituted benzoic acids, X-$C_6H_4CO_2C_6H_5$, in aqueous 50.9% (v/v) CH_3CN at 25°C (Table 2, Eqs. 14 and 15) also showed increase in the substituent polar effects

when going from water to solvent with decreased electrophilic solvating power as compared to water. In going from water to aqueous 50.9% (v/v) CH_3CN, the increase in the susceptibility to the *meta* and *para* polar effect by ca. 0.37 units of ρ was observed. In neat water and in aqueous 50.9% (v/v) CH_3CN at 25°C the values of $\rho_{m,p}$ were 1.72 [17] and 2.09, respectively (Table 2). In transition from water to aqueous 50.9% (v/v) CH_3CN, the increase in the susceptibility to the *ortho* inductive effect was ca. twice less as compared to *para* derivatives i.e. by ca. 0.2 units of ρ (Table 2). The increase in the *ortho* resonance effect with solvent was approximately 0.3 units of ρ what is comparable to that for *para* derivatives (Table 2).

In the previous work we found in the alkaline hydrolysis of substituted phenyl esters of benzoic acid, $C_6H_5CO_2C_6H_4$-X, containing substituents in the aryl moiety [12], that during transition from water to aqueous 50.9% (v/v) CH_3CN at 25°C the susceptibility to the *meta* and *para* polar effect ($\Delta\rho_{m,p}$ = 0.40 [12]) and *ortho* inductive effect grows exactly by the same extent ($(\Delta\rho_I)_{ortho}$ = 0.20) as we found that in the present paper for the alkaline hydrolysis of phenyl esters of substituted benzoic acids, X-$C_6H_4CO_2C_6H_5$. Though the polar effect of substituents in reaction series considered exhibited ca. 1.56-fold difference in water [12,17], the susceptibility to the *meta* and *para* polar effect and *ortho* inductive effect during transition from water to aqueous 50.9% (v/v) CH_3CN was found to change by the same magnitude of $\Delta\rho$.

In the alkaline hydrolysis of substituted phenyl benzoates, X-$C_6H_4CO_2C_6H_5$, the change in the *ortho*, *meta* and *para* substituent polar effects in going from water to aqueous 50.9% (v/v) CH_3CN is comparable with that when going from water to aqueous 0.5 M Bu_4NBr [37]. In aqueous 0.5 M Bu_4NBr at 25°C and aqueous 50.9% (v/v) CH_3CN at 25°C the corresponding the $\rho_{m,p}$, $(\rho_I)_{ortho}$, $(\rho_R)_{ortho}$ and δ values for the alkaline hydrolysis of substituted phenyl benzoates, X-$C_6H_4CO_2C_6H_5$, were 2.06, 2.20, 0.82, 2.96 and 2.09, 2.42, 0.55 and 2.93, respectively [37]. On moving from water (E_S = 21.74) to aqueous 0.5 M Bu_4NBr (E_S = 16.83 [4]) a decrease in the electrophilic solvating power ($\Delta E_S = E_S - E_{H20}$ = –4.91 [4]) similar to that for aqueous 50.9% (v/v) CH_3CN (ΔE_S = –5.84) was observed as well.

We found that rates in the alkaline hydrolysis of phenyl esters of *ortho*-substituted benzoic acids in aqueous 50.9% (v/v) CH_3CN reduced due to steric restrictions nearly by the same extent (δ = 2.93, steric substituent constants $E_s^B < 0$ used, Table 2) as earlier has been found in pure water (δ = 2.54, 2.67 [17]), aqueous 0.5 M Bu_4NBr (δ = 2.96 [37]), aqueous 1.0 M Bu_4NBr (δ= 2.84 [2,37]), aqueous 2.25 M Bu_4NBr (δ = 3.07 [37]), and aqueous 5.3 M $NaClO_4$ at 25°C (δ = 2.58 [37]). The susceptibility to the steric effect of *ortho* substituents found in the present work for the alkaline hydrolysis of substituted phenyl benzoates, X-$C_6H_4CO_2C_6H_5$, in aqueous 50.9% (v/v) CH_3CN (δ = 2.93), similarly to previous works [2,17], confirmed that the susceptibility to the steric effect is approximately independent of the solvent electrophilicity parameter.

4.2. Correlation of the rates of the alkaline hydrolysis of phenyl esters of substituted benzoic acids, X-$C_6H_4COOC_6H_5$, with the corresponding kinetic data for substituted phenyl benzoates, $C_6H_5COOC_6H_4$-X

To compare in substituted phenyl benzoates the influence of substituent effects from the benzoyl moiety with that in the aryl moiety, we correlated the rates of the alkaline hydrolysis of phenyl esters of *ortho*-, *meta*- and *para*-substituted benzoic acids, X-$C_6H_4COOC_6H_5$, in variuos media (aqueous 2.25 M Bu_4NBr [37], 0.5 M Bu_4NBr [37], 50.9% (v/v) CH_3CN, pure water [17], aqueous 5.3 M $NaClO_4$ [2]) with the corresponding kinetic data for *ortho*-, *meta*- and *para*-substituted phenyl benzoates, $C_6H_5COOC_6H_4$-X, in the same media at 25°C as follows (Table 3):

$$(\log k_{m,p})_{Ac} = (\log k_o)_{Ac} + c_1(\Delta\log k_{m,p})_{Ar} + c_2\Delta\sigma_R \quad (16)$$

$$(\log k_{ortho})_{Ac} = (\log k_o)_{Ac} + c_1(\Delta\log k_{ortho})_{Ar} + c_2\sigma^\circ_R + c_3E_s^B \quad (17)$$

where

$$(\Delta\log k_{m,p})_{Ar} = (\log k_{m,p})_{Ar} - \log k_H \quad (18)$$

$$(\Delta\log k_{ortho})_{Ar} = (\log k_{ortho})_{Ar} - \log k_H \quad (19)$$

In Eq. 16 $\Delta\sigma_R = \sigma_{para} - \sigma^\circ$ was used. In the case of the *meta* derivatives the resonance term equals to zero i.e. $c_2\Delta\sigma_R = 0$ In Eqs. 16-19 and in Table 3 by Ac is denoted phenyl esters of *ortho*-, *meta*- and *para*-substituted benzoic acids, X-$C_6H_4COOC_6H_5$, containing substituents in the benzoyl moiety and Ar denotes *ortho*-, *meta*- and *para*-substituted phenyl benzoates, $C_6H_5COOC_6H_4$-X, with substituents in aryl part. In the case of *para* and *ortho* derivatives in Eqs. 16 and 17 the additional resonance term was included. For the *ortho* derivatives besides the additional resonance term the steric term was included as well. The kinetic data of the alkaline hydrolysis of *ortho*-, *meta*- and *para*-substituted phenyl benzoates, $C_6H_5COOC_6H_4$-X, in aqueous 2.25 M Bu_4NBr, 0.5 M Bu_4NBr, 50.9% (v/v) CH_3CN, pure water,

Table 3. Results of the correlation of the kinetic data for alkaline hydrolysis of phenyl esters of *ortho*-, *meta*- and *para*-substituted benzoic acids, X-$C_6H_4COOC_6H_5$, in aqueous 2.25 M Bu_4NBr (1) [37], 0.5 M Bu_4NBr (2) [37], 50.9% (v/v) CH_3CN (3) (Table 1), pure water (4) [17] and aqueous 5.3 M $NaClO_4$ (5) [2] with corresponding kinetic data of *ortho*-, *meta*- and *para*-substituted phenyl benzoates, $C_6H_5COOC_6H_4$-X [1,12,38-40], with Eqs. 16 and 17 at 25°C.

Scales	log k_0	c_1	c_2	c_3	R[a]	s[b]	n[c]
	phenyl esters of *ortho*-substituted benzoic acids						
$\Delta\log k_{Ar}(1)$, σ°_R, E_s^B	–1.109 ± 0.118	1.14 ± 0.08	–0.923 ± 0.251	0.910 ± 0.334	0.991	0.097	6
	–1.107 ± 0.112	1.13 ± 0.07	–0.884 ± 0.241	0.948 ± 0.323	0.990	0.095	7[d]
$\Delta\log k_{Ar}(2)$, σ°_R, E_s^B	–0.639 ± 0.161	1.39 ± 0.16	–0.963 ± 0.400	1.70 ± 0.35	0.973	0.170	9
	–0.639 ± 0.143	1.39 ± 0.15	–0.977 ± 0.359	1.69 ± 0.32	0.975	0.156	10[e]
$\Delta\log k_{Ar}(3)$, σ°_R, E_s^B	–1.511 ± 0.168	1.29 ± 0.15	–1.16 ± 0.40	1.74 ± 0.37	0.969	0.181	9
	–1.511 ± 0.148	1.30 ± 0.14	–1.17 ± 0.36	1.74 ± 0.33	0.971	0.166	10[f]
$\Delta\log k_{Ar}(4)$, σ°_R, E_s^B	–0.360 ± 0.128	1.36 ± 0.14	–0.986 ± 0.297	1.47 ± 0.29	0.977	0.140	9
	–0.360 ± 0.114	1.36 ± 0.14	–0.985 ± 0.265	1.47 ± 0.26	0.978	0.128	10[g]
$\Delta\log k_{Ar}(5)$, σ°_R, E_s^B	–1.050 ± 0.051	1.34 ± 0.05	–0.801 ± 0.098	0.923 ± 0.157	0.996	0.045	6
	–1.052 ± 0.093	1.36 ± 0.10	–0.842 ± 0.178	0.871 ± 0.286	0.985	0.084	7[h]
	phenyl esters of *meta*- and *para*-substituted benzoic acids[i]						
$\Delta\log k_{Ar}(1)$, $\Delta\sigma_R$	–1.132 ± 0.073	1.19 ± 0.05	1.66 ± 0.76	–	0.994	0.116	8[j]
$\Delta\log k_{Ar}(2)$, $\Delta\sigma_R$	–0.689 ± 0.056	1.42 ± 0.07	2.19 ± 0.59	–	0.992	0.092	9
$\Delta\log k_{Ar}(3)$, $\Delta\sigma_R$	–1.633 ± 0.135	1.47 ± 0.16	2.35 ± 1.33	–	0.992	0.113	7[k]
$\Delta\log k_{Ar}(4)$, $\Delta\sigma_R$	–0.427 ± 0.057	1.41 ± 0.09	2.76 ± 0.38	–	0.992	0.094	10
$\Delta\log k_{Ar}(5)$, $\Delta\sigma_R$	–1.081 ± 0.057	1.57 ± 0.11	1.90 ± 0.70	–	0.987	0.105	8[l]

[a] *R is correlation coefficient.*
[b] *s is the standard deviation.*
[c] *n is the number of points remaining after exclusion of significantly deviating points.*
[d] *In aqueous 2.25 M Bu_4NBr for 2-Br derivative $\Delta\log k^{Ar} = 0.241$, obtained from $\log k_{Ar} = -0.855$ calculated with equation: $\log k_{Ar} = -1.016 + 2.19\sigma_I + 2.05\sigma^\circ_R + 1.61E_s^B$.*
[e] *In aqueous 0.5 M Bu_4NBr for 2-Br derivative $\Delta\log k_{Ar} = 0.14$ obtained from $\log k_{Ar} = -0.635$ what was calculated with equation: $\log k_{Ar} = -0.727 + 1.61\sigma_I + 1.37\sigma^\circ_R + 1.38E_s^B$ [1].*
[f] *In aqueous 50.9% MeCN for 2-Br derivative $\Delta\log k_{Ar} = 0.305$ determined from $\log k_{Ar} = -1.275$ what was calculated with equation: $\log k_{Ar} = -1.581 + 1.78\sigma_I + 1.34\sigma^\circ_R + 0.90E_s^B$ [12].* [g] *In pure water for 2-Br derivative used $\Delta\log k_{Ar} = 0.285$, obtained when $\log k_{Ar} = -0.155$ what was calculated with equation: $\log k^{Ar} = -0.393 + 1.58\sigma_I + 1.11\sigma^\circ_R + 0.97E_s^B$ [12].*
[h] *In aqueous 5.3 M $NaClO_4$ for 2-Br derivative $\Delta\log k_{Ar}$ was 0.275, obtained from $\log k_{Ar} = -0.635$ what was calculated according to equation: $\log k_{Ar} = -0.917 + 1.508\sigma_I + 0.661\sigma^\circ_R + 1.005E_s^B$ [40].*
[i] *$\Delta\sigma_R = \sigma_{para} - \sigma^\circ$ was used.*
[j] *In aqueous 2.25 M Bu_4NBr for 4-CH_3 and 4-OCH_3 derivatives $\Delta\log k_{Ar} = -0.338$ and $\Delta\log k_{Ar} = -0.361$ obtained using $\log k_{Ar} = -1.434$ and $\log k_{Ar} = -1.457$, respectively, calculated from equation: $\log k^{Ar} = -1.106 + 2.34\sigma^\circ$ [38].*
[k] *For 4-Cl derivative $\Delta\log k_{Ar} = 0.416$ obtained from $\log k_{Ar} = -1.167$ were used.*
[l] *In aqueous 5.3 M $NaClO_4$ for 4-CH_3 and 4-OCH_3 derivatives $\Delta\log k_{Ar} = -0.119$ and $\Delta\log k_{Ar} = -0.128$ calculated from $\log k^{Ar} = -1.029$ and $\log k_{Ar} = -1.039$ respectively, obtained from equation: $\log k_{Ar} = -0.894 + 0.961\sigma^\circ$ [40].*

and aqueous 5.3 M $NaClO_4$ at 25°C were taken from [1,12,38,39,40].

In the case of *meta* and *para* derivatives (Eq. 16, Table 3) the constant c_1 represents the ratio for the corresponding polar effects in two reaction series considered: $(c_1)_{m,p} = \rho^\circ_{Ac}/\rho^\circ_{Ar}$ and $(c_2)_{m,p} = (\rho_R)_{Ac} - c_1(\rho_R)_{Ar}$. In the case of *ortho* derivatives parameter c_1 (Eq. 17, Table 3) is the ratio for the corresponding inductive effects: $(c_1)_{ortho} = (\rho_I)_{Ac}/(\rho_I)_{Ar}$, $(c_2)_{ortho} = (\rho^\circ_R)_{Ac} - c_1(\rho^\circ_R)_{Ar}$, and $c_3 = \delta_{Ac} - c_1(\delta)_{Ar}$, where δ is the susceptibility to steric effect of *ortho* substituents.

When going from aqueous 5.3 M $NaClO_4$ ($E_S = 25.53$ [4]) to solvent with less hydrogen-bond donor capacity (electrophilicity) like aqueous 2.25 M Bu_4NBr ($E_S = 8.11$ [4]) in the case of both *meta*, *para* derivatives and *ortho* derivatives a considerable decrease in the relation $(c_1)_{m,p} = \rho^\circ_{Ac}/\rho^\circ_{Ar}$ and $(c_1)_{ortho} = (\rho_I)_{Ac}/(\rho_I)_{Ar}$, was detected (Table 3). In aqueous 5.3 M $NaClO_4$ the relation of the polar effects in the alkaline hydrolysis of phenyl esters of *meta*- and *para*-substituted benzoic acids, X-$C_6H_4COOC_6H_5$, and *meta*- and *para*-substituted phenyl benzoates, $C_6H_5COOC_6H_4$-X, was found to be $(c_1)_{m,p} = \rho^\circ_{Ac}/\rho^\circ_{Ar} = 1.57$ (Table 3), in aqueous 2.25 M Bu_4NBr the same ratio for *meta* and *para* derivatives was $(c_1)_{m,p} = \rho^\circ_{Ac}/\rho^\circ_{Ar} = 1.19$ (Table 3). In the case of *ortho* derivatives the variation of the relation, $(c_1)_{ortho} = (\rho_I)_{Ac}/(\rho_I)_{Ar}$, with solvent was less as compared to that for *para* and *meta* derivatives. For *ortho* derivatives

the magnitudes of $(c_1)_{ortho} = (\rho_I)_{Ac}/(\rho_I)_{Ar}$ in aqueous 5.3 M $NaClO_4$ and aqueous 2.25 M Bu_4NBr were 1.36 and 1.14, respectively (Table 3). Using for aqueous 2.25 M Bu_4NBr the values of $(\rho)_{Ac}$ = 2.71 [37] and ρ°_{Ar} = 2.34 [38] we obtained the magnitude $(c_1)_{m,p}$ = 1.16. The value of $(c_1)_{m,p}$ = 1.23 when ρ°_{Ar} = 2.19 [41] was used.

In the alkaline hydrolysis of phenyl benzoates in transition from water to solvent with the stronger electrophilic solvating power (S1) as compared to water (aqueous 5.3 M $NaClO_4$), the *para*, *meta* polar and *ortho* inductive effects were found to decrease as compared to water: $\rho_{S1} - \rho_{H2O} = -\Delta\rho$ [1,2,40]. In going from water to solvent with weaker electrophilic solvating power (S2) increase in the corresponding polar effects of *para*, *meta* and *ortho* substituents was observed: $\rho_{S1} - \rho_{H2O} = \Delta\rho$ [1,2,12,37]. Therefore for *para* and *meta* derivatives we found (Table 3):

$$[(\rho^\circ_{Ac})_{H2O} - (\Delta\rho^\circ_{Ac})_{S1}]/[(\rho^\circ_{Ar})_{H2O} - (\Delta\rho^\circ_{Ar})_{S1}] > > [(\rho^\circ_{Ac}/\rho^\circ_{Ar})_{H2O} = 1.41] > > [(\rho^\circ_{Ac})_{H2O} + (\Delta\rho^\circ_{Ac})_{S2}]/[(\rho^\circ_{Ar})_{H2O} + (\Delta\rho^\circ_{Ar})_{S2}] \quad (20)$$

In Eq. 20 the electrophilic power of solvents (S) diminishes as follows $E_{S1} > E_{H2O} > E_{S2}$.

The magnitudes of c_1 for various solvents (Table 3, Eqs. 16, 17, 20), varying with solvent electrophilicity, E_S, once more prove that the variation of the substituent polar effects in benzoyl part when going from one solvent to another, occurs approximately by the same extent as compared to that in aryl part and the change of the $\Delta\rho$ values is not proportional to the relation $c_1 = (\rho^\circ_{Ac}/\rho^\circ_{Ar})_{H2O}$ = 1.41 in water. Earlier [1,2] using multilinear relationships involving the log *k* values for various solvents (Eqs. 1, 2, 4, 5), the variation of the *meta, para* polar and *ortho* inductive substituent effects with the solvent electrophilicity, ΔE_S, was found to be nearly the same in both the alkaline hydrolysis of substituted phenyl benzoates, $C_6H_5COOC_6H_4$-X, and the alkaline hydrolysis of phenyl esters substituted benzoic acids, X-$C_6H_4COOC_6H_5$. The corresponding susceptibilities of the *meta*, *para* polar effect and *ortho* inductive effect to variation of solvent electrophilicity were: $(c_{m,p})_{Ar} = (-0.0741 \pm 0.0054)$, $(c_{ortho})_{Ar} = -(0.0299 \pm 0.0082)$ (Eqs. 4 and 5), $(c_{m,p})_{Ac} = (-0.0683 \pm 0.0055)$ and $(c_{ortho})_{Ac} = (-0.0164 \pm 0.0064)$ (Eqs. 1 and 2) at 25°C.

The constant $c_2 = (\rho^\circ_R)_{Ac} - c_1(\rho^\circ_R)_{Ar}$ for *ortho* derivatives (Eq. 17, Table 3) differs essentially from that for *para* derivatives. The magnitudes of c_2 for *ortho* derivatives appeared to be negative in the ranges (-1.17)-(-0.80), while in the case of *para* derivatives the corresponding c_2 values are positive in the ranges 1.66-2.76. In substituted phenyl benzoates with *ortho* substituents in benzoyl part the resonance term was found to be negligible (ρ°_R = 0.31 ± 0.13 in water at 25°C [37]). In phenyl benzoates containing substituents in aryl moiety the resonance term is comparable with that for *para* derivatives (ρ°_R = 1.070 ± 0.104 in water at 25°C [17]). Having in the case of *ortho* derivatives $(\rho^\circ_R)_{Ac} < (\rho^\circ_R)_{Ar}$ in Table 3, we obtained $(\rho^\circ_R)_{Ac} < c_1(\rho^\circ_R)_{Ar}$ as well. Although the contribution of the resonance term for *ortho* substituents in the benzoyl part of phenyl benzoates in water was negligible (ρ°_R = 0.31 ± 0.13 in water at 25°C [37]), the resonance term from the *ortho* position was found to vary with solvent approximately by the same extent as from the aryl part [2,3] (Table 2). In water, aqueous 5.3 M $NaClO_4$, 50.9% (v/v) CH_3CN, 0.5 M Bu_4NBr, 2.25 M Bu_4NBr for *ortho* derivatives the corresponding $(\rho^\circ_R)_{Ac}$ and $(\rho^\circ_R)_{Ar}$ at 25ºC were: 0.31 [37], 0 [2], 0.55 (Table 2), 0.82 [37], 1,42 [37] and 1.11 [12] or 0.95 [1], 0.66 [40], 1.34 [12], 1.37 [1], 2.27 [38], respectively.

4.3. Comparison of the experimental and predicted rates for the in alkaline hydrolysis of phenyl esters of substituted benzoic acids

To compare the experimental rate constants for the phenyl esters of substituted benzoic acids, X-$C_6H_4CO_2C_6H_5$, in aqueous 50.9% (v/v) acetonitrile (AN) at 25°C (v/v) (Table 1), with the predicted log k_{calc} values, we calculated the predicted log k_{calc} values as sum of the experimental log k_{exp} value for unsubstituted derivative (X = H) in aqueous 50.9% (v/v) acetonitrile (AN) at 25°C and the substituent effect component $(\Delta\log k^X_{AN})_{calc}$ as follows:

$$(\log k^X_{AN})_{calc} = (\log k^H_{AN})_{exp} + (\Delta\log k^X_{AN})_{calc} \quad (21)$$

In Eq. 21 the substituent effect term $(\Delta\log k^X_{AN})_{calc}$ was calculated from equation describing the variation of the substituent effect with the solvent electrophilicity parameter, ΔE, (Eqs. 1 and 2) using for aqueous 50.9% CH_3CN the solvent electrophilicity parameter, $\Delta E = E_{AN} - E_{H20} = -5.84$ [12]:

$$(\log k_{m,p})_{calc} = (\log k^H_{AN})_{exp} + 0.010 + 1.77\sigma - 0.0683\Delta E\sigma \quad (22)$$

$$(\log k_{ortho})_{calc} = (\log k^H_{AN})_{exp} + 0.059 + 2.19\sigma_I + 0.304\sigma^\circ_R + 2.79E_s^B - 0.0164\Delta E\sigma_I - 0.0854\Delta E\sigma^\circ_R \quad (23)$$

Comparison of the experimental rate constants and the predicted log k_{calc} values for phenyl esters of substituted benzoic acids, X-$C_6H_4CO_2C_6H_5$, in aqueous 50.9% (v/v) acetonitrile (AN) at 25°C (v/v) are shown

in Table 4. The predicted $(\log k^X)_{calc}$ values for *meta*, *para* and *ortho* derivatives calculated with Eqs. 21-23 coincide precisely with the log k_{exp} values determined experimentally for aqueous 50.9% (v/v) CH_3CN at 25°C in the present work (Eqs. 24 and 25, Table 4):

$$(\log k_{m,p})_{exp} = -(0.091 \pm 0.061) + (0.965 \pm 0.045)(\log k_{m,p})_{calc} \quad (24)$$

$R = 0.993$, $s = 0.101$, $s_o = 0.122$, $n/n_o = 8/8$

$$(\log k_{ortho})_{exp} = (0.062 \pm 0.059) + (1.030 \pm 0.037)(\log k_{ortho})_{calc} \quad (25)$$

$R = 0.994$, $s = 0.074$, $s_o = 0.107$, $n/n_o = 10/10$

4.4. Correlation of the log k values for alkaline hydrolysis of phenyl esters of substituted benzoic acids with the carbonyl IR stretching frequencies, $\Delta\nu_{CO}$, the carbonyl carbon ^{13}C NMR chemical shifts, $\Delta\delta_{CO}$, and the carbonyl oxygen ^{17}O NMR chemical shifts, $\Delta\delta(^{17}O)$

Similar to previous works [12,37] the substituent effects in the alkaline hydrolysis of phenyl esters of *para*- and *ortho*-substituted benzoic acids, X-$C_6H_4CO_2C_6H_5$, in aqueous 50.9% (v/v) CH_3CN at 25°C correlated precisely with the substituent effects in the corresponding carbonyl IR stretching frequencies, $\Delta\nu_{CO}$ [30], carbonyl carbon ^{13}C NMR chemical shifts, $\Delta\delta_{CO}$ [26], and carbonyl oxygen ^{17}O NMR chemical shifts, $\Delta\delta(^{17}O)$ [31] using Eqs. 8-13 (Table 5).

To compare the substituent effects on the rates of the alkaline hydrolysis of *ortho* derivatives with those in the corresponding IR carbonyl stretching frequencies, $\Delta\nu_{CO}$, substituent-induced carbonyl carbon ^{13}C NMR chemical shifts, $\Delta\delta_{CO}$, and the carbonyl oxygen ^{17}O NMR chemical shifts, $\Delta\delta(^{17}O)$, the additional resonance and steric terms were involved and in the case of the $\Delta\delta(^{17}O)$ values correlation was carried out separately for esters containing +*R* substituents (Eqs. 11-13, Table 5, $0.995 > R > 0.962$). The log *k* values for *para* derivatives correlated well with the corresponding values of $\Delta\nu_{CO}$, $\Delta\delta_{CO}$, and $\Delta\delta(^{17}O)$ values when the additional resonance term, $a_{2(para)}\,\Delta\sigma^+_R(s^+_R)$ was included (Eqs. 8-10, Table 5, $0.999 > R > 0.982$).

Correlation equations obtained (Table 5) enable to predict the rates of the alkaline hydrolysis of substituted benzoates, X-$C_6H_4CO_2C_6H_5$, in aqueous 50.9% (v/v) CH_3CN at 25°C using IR carbonyl stretching frequencies, $\Delta\nu_{CO}$, the carbonyl carbon ^{13}C NMR chemical shifts, $\Delta\delta_{CO}$, and the carbonyl ^{17}O NMR chemical shifts, $\delta(^{17}O)$, values for esters considered. Similarly, on the bases of correlations given in Table 5 the values of the $\Delta\nu_{CO}$, $\Delta\delta_{CO}$ and $\Delta\delta(^{17}O)$ values could be predicted using the corresponding log *k* values of the alkaline hydrolysis for phenyl benzoates, X-$C_6H_4CO_2C_6H_5$, in aqueous 50.9% (v/v) CH_3CN at 25°C.

The log *k* values of the alkaline hydrolysis for phenyl esters of *ortho*-substituted benzoic acids, X-$C_6H_4CO_2C_6H_5$, in aqueous 50.9% (v/v) at 25°C showed good correlations with the IR stretching frequencies, $\Delta\nu_{CO}$, the carbonyl carbon ^{13}C NMR chemical shifts, $\Delta\delta_{CO}$, and the carbonyl oxygen ^{17}O NMR chemical shifts, $\Delta\delta(^{17}O)$, as follows (Eqs. 26-28, Table 5):

$$\log k_{ortho} = (-1.567 \pm 0.132) + (0.153 \pm 0.008)\Delta\nu_{CO} + (0.730 \pm 0.124)\sigma^\circ_R + (6.62 \pm 0.25)E_s^B \quad (26)$$

$R = 0.995$, $s = 0.060$, $n = 8$

$$\log k_{ortho} = (-1.629 \pm 0.164) - (0.590 \pm 0.068)\Delta\delta_{CO} + (1.12 \pm 0.32)\sigma^\circ_R + (0.819 \pm 0.409)E_s^B \quad (27)$$

$R = 0.962$, $s = 0.187$, $n = 10$

For *ortho* derivatives with +*R* substituents (X = H, 2-F, 2-Cl, 2-Br, 2-CH_3, 2-OCH_3) we obtained (Eq. 28, Table 5):

$$\log k_{ortho} = (-1.608 \pm 0.245) + (0.126 \pm 0.008)\Delta\delta(^{17}O) - (1.28 \pm 0.17)\sigma_R + (12.6 \pm 0.7)E_s^B \quad (28)$$

$R = 0.992$, $s = 0.071$, $n = 6$

In the case of *para* derivatives we obtained (Table 5):

$$\log k_{para} = (-1.616 \pm 0.065) + (0.325 \pm 0.011)\Delta\nu_{CO} - (1.64 \pm 0.15)\Delta\sigma^+_R \quad (29)$$

$R = 0.999$, $s = 0.045$, $n = 5$

$$\log k_{para} = (-1.569 \pm 0.110) - (0.872 \pm 0.088)\Delta\delta_{CO} + (1.40 \pm 0.24)\Delta\sigma^+_R \quad (30)$$

$R = 0.987$, $s = 0.131$, $n = 6$

$$\log k_{para} = (-1.651 \pm 0.164) + (0.268 \pm 0.021)\Delta\delta(^{17}O) - (2.43 \pm 0.40)\Delta\sigma^+_R \quad (31)$$

$R = 0.992$, $s = 0.102$, $n = 6$

The slope a_1 in Eqs. 8-10, 29-31 (Table 5) for *para* derivatives represents the ratio of the polar effect in the alkaline hydrolysis and in the corresponding IR stretching frequencies, $\Delta\nu_{CO}$, the carbonyl carbon ^{13}C NMR chemical shifts, $\Delta\delta_{CO}$ and the carbonyl oxygen ^{17}O NMR chemical shifts, $\Delta\delta(^{17}O)$, respectively: $a_1 = \rho(AH)/\rho(IR)$, $a_1 = \rho(AH)/\rho(\delta_{CO})$, $a_1 = \rho(AH)/\rho(\delta(^{17}O))$.

In the case of *ortho* derivatives the parameter a_1 in Eqs. 11-13 and 26-28 (Table 5) is the ratio of the corresponding inductive effects: $a_1 = \rho_I(AH)/\rho_I(IR)$,

Table 4. The calculated and experimental log k values and differences Δ[a].

X	log k_{exp}	log k_{calc}	Δ	X	log k_{exp}	log k_{calc}	Δ
H	–1.583	–1.548	–0.035	H	–1.583	–1.584	0.001
2-NO_2	–0.979	–0.975	–0.004	4-NO_2	0.033	0.173	–0.140
2-CN	–0.138	–0.194	0.056	3-NO_2	–0.110	–0.044	–0.066
2-F	–0.932	–1.049	0.117	3-Cl	–0.959	–0.782	–0.177
2-Cl	–1.327	–1.288	–0.039	4-F	–1.355	–1.454	0.099
2-Br	–1.350	–1.401	0.051	4-Cl	–1.064	–1.085	0.021
2-I	–1.539	–1.566	0.027	4-CH_3	–1.928	–1.953	0.025
2-CF_3	–2.266	–2.161	–0.105	4-OCH_3	–2.318	–2.170	–0.148
2-CH_3	–2.469	–2.445	–0.014				
2-OCH_3	–2.015	–2.141	0.126				

[a] $\Delta = \log k_{exp} - \log k_{calc}$

Table 5. Correlation of the log *k* values for the alkaline hydrolysis of phenyl esters of *ortho*- and *para*-substituted benzoic acids, X-$C_6H_4CO_2C_6H_5$, in aqueous 50.9% (v/v) CH_3CN at 25°C with the carbonyl IR stretching frequencies [30], $\Delta\nu_{CO}$, the carbonyl carbon ^{13}C NMR chemical shifts [26], $\Delta\delta_{CO}$, and the carbonyl oxygen ^{17}O NMR chemical shifts [31], $\Delta\delta(^{17}O)$, using Eqs. 8-13.

Scales	log k_0	a_1	a_2	a_3	R[a]	s[b]	n[c]
			phenyl esters of *ortho*-substituted benzoic acids				
$\Delta\nu_{CO}$, σ^o_R, E_s^B	–1.486 ± 0.279	0.135 ± 0.016	0.391 ± 0.257	5.97 ± 0.53	0.972	0.146	9[d,e]
	–1.567 ± 0.132	0.153 ± 0.008	0.730 ± 0.124	6.62 ± 0.25	0.995	0.060	8[d,e,f]
$\Delta\delta_{CO}$, σ^o_R, E_s^B	–1.629 ± 0.164	–0.590 ± 0.068	1.12 ± 0.32	0.819 ± 0.409	0.962	0.187	10[g]
			+*R* substituents				
$\Delta\delta(^{17}O)$, σ_R, E_s^B	–1.608 ± 0.245	0.126 ± 0.008	–1.28 ± 0.17	12.6 ± 0.7	0.992	0.071	6[h]
$\Delta\delta(^{17}O)$, σ^+_R, E_s^B	–1.597 ±0.217	0.139 ± 0.007	–0.926 ± 0.097	14.0 ± 0.7	0.994	0.058	6[h]
			phenyl esters of *para*-substituted benzoic acids				
$\Delta\nu_{CO}$, $\Delta\sigma^+_R$	–1.616 ± 0.065	0.325 ± 0.011	–1.64 ± 0.15	–	0.999	0.045	5[i]
$\Delta\nu_{CO}$, $\Delta\sigma^+_R$	–1.602 ± 0.085	0.325 ± 0.015	–1.65 ± 0.21	–	0.997	0.062	6[j]
$\Delta\nu_{CO}$, σ^+_R	–1.555 ± 0.158	0.320 ± 0.029	–0.950 ± 0.242	–	0.990	0.117	6[j]
$\Delta\delta_{CO}$, $\Delta\sigma^+_R$	–1.569 ± 0.110	–0.872 ± 0.088	1.40 ± 0.24	–	0.987	0.131	6
$\Delta\delta_{CO}$, σ_R	–1.645 ± 0.122	–0.872 ± 0.103	1.23 ± 0.25	–	0.982	0.153	6
$\Delta\delta_{CO}$, σ^+_R	–1.585 ± 0.082	–0.865 ± 0.066	0.874 ± 0.110	–	0.993	0.099	6
$\Delta\delta(^{17}O)$, $\Delta\sigma^+_R$	–1.651 ± 0.164	0.268 ± 0.021	–2.43 ± 0.40	–	0.992	0.102	6
$\Delta\delta(^{17}O)$, σ^+_R	–1.504 ± 0.362	0.237 ± 0.047	–1.09 ± 0.55	–	0.954	0.246	6
	–1.620 ± 0.102	0.191 ± 0.014	–0.975 ± 0.143	–	0.992	0.064	5[k]

[a] *R is correlation coefficient.*
[b] *s is the standard deviation.*
[c] *n is the number of points remaining after exclusion of significantly deviating points.*
[d] *For 2-I derivative $\Delta\nu_{CO}$ = 13.3 was used (ν_{CO} = 1755.9 [26]).*
[e] *The 2-CH_3 derivative was omitted.*
[f] *The 2-OCH_3 derivative was excluded.*
[g] *For 2-Br derivative δ_{CO} = 164.12 [36], 2-I derivative δ_{CO} = 164.57 [36] and for unsubstituted derivative δ_{CO} = 165.04 [26] were used.*
[h] *The 2-I derivative was excluded.*
[i] *The 4-F derivative was excluded.*
[j] *For 4-F derivative $\Delta\nu_{CO}$ = –0.8 was used. The value of $\Delta\nu_{CO}$ = –0.8 for 4-F derivative was obtained using ν_{CO} = 1741.8 calculated from the relation: $\nu_{CO} = 1742.3 + 7.41\sigma^+$ [30].*
[k] *The 4-NO_2 derivative was excluded.*

$a_1 = \rho_I(AH)/\rho_I(\delta_{CO})$, $a_1 = \rho_I(AH)/\rho_I(\delta(^{17}O))$, $a_2 = \rho_R(AH) - a_1\rho_R(IR)$, $a_2 = \rho_R(AH) - a_1\rho_R(\delta_{CO})$, $a_2 = \rho_R(AH) - a_1\rho_R(\delta(^{17}O))$ and $a_3 = \delta(AH) - a_1\delta(IR)$, $a_3 = \delta(AH) - a_1\delta(\delta_{CO})$, $a_3 = \delta(AH) - a_1\delta(\delta(^{17}O))$, where alkaline hydrolysis is denoted by (AH), the infrared stretching frequencies by (IR), the carbonyl carbon ^{13}C NMR substituent chemical shifts by δ_{CO}, and the carbonyl ^{17}O NMR chemical shifts, by $\Delta\delta(^{17}O)$. The susceptibility to the steric influence of *ortho* substituents is denoted by δ.

The parameters a_1 found for *ortho* derivatives are lower as compared to the parameter a_1 for *para* derivatives. Therefore, in the case of *ortho* derivatives, the ratios $a_1 = \rho_I(AH)/\rho_I(IR)$ and $a_1 = \rho_I(AH)/\rho_I(\Delta\delta(^{17}O))$ are lower compared with the same ratios for *para* derivatives (Table 5).

The magnitudes of the parameters a_1, a_2, and a_3 found with Eqs. 11-13 (Table 5) coincide quite well with the magnitudes of a_1, a_2, and a_3 calculated using the corresponding ρ_I, ρ_R and δ values in the alkaline hydrolysis (AH), the IR frequencies of the carbonyl group, $\Delta\nu_{CO}$, the carbonyl carbon ^{13}C NMR substituent chemical shifts, $\Delta\delta_{CO}$, and the carbonyl ^{17}O NMR chemical shifts, $\Delta\delta(^{17}O)$. Using in the case of *ortho*-substituted benzoates $\rho_I(AH) = 2.42$, $\rho_R(AH) = 0.55$, $\delta(AH) = 2.93$ (Table 2), $\rho_I(IR) = 18.4$ [30], $\rho_R(IR) = 0$ [30], and $\delta(IR) = -23.2$ [30], we obtained $a_1 = 0.131$, $a_2 = 0.55$, and $a_3 = 5.97$. The corresponding values of a_1, a_2 and a_3 calculated with Eqs. (11) are 0.135, 0.391 and 5.97, respectively (Table 5). Using in phenyl esters of *ortho*-substituted benzoic acids for the carbonyl ^{17}O NMR chemical shifts, $\delta(^{17}O)$, the values $\rho_I(\delta(^{17}O)) = 17.3$, $\rho_R(\delta(^{17}O)) = 9.68$ and $\delta(\delta(^{17}O)) = -81.2$ we obtained the magnitudes of the parameters $a_1 = 0.140$, $a_2 = -0.795$ and $a_3 = 14.3$, respectively. The corresponding values of a_1, a_2 and a_3 calculated with Eq. 13 in Table 5 are 0.139, -0.926 and 14.0, respectively.

The positive values of the parameter a_1 in Eqs. 26, 28, 29, 31 and Table 5 prove that in phenyl esters of substituted benzoic acids the substituent-induced log *k* values of the alkaline hydrolysis, the IR carbonyl stretching frequencies, (ν_{CO}), and $\delta(^{17}O)$ values grow with increase of the inductive effects of substituents included. The negative value of the parameter a_1 in correlation of the log *k* values with the carbonyl carbon ^{13}C NMR chemical shifts, $\Delta\delta_{CO}$, (Eqs. 9, 12, 27, 30, Table 5) shows that in the alkaline hydrolysis the influence of inductive effect on the log *k* values is opposite to that on the ^{13}C NMR chemical shifts, $\Delta\delta_{CO}$. With increase in σ_I values of substituents the log *k* values of the alkaline hydrolysis were found to increase but the carbonyl carbon ^{13}C NMR chemical shifts, $\Delta\delta_{CO}$, were found to diminish when the electron-attracting substituents are involved [26].

Similarly to previous works [12,37] the obtained good correlations of the log *k* values of the alkaline hydrolysis of X-$C_6H_4CO_2C_6H_5$ in aqueous 50.9% (v/v) CH_3CN at 25°C with the corresponding IR carbonyl stretching frequencies, $\Delta\nu_{CO}$, carbonyl carbon ^{13}C NMR chemical shifts, $\Delta\delta_{CO}$, and the carbonyl oxygen NMR $\Delta\delta(^{17}O)$ values (Eqs. 26-31, Table 5) demonstrate that the same substituent factors (inductive, resonance, steric) are responsible for the substituent-induced effects in all four processes considered: the alkaline hydrolysis, the infrared stretching frequencies, the carbonyl carbon ^{13}C NMR chemical shifts, $\Delta\delta_{CO}$, and NMR $\Delta\delta(^{17}O)$ chemical shifts.

5. Conclusions

The experimental rate constants, *k*, measured in the present work for the alkaline hydrolysis of phenyl esters of *ortho-, para- and meta*-substituted benzoic acids with substituents in benzoyl moiety, X-$C_6H_4CO_2C_6H_5$ (X = H, 4-NO_2, 3-NO_2, 3-Cl, 4-Cl, 4-F, 4-CH_3, 4-OCH_3, 2-NO_2, 2-CN, 2-F, 2-Cl, 2-I, 2-Br, 2-CF_3, 2-OCH_3, 2-CH_3), in aqueous 50.9% (v/v) acetonitrile at 25°C (Table 1) coincided precisely with the corresponding predicted k_{calc} values. The values of the calculated rate constants, k_{calc}, were found with equation: $(\log k^X_{AN})_{calc} = (\log k^H_{AN})_{exp} + (\Delta\log k^X_{AN})_{calc}$, where the magnitude of the substituent effect, $(\Delta\log k^X_{AN})_{calc}$ was determined from the relationship characterizing the variation of the *meta*, *para* and *ortho* substituent effects with the solvent electrophilicity, ΔE_S, at 25°C (Eqs. 1, 2, 22, 23). For aqueous 50.9% (v/v) acetonitrile the solvent electrophilicity, $\Delta E = E_{AN} - E_{H20} = -5.84$ [12] was used. When going from pure water to aqueous 50.9% acetonitrile the *meta* and *para* polar substituent effects and *ortho* inductive and resonance effects in the alkaline hydrolysis of phenyl esters of substituted benzoic acids, X-$C_6H_4CO_2C_6H_5$, became stronger exactly to the same extent as it was found in the previous work for the alkaline substituted phenyl benzoates, $C_6H_5CO_2C_6H_4$-X, containing substituents in aryl moiety. Correlations of log *k* values in the alkaline hydrolysis of phenyl benzoates containing substituents in benzoyl moiety with the corresponding log *k* values for phenyl benzoates involving substituents in aryl part in various media (Eqs. 16 and 17, Table 3) once more demonstrate that in phenyl benzoates the polar effects of substituents vary with solvent approximately to the same extent in the case of substituents in the benzoyl part and in aryl part.

Good correlations obtained between the log *k* values of the alkaline hydrolysis of X-$C_6H_4CO_2C_6H_5$ in aqueous 50.9% (v/v) CH_3CN at 25°C and the corresponding IR

carbonyl stretching frequencies, $\Delta\nu_{CO}$, carbonyl carbon ^{13}C NMR chemical shifts, $\Delta\delta_{CO}$, and the carbonyl oxygen NMR $\Delta\delta(^{17}O)$ values (Eqs. 26-31, Table 5) demonstrate that the same substituent factors (inductive, resonance, steric) are responsible for the substituent-induced effects in all four processes considered: the alkaline hydrolysis, the infrared stretching frequencies, the carbonyl carbon ^{13}C NMR chemical shifts, $\Delta\delta_{CO}$, and NMR $\Delta\delta(^{17}O)$ chemical shifts.

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