

**SEPARATION OF *ortho* INDUCTIVE, RESONANCE AND STERIC TERMS IN ALKALINE HYDROLYSIS OF SUBSTITUTED PHENYL BENZOATES AND PHENYL TOSYLATES**Vilve NUMMERT<sup>1,\*</sup> and Mare PIIRSALU<sup>2</sup>*Institute of Chemical Physics, Tartu University, 51014 Tartu, Jakobi 2, Estonia;**e-mail: <sup>1</sup>vilven@ut.ee, <sup>2</sup>mare@chem.ut.ee*

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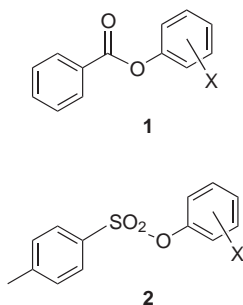
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The second-order rate constants  $k_2$  ( $\text{l mol}^{-1} \text{s}^{-1}$ ) for the alkaline hydrolysis of *meta*-, *para*- and *ortho*-substituted phenyl benzoates  $\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4\text{-X}$  and phenyl tosylates  $4\text{-CH}_3\text{-C}_6\text{H}_4\text{SO}_2\text{OC}_6\text{H}_4\text{-X}$  in aqueous 5.3 M  $\text{NaClO}_4$  have been measured spectrophotometrically at various temperatures. The  $\log k$  values at a single temperature were analysed according to the equations  $\log k_{\text{m,p}} = \log k_0 + (\rho)_{\text{m,p}}^\circ \sigma^\circ$ ,  $\log k_{\text{ortho}} = \log k_0 + (\rho_I)_{\text{ortho}} \sigma_I + (\rho_R)_{\text{ortho}} \sigma_R^\circ + \delta_{\text{ortho}} \upsilon$  and  $\log k_{\text{m,p,ortho}} = \log k_0 + (\rho_I)_{\text{ortho}} \sigma_I + (\rho_I)_{\text{meta}} \sigma_I + (\rho_I)_{\text{para}} \sigma_I + (\rho_R)_{\text{ortho}} \sigma_R^\circ + (\rho_R)_{\text{meta}} \sigma_R^\circ + (\rho_R)_{\text{para}} \sigma_R^\circ + \delta_{\text{ortho}} \upsilon$ . In the case of various temperatures, the equation for data processing involved the additional  $c_1(1/T)$  term and the cross term  $c_{\text{m,p}}(1/T)\sigma^\circ$  or  $c_2(1/T)\sigma_I$  and  $c_3(1/T)\sigma_R^\circ$  different for *ortho*-, *meta*- and *para*-substituted derivatives. As the measure of the steric influence from *ortho* position, the Charton  $\upsilon$  values were used. In the case of a single temperature, the sensitivity to the inductive effect of *ortho* substituents was found to be about 1.7 times (in water 1.5 times) stronger than that of *para* and *meta* substituents in both reaction series studied. The variation of the *ortho* inductive influence with temperature appeared to be more than twice larger than that for *para* substituents. Compared to water, in aqueous 5.3 M  $\text{NaClO}_4$  the inductive effect from *ortho* position was nearly unchanged while the *para* inductive effect was found to be about 0.13 units of  $\rho_I$  smaller in the case of both reaction series studied, though the polar effects in these reaction series differ about two-fold. Due to different variation of the *ortho* and *para* inductive effects with solvent and temperature, the relative increase in the *ortho* effect was observed when going from water to aqueous 5.3 M  $\text{NaClO}_4$ .

**Keywords:** Esters; Phenyl benzoates; Phenyl tosylates; Alkaline hydrolysis; Substituent effects; *ortho* Effects; Kinetics; Chemometrics; Steric effect.

The kinetics of substituted phenyl esters has been in the focus of our interest for many years. We have studied the temperature-dependent substituent effects, (especially *ortho* effect) in the alkaline hydrolysis of *ortho*-, *meta*- and *para*-substituted phenyl benzoates and tosylates in water<sup>1-3</sup>, in aqueous 2.25 M  $\text{Bu}_4\text{NBr}$ <sup>2-5</sup> and in 80% aqueous dimethyl sulfoxide<sup>3,6,7</sup>. For the further extension of our studies on substituent effects dependent on tempera-

ture, in the present paper the kinetics of the alkaline hydrolysis of substituted phenyl benzoates,  $\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4\text{-X}$  (esters **1**) ( $\text{X} = \text{H}$ , 4- $\text{NO}_2$ , 3- $\text{NO}_2$ , 3- $\text{Cl}$ , 4- $\text{F}$ , 3- $\text{CH}_3$ , 3- $\text{NH}_2$ , 2- $\text{NO}_2$ , 2- $\text{F}$ , 2- $\text{Cl}$ , 2- $\text{CH}_3$ , 2- $\text{OCH}_3$ ) and phenyl tosylates, 4- $\text{CH}_3\text{-C}_6\text{H}_4\text{SO}_2\text{OC}_6\text{H}_4\text{-X}$  (esters **2**) ( $\text{X} = \text{H}$ , 4- $\text{NO}_2$ , 3- $\text{NO}_2$ , 3- $\text{Cl}$ , 4- $\text{Cl}$ , 4- $\text{F}$ , 2- $\text{NO}_2$ , 2- $\text{F}$ , 2- $\text{Cl}$ , 2- $\text{CH}_3$ , 2- $\text{OCH}_3$ ) in aqueous 5.3 M  $\text{NaClO}_4$  in broad temperature range has been studied. The purpose of our work was to separate the influence of the induction, resonance and steric terms of *ortho*, *meta* and *para* substituents and to check up, how these terms at a single temperature and dependent on temperature vary during transition from water to aqueous 5.3 M  $\text{NaClO}_4$  which electrophilic solvating power is higher compared to water. It is of interest to compare how vary the inductive and resonance terms with temperature and solvent in the case of the alkaline hydrolysis of benzoates and tosylates as polar effects in these reaction were found to differ in water nearly twice.



<b>1</b>	<b>2</b>	<b>X</b>
<b>a</b>	<b>a</b>	4- $\text{NO}_2$
<b>b</b>	<b>b</b>	3- $\text{NO}_2$
<b>c</b>	<b>c</b>	3- $\text{Cl}$
<b>d</b>	<b>d</b>	4- $\text{F}$
	<b>e</b>	4- $\text{Cl}$
<b>f</b>		3- $\text{CH}_3$
<b>g</b>		3- $\text{NH}_2$
<b>h</b>	<b>h</b>	H
<b>i</b>	<b>i</b>	2- $\text{NO}_2$
<b>j</b>	<b>j</b>	2- $\text{F}$
<b>k</b>	<b>k</b>	2- $\text{Cl}$
<b>l</b>	<b>l</b>	2- $\text{CH}_3$
<b>m</b>	<b>m</b>	2- $\text{OCH}_3$

The log  $k$  values of both the alkaline hydrolysis of tosylates and benzoates in the case of *meta* and *para* substituents were found to be correlated with the  $\sigma^\circ$  substituent constants, but the susceptibility to the polar substituent effect in water exhibited a two-fold difference  $(\rho^\circ_{\text{m,p}})_{\text{Tos}}/(\rho^\circ_{\text{m,p}})_{\text{Benz}} \approx 2$ . In water in both reactions considered, the inductive influence from *ortho* position was found to be 1.5-fold stronger than that from *para* and *meta* position and exhibited two-fold difference as well:  $[(\rho)_{\text{ortho}}]_{\text{Tos}}/[(\rho)_{\text{ortho}}]_{\text{Benz}} \approx 2$ . During transition from water to aqueous 2.25 M  $\text{Bu}_4\text{NBr}$  and aqueous 80% aqueous DMSO media, which electrophilic solvating power is reduced compared to water, the polar effect of *para* and *meta* substituents was enhanced by about 1.0 units of the  $\rho^\circ$  scale in both reaction series considered. The variation of the *ortho* inductive term with solvent and the temperature appeared to be half that of *para* substituents<sup>2</sup>. Due to reduced variation of

*ortho* inductive effect with solvent, compared to that of *para* substituents, a considerable decrease in the *ortho* effect (i.e. the difference  $\log k_{\text{ortho}}^X - \log k_{\text{para}}^X$ ) caused inductive influence, has been observed when going from water to less electrophilic media (aqueous 2.25 M Bu<sub>4</sub>NBr and 80% DMSO).

Therefore it was interesting to check up whether the *ortho* effect, caused by inductive influence, should become in inorganic salt like aqueous 5.3 M NaClO<sub>4</sub> more positive compared to pure water.

Recently kinetics of the alkaline hydrolysis of phenyl benzoates in the micelles of sodium dodecyl sulfate and hexadecyl(trimethyl)ammonium bromide, in 31% aqueous acetonitrile and in 50% aqueous dimethyl sulfoxide has been studied<sup>8-13</sup>. In literature, there are, to our knowledge, no kinetic data on the alkaline hydrolysis of substituted phenyl benzoates and tosylates in aqueous 5.3 M NaClO<sub>4</sub> in broad temperature range. Earlier the rates of the alkaline hydrolysis of substituted phenyl benzoates and tosylates, with few of uncharged substituents, have been measured dependent on the additions of NaClO<sub>4</sub> and NaCl at a single temperature only<sup>14-17</sup>. When going from water to aqueous 5.3 M NaClO<sub>4</sub>, there was found a decrease in the  $(\rho^0)_{\text{m,p}}$  value for the alkaline hydrolysis of substituted phenyl tosylates at 75 °C (for water  $\rho^0_{\text{m,p}} = 1.67$  and for 5.3 M NaClO<sub>4</sub>  $\rho^0_{\text{m,p}} = 1.36$ )<sup>17-19</sup>. The decrease in the  $\rho$  value when going from water to medium which has more pronounced electrophilic properties, is in accordance with the relationship  $(\rho^0_{\text{s}} - \rho^0_{(\text{H}_2\text{O})}) = (-0.0842 \pm 0.0056)(E_{\text{s}} - E_{\text{H}_2\text{O}})$  characterizing the variation of the  $\rho^0$  values with the solvent electrophilicity  $E_{\text{s}}$ -parameters<sup>17,19</sup>.

Earlier<sup>1,3,6</sup> in order to study the substituent effects, especially *ortho* effect dependent on temperature, the  $\log k$  values for the alkaline hydrolysis of *ortho*-, *meta*- and *para*-substituted phenyl tosylates and benzoates at various temperatures have been treated according to the multilinear relationship

$$\begin{aligned} \log k_{\text{m,p,ortho}} &= \log k_0^{\circ} + c_{\text{x(o)m,p,ortho}} \sigma^{\circ} + c_{\text{x(l)ortho}} \sigma_{\text{I}} + c_{\text{T}}(1/T) + \\ &+ c_{\text{x(o)m,p,ortho}}(1/T) \sigma^{\circ} + c_{\text{x(l)ortho}}(1/T) \sigma_{\text{I}} . \end{aligned} \quad (1)$$

The inductive influence of *ortho* substituents was assumed to be different from that of *para* substituents. Therefore the additional  $c_{\text{x(l)ortho}}\sigma_{\text{I}}$  and  $(c_{\text{x(l)T}})_{\text{ortho}}(1/T)\sigma_{\text{I}}$  terms for *ortho*-substituted derivatives were included. In the alkaline hydrolysis of substituted phenyl benzoates<sup>1,6</sup> the corresponding steric terms  $(c_{\text{x(s)}})_{\text{ortho}}E_{\text{s}}^{\text{B}}$  and  $(c_{\text{x(s)T}})_{\text{ortho}}(1/T)E_{\text{s}}^{\text{B}}$  were included as well

( $E_s^B = \log k_{H+X} - \log k_{H+H}$ , 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<sup>2,4,20</sup>). In Eq. (1)  $c_{x(o)m,p,ortho}$  is the susceptibility of the substituent polar effect to temperature variation, common for *ortho*, *meta* and *para* substituents. The whole susceptibility of *ortho* inductive term to variation of temperature is represented as sum ( $c_{x(o)m,p,ortho} + c_{x(l)ortho}$ ). The steric term appeared to be independent of temperature and medium. In pure water, the log *A* values for *meta*- and *para*-substituted derivatives were nearly constant, being independent of the substituent effect (isoentropic reaction series) both in the case of the alkaline hydrolysis of benzoates and tosylates. In water the dependence of the *ortho* inductive term on temperature appeared to correspond to the isokinetic relationship.

The aqueous solutions of inorganic salts are quite different from that of organic salts considering them as the medium for organic reactions. The addition of Bu<sub>4</sub>NBr to water increases the solubility of esters considerably compared to pure water<sup>2</sup> (salting-in effect<sup>21</sup>), but the additions of inorganic salts salt them out. Concentrated quaternary ammonium salts like Bu<sub>4</sub>NBr drastically reduce the electrophilicity of water, changing the value of electrophilicity *E* from 21.7 in water to 9.4 in aqueous 2.25 M Bu<sub>4</sub>NBr<sup>22</sup>. The magnitude of the electrophilicity *E* parameter for aqueous 2.25 M Bu<sub>4</sub>NBr solution is similar to that for aqueous 80% DMSO (*E* = 7.9). It was shown that addition of salts with relatively small inorganic cations, such as NaClO<sub>4</sub> and NaCl, tends to increase the electrophilic solvating power of aqueous methanol ( $N_{MeOH} = 0.216$ ) by 3.8 and 0.7 units for 5 M NaClO<sub>4</sub> and 4 M NaCl, respectively.

## EXPERIMENTAL

The preparation and characteristics of substituted phenyl benzoates (esters **1**) and phenyl tosylates (esters **2**) as well as the technique of kinetic measurements were described earlier<sup>2,4,23-27</sup>. As a reagent, NaOH (Chemapol, analytical grade) was used. A carbon dioxide-free hydroxide solution was prepared<sup>28</sup> from saturated aqueous solution of NaOH by diluting to approximately 0.3 M solution. This solution was refluxed with Ba(OH)<sub>2</sub> to precipitate BaCO<sub>3</sub> and passed through a cation-exchange column (KY-2) in argon atmosphere. The salt, NaClO<sub>4</sub> (Sigma, anhydrous minimum 99%), was dried at an elevated temperature for 12 h and kept in a desiccator over P<sub>2</sub>O<sub>5</sub>. All solutions were prepared using water double distilled from glass and degassed.

The kinetics was measured spectrophotometrically. The reactions were followed using a CF-4A spectrophotometer CF-4A equipped with a photoelectric multiplier and a recorder of the LP type. The slower kinetics of alkaline hydrolysis of phenyl tosylates were followed using a CF-4 spectrophotometer equipped with thermostatted cylindrical cell-holders allowing carry out kinetics at elevated temperatures. All the reactions were carried out in aqueous

5.3 M NaClO<sub>4</sub> medium under the pseudo-first-order conditions using at least a 10-fold sodium hydroxide excess. To avoid the influence of salt effect on the kinetic measurements, a nearly constant alkali concentration was used. Concentrations of NaOH 0.0271 and 0.108 mol l<sup>-1</sup> were used in the kinetic measurements phenyl benzoates (esters **1**) and phenyl tosylates (esters **2**), respectively.

The pseudo-first-order rate constants,  $k_1$  (s<sup>-1</sup>), were determined using the least squares computer program. The second-order rate constants  $k_2$  (l mol<sup>-1</sup> s<sup>-1</sup>) were calculated by dividing the pseudo-first-order rate constants  $k_1$  (s<sup>-1</sup>) by alkali concentration. The kinetic measurements were repeated more than three times for each derivative and the average values of the second-order rate constants  $k_2$  (l mol<sup>-1</sup> s<sup>-1</sup>) were calculated. The  $k_2$  values for substituted phenyl benzoates (esters **1**) and phenyl tosylates (esters **2**) in 5.3 M NaClO<sub>4</sub>, the number of measurements and the wavelength  $\lambda$  used at spectrophotometric kinetic measurements are given in Table I.

### DATA PROCESSING

For study the substituent effects on a single temperature, the log  $k$  values of the alkaline hydrolysis of substituted phenyl benzoates (esters **1**) and phenyl tosylates (esters **2**) at 25 °C were treated according to the Taft Eq. (2) and the modified Charton<sup>29</sup> Eqs (3):

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

$$\log k_{m,p} = \log k_0 + (\rho)_{m,p}^{\circ} \sigma^{\circ} \quad (2)$$

$$\begin{aligned} \log k_{m,p,\text{ortho}} = \log k_0 + (\rho_I)_{\text{ortho}} \sigma_I + (\rho_I)_{\text{meta}} \sigma_I + (\rho_I)_{\text{para}} \sigma_I + \\ + (\rho_R)_{\text{ortho}} \sigma_R^{\circ} + (\rho_R)_{\text{meta}} \sigma_R^{\circ} + (\rho_I)_{\text{para}} \sigma_R^{\circ} + \delta_{\text{ortho}} S. \end{aligned} \quad (3)$$

The activation parameters log  $A$  and activation energy  $E$  values were calculated according to Eq. (4)

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

$$\log k = \log A - (E/2.3RT) . \quad (4)$$

For separation of the influence of the inductive, resonance and steric terms dependent on substitution and temperature, the log  $k$  values were submitted to a regression analysis using Eqs (5) and (6):

TABLE I

The second-order rate constants  $k_2$  for the alkaline hydrolysis of substituted phenyl benzoates (esters **1**) and phenyl tosylates (esters **2**) in aqueous 5.3 M NaClO<sub>4</sub> at various temperatures<sup>a</sup>

Compound	$\lambda^b$ , nm	$T$ , °C	$k_2^c \times 10^3$ mol <sup>-1</sup> s <sup>-1</sup>	$n^d$	Compound	$\lambda^b$ , nm	$T$ , °C	$k_2^c \times 10^3$ mol <sup>-1</sup> s <sup>-1</sup>	$n^d$
<b>1a</b>	404	50	3820±40	9	<b>1g</b>	242	60	1100±20	4
		40	2370±90	4			50	627±6	6
		30	1100±20	4			40	348±10	4
		25	849±10	7			30	171±1	3
		20	617±13	3			25	118±1	3
		15	433±19 <sup>e</sup>	3			15	54.6±1.7	3
<b>1b</b>	272	50	2790±60	8	<b>1h</b>	292	60	1200±60	3
		40	1490±40	3			50	669±11	4
		30	823±15	4			40	377±7	3
		25	587±12	6			30	172±5	4
		20	430±19	4			25	123±3	4
		15	270±6	4			15	59.4±5.0	4
<b>1c</b>	295	60	2820±130	4	<b>1i</b>	420	50	2660±90	3
		50	1510±60	9			40	1550±30	3
		40	850±13	3			30	848±1	3
		25	304±26	6			25	605±7	3
		15	150±11	3			20	468±13	3
<b>1d</b>	300	60	1460±20	3	<b>1j</b>	280	15	318±8	3
		50	897±14	4			60	2530±10	3
		40	466±18	3			50	1390±110	3
		30	234±11	3			40	818±22	3
		25	165±3	3			30	419±26	3
<b>1f</b>	292	60	908±40	3			25	306±22	3
		50	554±9	4			15	132±1	3
		40	321±7	3					
		30	123±2	3					
		25	98.0±1.6	3					

TABLE I  
(Continued)

Compound	$\lambda^b$ , nm	$T$ , °C	$k_2^c \times 10^3$ mol <sup>-1</sup> s <sup>-1</sup>	$n^d$	Compound	$\lambda^b$ , nm	$T$ , °C	$k_2^c \times 10^3$ mol <sup>-1</sup> s <sup>-1</sup>	$n^d$
1k	296	60	1940±20	3	2e	245	50	2.70±0.28 <sup>g</sup>	5
		50	1190±10	3			75	11.8±0.9	4
		40	775±15	3			60	3.66±0.10	3
		25	260±15	6			50	1.52±0.06 <sup>g</sup>	4
		15	123±10	3	2g	237	75	3.94±0.14	3
1l	290	60	467±21	3	2h	290	75	4.51±0.27	8
		50	288±24	4			60	1.56±0.03	3
		40	147±12	5			50	0.605±0.031 <sup>g</sup>	3
		30	69.0±0.4	3			40	0.227±0.001	3
		25	48.2±4.0	9	2i	410	75	443±18	3
1m	292	60	726±10	4			50	95.7±4.0	3
		50	426±7	3			40	46.6±0.5	3
		40	242±1	3			25	12.8±1.5	3
		30	115±4	3	2j	290	75	47.0±1.5	4
2a	410	25	74.6±2.9	3			60	15.1±0.3	3
		15	37.1±0.3	3			50	6.94±0.10	3
		75	97.9±3.2	6			40	3.31±0.32	6
		60	35.3±0.5	3	2k	290	75	34.6±2.6	5
2b	270	50	18.5±0.4	3			60	12.4±0.5	3
		40	6.81±0.44	3			50	5.13±0.02 <sup>g</sup>	4
		25	1.85±0.03	3	2l	290	75	2.76±0.46	3
		75	75.3±2.7	6			60	0.850±0.178 <sup>g</sup>	4
2c	290	60	28.2±1.2	3			50	0.332±0.036 <sup>g</sup>	3
		50	12.8±0.1	3	2m	290	75	5.55±0.36	5
		40	5.18±0.11	3			60	1.97±0.01	4
		75	19.3±0.6 <sup>f</sup>	7			50	0.798±0.027 <sup>g</sup>	4
		60	6.40±0.44	5			40	0.302±0.004 <sup>g</sup>	4

<sup>a</sup> Aqueous 0.0271 M NaOH for esters **1** and aqueous 0.108 M NaOH for esters **2** was used. <sup>b</sup>  $\lambda$  is the wavelength used in kinetic measurements. <sup>c</sup>  $k_2$  is the arithmetic mean value of the second-order rate constants (l mol<sup>-1</sup> s<sup>-1</sup>). <sup>d</sup>  $n$  equals to the number of the remaining  $k_2$  values after exclusion of significantly deviating rate constants in the calculations of arithmetic mean values. <sup>e</sup> The values of rate constants  $k_2$  measured in 0.0108 M NaOH. <sup>f</sup> The values of rate constant  $k_2$  measured in 0.054 M NaOH. <sup>g</sup> 0.195 M NaOH was used.

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

$$\log k_{m,p} = c_0 + c_1\sigma^\circ + c_2(1/T) + c_3(1/T)\sigma^\circ \quad (5)$$

$$\begin{aligned} \log k_{m,p,ortho} = & c_0 + c_{1(ortho)}\sigma_I + c_{2(meta)}\sigma_I + c_{3(para)}\sigma_I + c_{4(ortho)}\sigma_R^\circ + \\ & + c_{5(meta)}\sigma_R^\circ + c_{6(para)}\sigma_R^\circ + c_{7(ortho)}S + c_8(1/T) + c_{9(ortho)}(1/T)\sigma_I + \\ & + c_{10(meta)}(1/T)\sigma_I + c_{11(para)}(1/T)\sigma_I + c_{12(ortho)}(1/T)\sigma_R^\circ + c_{13(meta)}(1/T)\sigma_R^\circ + \\ & + c_{14(para)}(1/T)\sigma_R^\circ. \end{aligned} \quad (6)$$

Equations (2) and (3) include data at a single temperature, Eqs (5) and (6) at various temperatures, respectively. The data only for *meta*- and *para*-substituted derivatives were correlated with Eqs (2) and (5), the data for *meta*- and *para*-substituted phenyl esters simultaneously with *ortho*-substituted esters were treated according to Eqs (3) and (6). The data for only *ortho*-substituted derivatives were treated according to Eqs (3) and (6) to compare the susceptibilities obtained for the inductive, resonance and steric terms for *ortho* substituents with those determined with the simultaneous use of data for *ortho*-, *meta*- and *para*-substituted derivatives. In processing of data for *ortho*-substituted derivatives with Eqs (3) and (6) the  $\log k$  value for the unsubstituted derivative ( $X = H$ ) as standard was included besides the *ortho*-substituted derivatives. The different sensitivity towards substituent effects from *ortho*, *meta* and *para* positions was assumed. In the case of the alkaline hydrolysis of substituted phenyl tosylates (series 2) the steric term  $c_{7(ortho)}S$  was omitted. The steric term of *ortho* substituents in the alkaline hydrolysis of phenyl benzoates was considered independent of temperature and the corresponding cross term  $(1/T)S$  was not included. The Taft polar  $\sigma^\circ$ <sup>30</sup>, inductive  $\sigma_I$ <sup>31</sup>, the resonance  $\sigma_R^\circ$  [ $\sigma_R^\circ = (\sigma^\circ)_{para} - \sigma_I$ ]<sup>32</sup> scales were used at the data processing (see Table II). For comparison, two steric scales were involved: the Charton steric  $\nu$  constants<sup>33</sup> based on van der Waals radii and  $E_s^B$  scale<sup>4</sup> determined as the Taft steric constants  $E_0$ , but for *ortho* substituents in alkyl part of phenyl benzoates (esters 1). Two steric scales gave nearly identical results if  $\nu = 1.39$  for *ortho*-nitro group was used. When the  $\nu$  value for nitro group was 0.35, in data treatment according to Eq. (3) the steric scale for *ortho* substituents was excluded as insignificant.

To the data processing according to Eqs (2) and (3) were submitted the second-order rate constants  $k_2$  of the alkaline hydrolysis of substituted phenyl benzoates (esters 1) and phenyl tosylates (esters 2) at 25 °C in 5.3 M aqueous NaClO<sub>4</sub>, calculated according to the Arrhenius Eq. (4) using the values of activation parameters  $E$  and  $\log A$  listed in Table II. When correlated according to Eqs (5) and (6), the experimental second-order rate constants  $k_2$ , reported in Table I, were used.

The data treatment was carried out using a multiple parameter linear least squares (LLSQ) procedure<sup>34,35</sup>. Significantly deviating points were excluded using a Student criterion. Exclusion of the significantly deviating points was performed on different confidence levels of the  $t$ -test.

The activation parameters for the alkaline hydrolysis of substituted phenyl benzoates and phenyl tosylates in 5.3 M NaClO<sub>4</sub> solution are listed in Table II. The parameters calculated with Eqs (2) and (3) are presented in Table III, the results of data processing, obtained using Eqs (5) and (6) are shown in Table IV.

TABLE II

Substituent parameters used for correlations and the values of activation energy  $E$  (kJ mol<sup>-1</sup>) and  $\log A$  for the alkaline hydrolysis of substituted phenyl benzoates (esters 1) and phenyl tosylates (esters 2) in aqueous 5.3 M NaClO<sub>4</sub> calculated using Eq. (4)

X	$\sigma^O$	$\sigma_I$	$\sigma_R^O$	$\nu$	$E_s^B$	Benzoates <sup>a</sup>		Tosylates <sup>a</sup>	
						$E$ , kJ mol <sup>-1</sup>	$\log A$	$E$ , kJ mol <sup>-1</sup>	$\log A$
4-NO <sub>2</sub>	0.81	0.63	0.19	-	-	48.90±1.49	8.499±0.256	68.86±1.93	9.344±0.315
3-NO <sub>2</sub>	0.71	0.63	0.19	-	-	50.43±1.14	8.598±0.197	69.09±2.24	9.258±0.356
3-Cl	0.37	0.47	-0.20	-	-	51.87±0.48	8.575±0.080	73.27±1.80	9.280±0.283
4-F	0.21	0.52	-0.35	-	-	52.12±1.22	8.353±0.202	-	-
4-Cl	0.28	0.47	-0.20	-	-	-	-	76.35±1.05	9.526±0.166
3-CH <sub>3</sub>	-0.07	-0.05	-0.10	-	-	54.63±3.51	8.557±0.585	-	-
3-NH <sub>2</sub>	-0.14	0.10	-0.48	-	-	53.36±0.71	8.423±0.121	-	-
H	0	0	0	-	-	53.80±0.86	8.523±0.145	77.54±2.93	9.311±0.467
2-NO <sub>2</sub>	0.81	0.63	0.19	1.39	-0.374	46.76±0.67	7.985±0.114	60.83±1.78	8.790±0.292
2-F	0.21	0.52	-0.35	0.27	-0.155	51.47±1.17	8.478±0.198	68.76±1.74	8.974±0.278
2-Cl	0.28	0.47	-0.20	0.55	-0.243	49.23±2.16	8.037±0.365	70.85±3.75	9.176±0.588
2-CH <sub>3</sub>	-0.14	-0.05	-0.10	0.52	-0.264	54.55±1.70	8.248±0.286	78.78±2.49	9.265±0.389
2-OCH <sub>3</sub>	-0.15	0.25	-0.41	0.36	-0.308	53.59±1.25	8.286±0.212	75.37±2.93	9.076±0.464

<sup>a</sup> In the data processing according to Eq. (4) the values of  $s$  were in range from 0.01 to 0.04.

TABLE III

Results of correlation with Eqs (2) and (3) for the alkaline hydrolysis of substituted phenyl benzoates (esters 1) and phenyl tosylates (esters 2) in aqueous 0.5 M NaClO<sub>4</sub> at 25 °C<sup>a</sup>

Reaction constant	Benzoates, Eq. (3)				Tosylates, Eq. (3)	
	Eq. (2)	Steric scale $\nu$		Eq. (2)	values of $\rho^d$	weight
		values of $\rho^b$	weight			
log $k_0$	-0.894±0.033	-0.918±0.023		-4.32±0.06	-4.25±0.11	
$\rho^o$ / <sub>m,p</sub>	0.961±0.075	-	-	2.00±0.10	-	
( $\rho$ )/ortho	-	1.657±0.040	0.345	-	3.21±0.18	0.603
( $\rho$ )/meta	-	0.995±0.032	0.211	-	1.92±0.20	0.096
( $\rho$ )/para	-	1.013±0.031	0.206	-	1.77±0.20	0.069
( $\rho^o$ )/ortho	-	1.108±0.044	0.172	-	1.68±0.16	0.152
( $\rho^o$ )/meta	-	0.251±0.039	0.030	-	1.64±0.17	0.012
( $\rho^o$ )/para	-	1.107±0.043	0.101	-	1.04±0.42	0.067
$\delta$	-	-0.392±0.026	-0.065	-	-	
n	7	12		5	10	
s	0.070	0.018		0.069	0.113	
s <sub>0</sub>	0.189	0.046		0.104	0.138	
R	0.982	0.999		0.994	0.991	
ortho-Substituted derivatives, Eq. (3)						
log $k_0$	-0.903±0.018	-0.909±0.015		-4.25±0.09		
( $\rho$ )/ortho	1.661±0.026	1.035	1.467±0.021 <sup>e</sup>	3.21±0.18		0.846
( $\rho^o$ )/ortho	1.139±0.033	0.243	0.683±0.023	1.68±0.23		0.154
$\delta$	-0.409±0.019	-0.278	-0.946±0.019	-		
n	6	6		6		
s	0.012		0.012	0.113		
s <sub>0</sub>	0.028		0.028	0.114		
R	0.999		0.999	0.993		

<sup>a</sup> The log  $k$  values were calculated according to the Arrhenius Eq. (4), log  $A$  and  $E$  values in Table II were used. <sup>b</sup> When the experimental log  $k$  values were used: log  $k_0 = -0.914 \pm 0.031$ , ( $\rho$ )/ortho = 1.709 ± 0.055, ( $\rho$ )/meta = 0.991 ± 0.043, ( $\rho$ )/para = 1.002 ± 0.042, ( $\rho^o$ )/ortho = 1.136 ± 0.060, ( $\rho^o$ )/meta = 0.265 ± 0.053, ( $\rho^o$ )/para = 1.112 ± 0.063,  $\delta = -0.428 \pm 0.036$ ,  $s = 0.024$ ,  $s_0 = 0.062$ ,  $R = 0.998$ . <sup>c</sup> When the experimental log  $k$  values were used: log  $k_0 = -0.917 \pm 0.018$ , ( $\rho$ )/ortho = 1.508 ± 0.028, ( $\rho$ )/meta = 0.996 ± 0.028, ( $\rho$ )/para = 1.007 ± 0.027, ( $\rho^o$ )/ortho = 0.661 ± 0.030, ( $\rho^o$ )/meta = 0.260 ± 0.034, ( $\rho^o$ )/para = 1.112 ± 0.040,  $\delta = 1.005 \pm 0.054$ ,  $s = 0.016$ ,  $s_0 = 0.040$ ,  $R = 0.999$ . <sup>d</sup> Data treatment for water gave log  $k_0 = -3.91 \pm 0.03$ , ( $\rho^o$ )/m,p = 2.05 ± 0.05, ( $\rho$ )/ortho = 3.34 ± 0.10, ( $\rho^o$ )/ortho = 2.05 ± 0.05, <sup>e</sup> ( $\rho$ )/ortho = 1.522 ± 0.062 found when the values of log  $k$  ortho - 1.2  $E_s$  were treated (similarly to water).

TABLE IV  
Correlation with Eqs (5) and (6) for the alkaline hydrolysis of benzoates (esters 1) and tosylates (esters 2)

Scale	Reaction constant	Benzoates				Tosylates <sup>a</sup>	
		Steric scale $\nu$		Steric scale $E_s^B$		values of c	weight
		values of c	weight	values of c	weight		
meta- and para-Substituted derivatives, Eq. (5)							
Intercept	c <sub>0</sub>	8.346±0.222				9.30±0.25	
$\sigma^o$	c <sub>1</sub>	0				0	
10 <sup>3</sup> /T	c <sub>2</sub>	-2.750±0.068	0.639			-4.052±0.082	0.462
$\sigma^o$ 10 <sup>3</sup> /T	c <sub>3</sub>	0.284±0.009	0.361			0.589±0.011	0.538
n/n <sub>0</sub>		39/39				19/20	
R		0.991				0.998	
s		0.062				0.046	
s <sub>0</sub>		0.132				0.067	
t		0.99				0.95	
ortho-, meta- and para-Substituted derivatives, Eq. (6)							
Intercept	c <sub>0</sub>	8.52±0.06		8.47±0.05		9.34±0.40	
( $\sigma$ ) <sub>ortho</sub>	c <sub>1</sub> (ortho)	0	-	0	-	-1.51±0.70	-0.207
( $\nu$ ) <sub>ortho</sub>	c <sub>7</sub> (ortho)	-0.415±0.013	-0.014	-	-	-	-
( $E_s^B$ ) <sub>ortho</sub>	c <sub>7</sub> (ortho)	-	-	0.979±0.026	0.033	-	-
10 <sup>3</sup> /T	c <sub>8</sub>	-2.808±0.017	0.583	-2.793±0.015	0.588	-4.055±0.083	0.294
( $\sigma$ ) 10 <sup>3</sup> /T <sub>ortho</sub>	c <sub>9</sub> (ortho)	0.499±0.006	0.096	0.440±0.004	0.117	1.45±0.23	0.587
( $\sigma$ ) 10 <sup>3</sup> /T <sub>meta</sub>	c <sub>10</sub> (meta)	0.288±0.005	0.081	0.289±0.004	0.088	0.576±0.016	0.091
( $\sigma$ ) 10 <sup>3</sup> /T <sub>para</sub>	c <sub>11</sub> (para)	0.293±0.005	0.107	0.291±0.004	0.084	0.543±0.015	0.054
( $\sigma_R^o$ 10 <sup>3</sup> /T) <sub>ortho</sub>	c <sub>12</sub> (ortho)	0.341±0.006	0.100	0.201±0.004	0.051	0.484±0.017	0.124
( $\sigma_R^o$ 10 <sup>3</sup> /T) <sub>meta</sub>	c <sub>13</sub> (meta)	0.081±0.006	0.016	0.079±0.005	0.016	0.305±0.033	0.015
( $\sigma_R^o$ 10 <sup>3</sup> /T) <sub>para</sub>	c <sub>14</sub> (para)	0.335±0.007	0.032	0.330±0.006	0.022	0.621±0.033	0.040

TABLE IV  
(Continued)

Scale	Reaction constant	Benzoates				Tosylates <sup>a</sup>	
		Steric scale $\nu$		Steric scale $E_s^B$		values of $c$	weight
		values of $c$	weight	values of $c$	weight		
ortho-, meta- and para-Substituted derivatives, Eq. (6)							
$n/n_0$		64/67		60/67		36/37	
R		0.999		0.999		0.998	
s		0.020		0.017		0.049	
$s_0$		0.041		0.034		0.063	
t		0.97		0.95		0.99	
ortho-Substituted derivatives, Eq. (6)							
Intercept	$c_0$	8.541±0.085		8.464±0.066		9.62±0.49	
$(\sigma_I)_{ortho}$	$c_1(ortho)$	0	–	0		–1.94±1.19(–1.6)	0.695
$(\sigma_R^3)_{ortho}$	$c_4(ortho)$	0		0		1.48±0.06(0.21)	0.123
$(\nu)_{ortho}$	$c_7(ortho)$	–0.416±0.015	–0.119	–		–	
$(E_s^B)_{ortho}$	$c_7(ortho)$	–		0.977±0.027	–0.017	–	
$10^3/T$	$c_8$	–2.814±0.026	0.602	–2.793±0.015	0.583	–4.148±0.161	0.181
$(\sigma_I^3)_{ortho}$	$c_9(ortho)$	0.499±0.006	0.096	0.440±0.004	0.370	1.59±0.39(1.5)	0.001
$(\sigma_R^3)_{ortho}$	$c_{12}(ortho)$	0.341±0.008	0.121	0.201±0.004	0.064	0(0.42)	
$n/n_0$		33/34		30/34		21/22	
R		0.999		0.999		0.998	
s		0.022		0.016		0.061	
$s_0$		0.044		0.032		0.068	
t		0.97		0.95		0.95	

<sup>a</sup> The values of reaction constants obtained before excluding significantly deviating ( $\sigma_R^3(10^3/T)$ ) scale are shown in brackets.

## RESULTS AND DISCUSSION

The alkaline hydrolysis rates of all substituted phenyl benzoates (esters **1**) and phenyl tosylates (esters **2**) were found to decrease when going from water to aqueous 5.3 M NaClO<sub>4</sub>. For esters with electron withdrawing substituents the retardation appeared to be bigger than in case of esters with electron-donating groups. For instance, the log *k* value for ester **1a** at 50 °C decreased by about 0.5 units and log *k* value for ester **1g** decreased by 0.3 units compared with values in water. In both reaction series benzoates and tosylates the second-order rate constant *k*<sub>2</sub> for non-substituted esters at 50 °C was found to be about 0.35 log *k* units lower than the corresponding value in water.

The alkaline hydrolysis of *ortho*-substituted tosylates was accelerated by additional inductive effects of *ortho* substituents in comparison with those of *para* ones. For *ortho*-substituted benzoates, two effects influenced the rate of the process in the opposite directions: compared with *para* substituents, process was accelerated by additional inductive effect but retarded by the steric effect.

The values of reaction constants for *ortho*-substituted derivatives ( $\rho_I$ )<sub>ortho</sub>, ( $\rho^\circ_R$ )<sub>ortho</sub> and  $\delta_{ortho}$ , calculated with Eq. (3) separately for *ortho*-substituted derivatives appeared to be approximately the same when calculated simultaneously with for *ortho*-, *meta*- and *para*-substituted derivatives (Table III).

The separation of the total substituent effect into contributions of the inductive, resonance and steric terms according to Eq. (3) (Table III) confirmed the Taft postulate ( $\rho_I$ )<sub>meta</sub> ≈ ( $\rho_I$ )<sub>para</sub> ≈ ( $\rho^\circ_R$ )<sub>para</sub> ≈ 2( $\rho^\circ_R$ )<sub>meta</sub> ≈  $\rho^\circ_{m,p}$ . The susceptibility to the polar influence of *meta* and *para* substituents, ( $\rho^\circ$ )<sub>m,p</sub>, and similarly the ( $\rho_I$ )<sub>meta</sub>, ( $\rho_I$ )<sub>para</sub> and ( $\rho^\circ_R$ )<sub>para</sub> values appeared to decrease approximately 0.13 units only, when going from water to aqueous 5.3 M NaClO<sub>4</sub> solution, in both the alkaline hydrolysis of benzoates and tosylates, depending on temperature considered (Table III). The ( $\rho^\circ$ )<sub>m,p</sub> value for the alkaline hydrolysis of substituted phenyl benzoates at 25 °C was found to be equal to 0.96 and 1.08 in 5.3 M NaClO<sub>4</sub> <sup>2</sup> and in pure water, respectively. The corresponding values for ( $\rho^\circ$ )<sub>m,p</sub> for the alkaline hydrolysis of phenyl tosylates at 25 °C are 1.9 and 2.05.

In both reaction series the inductive influence from *ortho* position for aqueous 5.3 M NaClO<sub>4</sub> appeared to be unchanged compared to pure water. For alkaline hydrolysis of substituted phenyl benzoates the corresponding ( $\rho_I$ )<sub>ortho</sub> values at 25 °C are 1.50 and 1.53 <sup>2</sup> and for tosylates 3.2 and 3.3 °C, respectively.

When going from water to aqueous 5.3 M NaClO<sub>4</sub> the relation  $(\rho_I)_{ortho}/(\rho_I)_{para}$  was found to be increased from 1.6 to 1.7 for tosylates reaction series and from 1.5 to 1.7 (as steric constant  $\nu$  was used) for benzoates reaction series.

Though the decrease in the polar effect of *meta* and *para* substituents appeared to be minimal (only 0.13 units of  $\rho$ ) and the inductive influence from *ortho* position was observed nearly unchanged when going from water to aqueous 5.3 M NaClO<sub>4</sub>, we detected the increase in *ortho* effect ( $\log k_{ortho}^X - \log k_{para}^X$ ) by transfer from water to more electrophilic media (compared to pure water) in both reaction series studied.

When going from water to less electrophilic media like aqueous 2.25 M Bu<sub>4</sub>NBr or 80% DMSO, a considerable decrease in the relation  $(\rho_I)_{ortho}/(\rho_I)_{para}$  was detected<sup>2</sup>. In 2.25 M Bu<sub>4</sub>NBr  $(\rho_I)_{ortho}/(\rho_I)_{para} \approx 0.9$  for the alkaline hydrolysis of benzoates at 25 °C [ $(\rho_I)_{ortho} = 2.09$  and  $(\rho_I)_{para} = 2.27$ ] and  $(\rho_I)_{ortho}/(\rho_I)_{para} \approx 1.24$  for phenyl tosylates [ $(\rho_I)_{ortho} = 3.59$  and  $(\rho_I)_{para} = 2.90$ ].

The observed variation of  $(\rho_I)_{ortho}/(\rho_I)_{para}$  when going from water to aqueous 5.3 M NaClO<sub>4</sub>, once more prove that the inductive term of *ortho* substituents varies with solvent less (nearly twice<sup>2</sup>) than the inductive term of *para* substituents.

Similarly to our previous works, both the magnitude of the resonance from *ortho* position and the variation of *ortho* resonance term with solvent appeared to be nearly the same as for *para* substituents [ $(\rho^\circ_R)_{para} \approx (\rho^\circ_R)_{ortho}$ ] in both reaction series considered.

In previous works we used for the data treatment the  $E_s^B$  scale determined from the acidic hydrolysis experimental data for substituted phenyl benzoates. To compare the steric term for aqueous 5.3 M NaClO<sub>4</sub> with those obtained in previous works for other media, in present work besides the Charton steric  $\nu$  scale, the steric  $E_s^B$  scale was involved. Two steric scales gave nearly identical results if  $\nu = 1.39$  for *ortho*-nitro group was used. In the case of the  $\nu$  values, the resonance from *ortho* position appeared to be exactly equal to resonance from *para* position and the inductive influence from *ortho* position observed a little stronger than in case the  $E_s^B$  constants used (Table III). In the case the  $E_s^B$  constants, the resonance term from *ortho* position appeared to be equal to or a little less than that for *para* substituents.

When to use in correlations the steric  $E_s^B$  scale, for *ortho*-substituted benzoates in aqueous 5.3 M NaClO<sub>4</sub> the susceptibility to the steric influence was found to be equal to 1.0, nearly equal to that in water, aqueous 2.25 M

$\text{Bu}_4\text{NBr}$  and 80% DMSO. When the Charton  $\nu$  scale was involved, the susceptibility to the steric influence was found to be  $-0.40$ .

Though the inductive and resonance terms in the benzoates and tosylates reaction series differ about two-fold, the variation of the inductive and resonance terms for *ortho*, *meta* and *para* substituents with solvent was observed by the same extent in the two reactions considered. Similar variation of substituent effects with solvent has been found in our previous papers involving media which electrophilic power is reduced compared to water<sup>2</sup>.

The separation of the inductive, resonance and the steric terms dependent simultaneously on substitution and temperature was performed using Eqs (5) and (6) (Table IV). Equation (5) includes data only for *meta*- and *para*-substituted derivatives, Eq. (6) includes those simultaneously for *ortho*-*meta*- and *para*-substituted derivatives at various temperatures. For the sake of comparison data processing with Eq. (6) was performed separately for *ortho*-substituted esters. The calculated susceptibilities for the inductive, resonance and steric terms for *ortho*, *meta* and *para* substituents obtained using Eq. (6), appeared to be the same as calculated separately for *meta*-, *para*- and *ortho*-substituted derivatives.

Equations (5) and (6) are the multilinear relationships with cross terms. Palm and Istomin demonstrated<sup>1,30,36</sup> that this kind of equations exhibit a remarkable property called isoparametricity. The phenomenon of isoparametrical relationship is possible if there are represented the cross terms in correlation equation. The isoparametrical point for temperature  $T$  is the known as isokinetical (or isoequilibrium) temperature.

In aqueous 5.3 M  $\text{NaClO}_4$ , the variation of the inductive and resonance terms with temperature only slightly differs from those obtained earlier for pure water<sup>1</sup>. In 5.3 M  $\text{NaClO}_4$ , similarly to water, the dependence of inductive and resonance terms on temperature in the case of *meta* and *para* substituents in both the benzoates and tosylates reaction series, appeared to be isoentropic as the corresponding terms in Eqs (5) and (6) were excluded as insignificant (in Eq. (5)  $c_1 = 0$  and in Eq. (6)  $c_{2(\text{meta})} = c_{3(\text{para})} = c_{5(\text{meta})} = c_{6(\text{para})} = 0$ ). The dependence of the *ortho* resonance term on temperature, similar to that of *para* substituents, was found to be isoentropic ( $c_{4(\text{ortho})} = 0$ ). In aqueous 5.3 M  $\text{NaClO}_4$ , similarly to pure water, the dependence of the *ortho* inductive term on temperature for the tosylates series corresponds to the isoparametric relationship, *i.e.* belongs to isokinetical relationship as much the terms  $c_{1(\text{ortho})}\sigma_I$  and  $c_{9(\text{ortho})}(1/T)\sigma_I$  in Eq. (6) appeared to be present ( $c_{1(\text{ortho})} = -1.51$ ,  $c_{7(\text{ortho})} = 1.45 \times 10^3$ ). In water, the *ortho* inductive term in benzoates reaction series corresponds to isokinetic relationship (the

value of  $c_{1(\text{ortho})}$  in range from  $-0.4$  to  $-0.8$ ). In aqueous  $5.3 \text{ M NaClO}_4$ , the  $c_{1(\text{ortho})}$  value was found to be different from zero (nearly  $-0.4$ ) in the preliminary solution. Due to relatively large deviations, the  $c_{1(\text{ortho})}\sigma_1$  term for benzoates reaction series was excluded as insignificant and the corresponding relationship should be considered as isoentropic one. If the data treatment procedure involved the cross terms, formed from centred basic argument scales<sup>3</sup>, the  $c_{1(\text{ortho})}$  value was found to be about  $-0.6$  and  $c_{9(\text{ortho})} = 0.56 \times 10^3$  for the benzoates reaction series. Performing the data treatment that way, the calculated resonance term for *meta* and *para* substituents appeared to be independent of temperature. Therefore, similar solution could be regarded "unreasonable" as well. Hence, in aqueous  $5.3 \text{ M NaClO}_4$  for the *ortho*-inductive term in benzoates reaction series, two alternative relationships, isoentropic and isokinetic could be considered as indistinguishable ones.

In both reaction series studied in the case of *meta* and *para* substituents the inductive term and the resonance of *para* substituents vary with temperature equally, but for *meta* substituents the variation of the resonance term with temperature appeared to be nearly twice smaller than that for *para* substituents: ( $c_{10(\text{meta})} = c_{11(\text{para})} = c_{14(\text{para})} \approx 2c_{13(\text{meta})}$ ). In the case of the alkaline hydrolysis of substituted phenyl tosylates, the variation of the inductive and resonance terms with temperature was found to be about twice stronger than that in the alkaline hydrolysis of substituted phenyl benzoates:

$$[c_{10(\text{meta})} = c_{11(\text{para})} = c_{14(\text{para})} \approx c_{12(\text{ortho})} \approx 2c_{13(\text{meta})} \approx 0.56 \times 10^3]_{\text{Tos}} \approx 2[c_{10(\text{meta})} = c_{11(\text{para})} = c_{14(\text{para})} \approx c_{12(\text{ortho})} \approx 2c_{13(\text{meta})} \approx 0.29 \times 10^3]_{\text{Benz}}.$$

In water<sup>1,3</sup> in both reaction series considered, the sensitivity of the *ortho* inductive effect towards the temperature variation observed about two times stronger than for *meta*- and *para*-substituted derivatives, dependence itself in the alkaline hydrolysis of phenyl tosylates was found to be twice larger than in the alkaline hydrolysis of phenyl benzoates:

$$[c_{9(\text{ortho})} = 1.41 \times 10^3]_{\text{Tos}}/[c_{9(\text{ortho})} = 0.72 \times 10^3]_{\text{Benz}} \approx 2.$$

In aqueous  $5.3 \text{ M NaClO}_4$ , similarly to pure water, in the case of *ortho* substituents, the dependence of the inductive influence on temperature appeared to be about twice as large as the same dependence for *para* and *meta* substituents in both reaction series studied. The magnitude of the relation  $[c_{9(\text{ortho})} = (1.45 \pm 0.23) \times 10^3]_{\text{Tos}}/[c_{9(\text{ortho})} = 0.5 \times 10^3]_{\text{Benz}} = 2.9$  could be con-

sidered as too high. Due to large deviations, the  $[c_{1(\text{ortho})}]_{\text{Benz}}$  constant was excluded and the data processing gave for the reaction constant  $[c_{9(\text{ortho})}]_{\text{Benz}}$  lower value than expected.

When going from water to aqueous 5.3 M  $\text{NaClO}_4$ , the temperature dependence of inductive and resonance effects in the case of *meta* and *para* substituents appeared to be decreased about  $0.06 \times 10^3$  units (Table IV) in case of both reaction series considered (for benzoates in water<sup>1</sup>  $c_{10(\text{meta})} = c_{11(\text{para})} = 0.320$ , for tosylates<sup>3</sup>  $c_{10(\text{meta})} = c_{11(\text{para})} = 0.600$ ). By transfer from water to 5.3 M  $\text{NaClO}_4$ , in the case of *ortho* substituents the dependence of the inductive influence on temperature appeared to be practically unchanged compared to water in tosylates reaction series [in aqueous 5.3 M  $\text{NaClO}_4$   $c_{1(\text{ortho})} = (-1.51 \pm 0.70)$  and  $c_{9(\text{ortho})} = (1.45 \pm 0.23)$ , in water  $c_{1(\text{ortho})} = (-1.46 \pm 0.46)$  and  $c_{9(\text{ortho})} = (1.41 \pm 0.11)$ ].

The variation of the reaction rate with the substituent and temperature in the alkaline hydrolysis of substituted alkyl benzoates and tosylates appeared to be nicely described by Eqs (5) and (6). The comparison of the predicted  $\log k$  values ( $\log k_{\text{calc}}$ ) calculated according to Eq. (6) and the experimental  $\log k$  values (Table I) for the alkaline hydrolysis of substituted phenyl benzoates and tosylates is shown in Figs 1–4. For the alkaline hydrolysis of substituted phenyl benzoates in 5.3 M  $\text{NaClO}_4$  we found (Fig. 1):

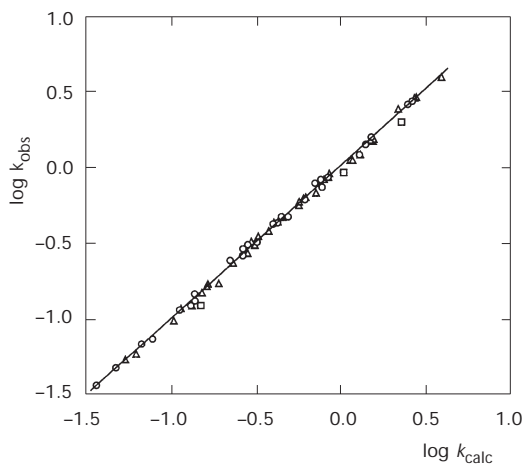


FIG. 1

Plot of  $\log k_{\text{obs}}$  vs  $\log k_{\text{calc}}$  for the alkaline hydrolysis of substituted phenyl benzoates (esters **1**) in aqueous 5.3 M  $\text{NaClO}_4$  (Eq. (7)).  $\log k_{\text{obs}}$  are the  $\log k$  values of the experimental values of the second-order rate constants at various temperatures given in Table I.  $\log k_{\text{calc}}$  were calculated using Eq. (8) (Table IV).  $\circ$  *ortho*-Substituted derivatives,  $\Delta$  *meta*- and *para*-substituted derivatives,  $\square$  points excluded during the data treatment

$$\log k_{\text{obs}} = -(0.010 \pm 0.004) + (1.000 \pm 0.006) \log k_{\text{calc}} \quad (7)$$

$$R = 0.999, s = 0.026, s_0 = 0.052, n/n_0 = 67/67.$$

The  $\log k_{\text{calc}}$  values for benzoates were calculated according to Eq. (8) (Table IV) using the steric parameter  $\nu = 1.39$  for *ortho*-nitro group:

$$\begin{aligned} (\log k_{\text{calc}})_{\text{o,m,p}} = & 8.52 - (0.415\nu)_{\text{ortho}} - 2.808(10^3/T) + [0.499(10^3/T)\sigma_{\text{I}}]_{\text{ortho}} + (8) \\ & + [0.288(10^3/T)\sigma_{\text{I}}]_{\text{meta}} + [0.293(10^3/T)\sigma_{\text{I}}]_{\text{para}} + [0.341(10^3/T)\sigma_{\text{R}}^{\circ}]_{\text{ortho}} + \\ & + [0.081(10^3/T)\sigma_{\text{R}}^{\circ}]_{\text{meta}} + [0.335(10^3/T)\sigma_{\text{R}}^{\circ}]_{\text{para}} . \end{aligned}$$

Only for *ortho*-substituted phenyl benzoates we found (Fig. 2):

$$\log k_{\text{obs}} = -(0.0003 \pm 0.0502) + (1.000 \pm 0.007) \log k_{\text{calc}} \quad (9)$$

$$R = 0.999, s = 0.021, s_0 = 0.042, n/n_0 = 33/34, \text{excluded 2-Cl derivative at } 60^\circ\text{C}.$$

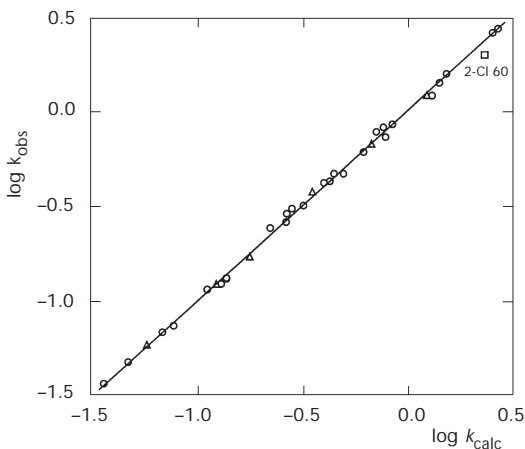


FIG. 2

Plot of  $\log k_{\text{obs}}$  vs  $\log k_{\text{calc}}$  for the alkaline hydrolysis of *ortho*-substituted phenyl benzoates (esters 1) in aqueous 5.3 M  $\text{NaClO}_4$  (Eq. (9)).  $\log k_{\text{obs}}$  are the  $\log k$  values of the experimental values of the second-order rate constants at various temperatures given in Table I.  $\log k_{\text{calc}}$  were calculated using Eq. (10) (Table IV)  $\circ$  *ortho*-Substituted derivatives,  $\Delta$  unsubstituted derivative (phenyl benzoate),  $\square$  point excluded during the data treatment

The  $\log k_{\text{calc}}$  values for *ortho*-substituted benzoates were calculated according to Eq. (10) (Table IV) using the steric parameter  $\nu = 1.39$  for *ortho*-nitro group:

$$\log k_{\text{ortho}} = 8.541 - (0.416\nu)_{\text{ortho}} + 2.814(10^3/T) + \quad (10)$$

$$[0.499(10^3/T)\sigma_{\text{I}}]_{\text{ortho}} + [0.341(10^3/T)\sigma_{\text{R}}^{\circ}]_{\text{ortho}}.$$

For the alkaline hydrolysis of substituted phenyl tosylates in 5.3 M NaClO<sub>4</sub> it was found (Fig. 3):

$$\log k_{\text{obs}} = -(0.007 \pm 0.029) + (0.996 \pm 0.012) \log k_{\text{calc}} \quad (11)$$

$$R = 0.997, s = 0.058, s_0 = 0.076, n/n_0 = 38/38.$$

The  $\log k_{\text{calc}}$  values for tosylates reaction series were calculated according to Eq. (12) (Table IV):

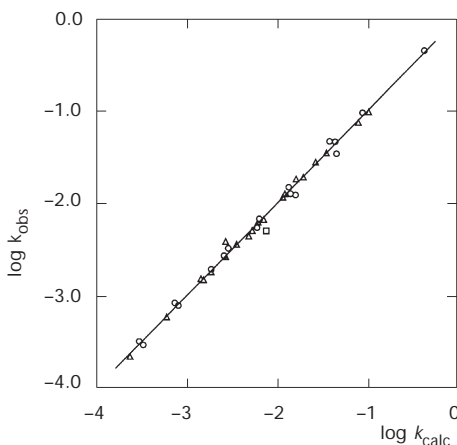


FIG. 3

Plot of  $\log k_{\text{obs}}$  vs  $\log k_{\text{calc}}$  for the alkaline hydrolysis of substituted phenyl tosylates (esters **2**) in aqueous 5.3 M NaClO<sub>4</sub> (Eq. (11)).  $\log k_{\text{obs}}$  are the  $\log k$  values of the experimental values of the second-order rate constants at various temperatures given in Table I.  $\log k_{\text{calc}}$  were calculated using Eq. (12) (Table IV).  $\circ$  *ortho*-Substituted derivatives,  $\Delta$  *meta*- and *para*-substituted derivatives,  $\square$  point excluded during the data treatment

$$\begin{aligned}
 (\log k_{\text{calc}})_{\text{o,m,p}} = & 9.34 - (1.51\sigma_{\text{I}})_{\text{ortho}} - 4.055(10^3/T) + [1.45(10^3/T)\sigma_{\text{I}}]_{\text{ortho}} + \quad (12) \\
 & + [0.576(10^3/T)\sigma_{\text{I}}]_{\text{meta}} + [0.543(10^3/T)\sigma_{\text{I}}]_{\text{para}} + [0.484(10^3/T)\sigma_{\text{R}}^{\circ}]_{\text{ortho}} + \\
 & + [0.305(10^3/T)\sigma_{\text{R}}^{\circ}]_{\text{meta}} + [0.621(10^3/T)\sigma_{\text{R}}^{\circ}]_{\text{para}} .
 \end{aligned}$$

Only for *ortho*-substituted phenyl tosylates we found (Fig. 4):

$$\log k_{\text{obs}} = (0.015 \pm 0.035) + (1.003 \pm 0.014) \log k_{\text{calc}} \quad (13)$$

$R = 0.998$ ,  $s = 0.056$ ,  $s_0 = 0.064$ ,  $n/n_0 = 21/22$ , excluded 2-Cl at 50 °C.

The  $\log k_{\text{calc}}$  values for *ortho*-substituted phenyl tosylates were calculated according to Eq. (14) (Table IV):

$$\log k_{\text{ortho}} = 9.62 - 1.94(\sigma_{\text{I}})_{\text{ortho}} + 1.48(\sigma_{\text{R}}^{\circ})_{\text{ortho}} + 4.148(10^3/T) + [1.59(10^3/T)\sigma_{\text{I}}]_{\text{ortho}} . \quad (14)$$

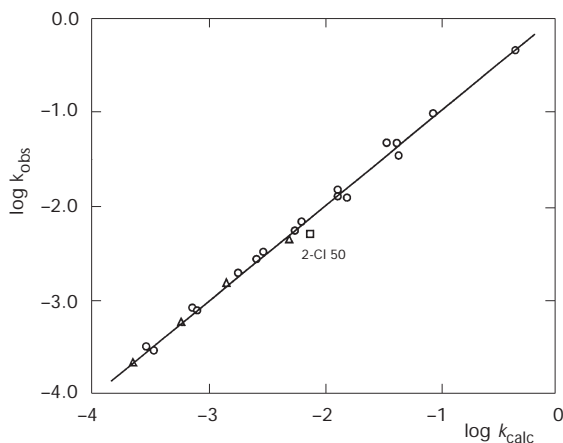


FIG. 4

Plot of  $\log k_{\text{obs}}$  vs  $\log k_{\text{calc}}$  for the alkaline hydrolysis of *ortho*-substituted phenyl tosylates (esters 2) in aqueous 5.3 M NaClO<sub>4</sub> (Eq. (13)).  $\log k_{\text{obs}}$  are the  $\log k$  values of the experimental values of the second-order rate constants at various temperatures given in Table I.  $\log k_{\text{calc}}$  were calculated using Eq. (14) (Table IV).  $\circ$  *ortho*-Substituted derivatives,  $\Delta$  unsubstituted derivative (phenyl benzoate),  $\square$  point excluded during the data treatment

The polar effects of *ortho*, *meta* and *para* substituents in the alkaline hydrolysis of substituted phenyl tosylates (esters **2**) for water were found to be approximately twice higher than same effects in the alkaline hydrolysis of substituted phenyl benzoates (esters **1**)<sup>1</sup>. The slope of the similar dependence in aqueous 5.3 M NaClO<sub>4</sub> (Eq. (15)) was found to be equal to 2.19 (Fig. 5) when log *k* values for the *ortho*-, *meta*- and *para*-substituted derivatives at 25, 40, 50 and 60 °C were included:

$$(\log k_X - \log k_H)^{\text{Tos}} = (-0.048 \pm 0.039) + (2.19 \pm 0.07)(\log k_X - \log k_H - 0.979E_s^{\text{B}})^{\text{Benz}} \quad (15)$$

$$R = 0.989, s = 0.121, s_0 = 0.149, n = 23.$$

The slope of the dependence (Eq. (15)) for 5.3 M NaClO<sub>4</sub> appeared to be slightly larger than the same slope for water (1.98) what is in accordance with our point of view that the substituent polar effects in benzoates and tosylates reaction series change by the same magnitude of Δρ (for 5.3 M NaClO<sub>4</sub> Δρ nearly -0.13 units of ρ) when going from water to another solvent. It should be remind that the slope of the dependence (log *k*<sub>T</sub><sup>X</sup> - log *k*<sub>T</sub><sup>H</sup>)<sup>T</sup> on (log *k*<sub>T</sub><sup>X</sup> - log *k*<sub>T</sub><sup>H</sup> - 1.2*E*<sub>s</sub><sup>B</sup>)<sup>B</sup> (Eq. (15)) was found to decrease considerably when going from water to media like 2.25 M Bu<sub>4</sub>NBr and 80% DMSO (the

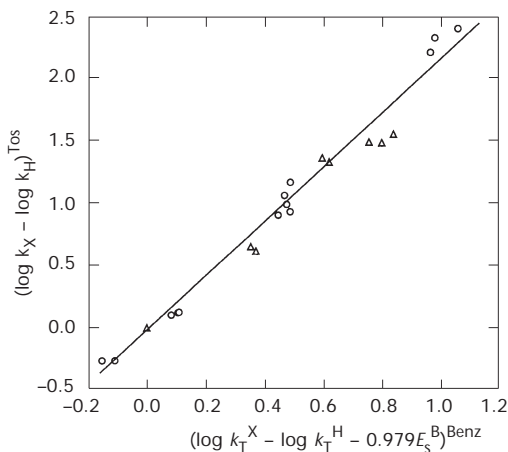


FIG. 5

Dependence of  $(\log k_X - \log k_H)^{\text{Tos}}$  on  $(\log k_T^X - \log k_T^H - 0.979E_s^{\text{B}})^{\text{Benz}}$ , Eq. (15). ○ *ortho*-Substituted derivatives, Δ *meta*- and *para*-substituted derivatives; Benz denotes esters **1**, Tos denotes esters **2**

slope nearly 1.5) which electrophilic solvation properties are considerably lower than for water.

The slight negative salt effects on the alkaline hydrolysis of esters, observed when going from water to aqueous 5.3 M NaClO<sub>4</sub>, are consistent with the ion-dipolar molecule rate theory<sup>37,38</sup>. According to Loupy<sup>39</sup> the influence of the neutral salts on the rates of alkaline hydrolysis of aromatic esters could be considered as sum of two opposite effects: association of the nucleophile OH<sup>-</sup> with M<sup>+</sup> leading to rate decrease and =C=O-M<sup>+</sup> complexation in ester inducing the rate increase. We assume that slight negative salt effects on the alkaline hydrolysis of phenyl benzoates and tosylates, observed in aqueous 5.3 M NaClO<sub>4</sub>, could be caused mainly by the association of the nucleophile OH<sup>-</sup> with Na<sup>+</sup> leading to rate decrease and less extent by the complexation of Na<sup>+</sup> ions to the minus charged transition state, inducing a rate increase.

The relative importance of the complexation of Na<sup>+</sup> ions to transition state depends on the nature of the ester. If the substituent X in phenyl group is an electron repelling, in the transition state the minus charge is more located in the phenolic oxygen and in protic solvents the electrophilic solvation stabilizes the transition state more extent than in the case of electron-attracting substituents. The complexation of Na<sup>+</sup> ions to the minus charged transition state could be considered responsible for the observed substituent polar effect, which is a slightly decreased compared to pure water. It follows from Eq. (16)<sup>40</sup>

$$\rho = \text{const}(\sigma_y - \sigma_y^\ddagger) \quad (16)$$

that the  $\rho$  value is depending on the  $\sigma$  value for the reaction centre in the initial state ( $\sigma_y$ ) and the transition state ( $\sigma_y^\ddagger$ ). In the case of ester hydrolysis in inorganic salt solution the  $\sigma_y^\ddagger$  value should become more positive due to complexation of M<sup>+</sup> to negatively charged transition state and  $\rho$  should decrease compared to water. In concentrated organic salt solution of 2.25 M Bu<sub>4</sub>NBr and 80% DMSO the sensitivity to the polar effect of substituents in the alkaline hydrolysis of benzoates and tosylates increased by about 1.0 units of  $\rho$  compared to water<sup>1</sup>. In 2.25 M Bu<sub>4</sub>NBr and 80% DMSO the transition state of ester hydrolysis involving minus charge, could be considered as very few solvated electrophilically what leads to essentially increased  $\rho$  values compared to pure water. In the concentrated aqueous Bu<sub>4</sub>NBr solution there are very few of the active water molecules capable for hydrogen

bondings with the negative charged transition state and the large  $\text{Bu}_4\text{N}^+$  ions are not able for the complexations to the partly charged phenolic oxygen as do little  $\text{M}^+$  cations.

The dependence of the activation energies  $E$  on substituent effects in the alkaline hydrolysis of *meta*- and *para*-substituted as well as *ortho*-substituted phenyl benzoates (esters **1**) and tosylates (esters **2**) is completely caused by polar effects of substituents whereas the electron-withdrawing substituents decreased the activation energy  $E$ , the electron-donating substituents increased it. In aqueous 5.3 M  $\text{NaClO}_4$  the activation energies  $E$  of the alkaline hydrolysis of benzoates and tosylates increased in the case of all substituents in comparison with the activation energies in water (see Table II). Because of the additional inductive effect of *ortho* substituents in comparison with *para* substituents, the activation energies  $E$  of the alkaline hydrolysis of *ortho*-substituted derivatives, except esters **11** and **21** were lower than for *para*-substituted ones in water as well as in aqueous 5.3 M  $\text{NaClO}_4$ . The sensitivity of the activation energies  $E$  of the alkaline hydrolysis of *meta*- and *para*-substituted phenyl benzoates and phenyl tosylates to the polar substituent effects decreased in aqueous 5.3 M  $\text{NaClO}_4$ , in comparison with the sensitivity for water<sup>1,3</sup>. In aqueous 5.3 M  $\text{NaClO}_4$  the lowered susceptibility of the activation energy to the polar influence of substituents could be considered caused by the complexation of  $\text{Na}^+$  ions to the transition state involving negative charge what makes the activation energy of esters with electron repelling substituents lower and for esters with electron attracting substituents higher compared with unsubstituted derivative.

The log  $A$  values for *meta*- and *para*-substituted derivatives were nearly constant, being independent of the substituent effects in aqueous 5.3 M  $\text{NaClO}_4$  for both reaction series (see Table II). But all the values of log  $A$  found in aqueous 5.3 M  $\text{NaClO}_4$  for substituted phenyl esters were significantly higher than those in water. Similar values for *ortho* substituents were smaller in both reaction series than those observed for the *para* substituents in water as well as in aqueous 5.3 M  $\text{NaClO}_4$  (see Table II). It was shown earlier<sup>2</sup> that if the steric factor was temperature-independent, it could influence merely the log  $A$  value, *i.e.*, only the entropy of the reaction.

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