

Enthalpy and Entropy Relations in Reactions of 2,4-Dinitrophenyl Benzoate with Phenols in the Presence of Potassium Carbonate in Dimethylformamide

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Received January 16, 2008

Abstract—By means of competing reactions procedure the temperature dependence of the relative reactivity of phenols in reactions with 2,4-dinitrophenyl benzoate in the presence of potassium carbonate and DMF was examined. The correlation analysis of the relative rate constants k_{ArOH}/k_{PhOH} and the difference in the activation parameters ($\Delta\Delta H^\ddagger$ and $\Delta\Delta S^\ddagger$) of the competing reactions revealed the existence of three isokinetic series. The interpretation of the transesterification mechanism was performed applying the approach underlain by the analysis of the effect of substituents nature on the activation parameters.

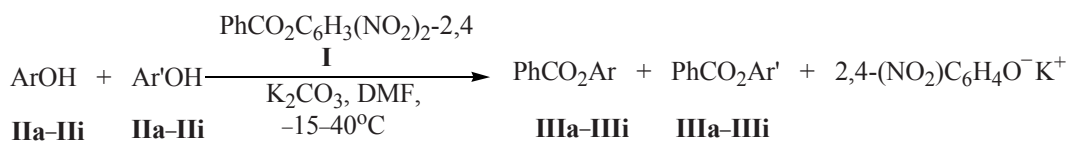
DOI: 10.1134/S1070428008110092

The nucleophilic substitution at the carbonyl carbon atom is the key stage of many complex biochemical reactions [1]. Model reactions are widely used to obtain the necessary information on the probable mechanisms of these processes [2]. In the framework of this procedure the transesterification reactions are important objects of the study revealing the effect of the substrate and reagent structural features on the mechanism of the nucleophilic substitution [3, 4]. It is known that in event of the easily departing eliminated groups, like 4-nitro- and 2,4-dinitrophenoxy groups, the transesterification proceeds not only by the addition-elimination mechanism $A_N + D_N$ (with the limiting first or second stage) but also by the concerted mechanism $A_N D_N$, and sometimes even through elimination–addition $D_N + A_N$. For instance, the latter mechanism was observed in the reaction of (2',4'-dinitrophenyl) 4-methoxy-2,6-dimethylbenzoate with phenolate anions in water environment [5]. Similar transesterifications of 2,4-dinitrophenyl acetate and 4-nitrophenyl acetates occur along the concerted mechanism $A_N D_N$ [5, 6]. Stage mechanism $A_N + D_N$ is characteristic of the reaction of 4'-nitrophenyl benzoate with potassium phosphate in aqueous DMSO [7]. The transesterification of substituted 4-nitrophenyl benzoates effected by the complex of 4-chlorophenol with K_2CO_3 in DMF in a hetero-

phase conditions proceeded through a limiting stage of a tetrahedral intermediate formation [8]. Evidently the study of the effect of the substituents in phenols on the reactivity of their complexes with K_2CO_3 provides a possibility to obtain a more complete information on the reaction mechanism. To this end we studied the transesterification reaction of 2,4-dinitrophenyl benzoate (**I**) with phenols **IIa–III** in the presence of potassium carbonate in DMF. The anhydrous potassium carbonate is extensively used in the organic synthesis as a non-nucleophilic agent for the generation of charged nucleophiles in situ in versatile nucleophilic reactions including the organic reactions under the phase-transfer catalysis in systems liquid-solid [9]. Evidently the presence of a solid phase in the reaction system impedes the application of a direct kinetic procedure of the reaction investigation. Yet the procedure of competing reactions proved to be valid in the examination of the effect of the substrate structural features on the transesterification rate in the system 4-ClC₆H₄OH– K_2CO_3 [8].

We studied by means of competing reactions procedure the temperature dependence of the relative reactivity of phenols **IIa–III** in reactions with benzoate **I** in the presence of potassium carbonate in DMF

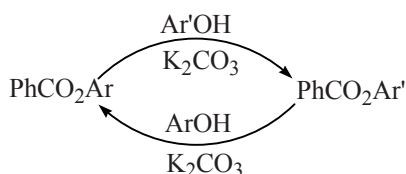
Scheme 1.



Ar, Ar' = RC₆H₄; R = 4-MeO (a), 4-Me (b), 3-Me (c), H (d), 4-Cl (e), 3-Br (f), 3-NO₂ (g), 4-CN (h), 4-NO₂ (i).

(Scheme 1). The corresponding phenol pairs and the rate constants ratios are compiled in Table 1.

Esters **III** arising in the course of the competing reactions are also capable to be involved into the transesterification (Scheme 2).



The error in the calculation by Scheme 1 of the ratio of rate constants corresponding to the competing reactions was reduced by selecting the reaction conditions where the subsequent transformations of esters **III** (Scheme 2) did not affect the ratio of their molar concentration more than by 5% (see EXPERIMENTAL).

As follows from the data of Table 2 in the studied temperature range the ratio $k_{\text{ArOH}}/k_{\text{PhOH}}$ varies from 0.62 to 5.04. For all selected phenols the values $\log(k_{\text{ArOH}}/k_{\text{PhOH}})$ are linearly dependent on the reciprocal $1/T$ ($r=0.997$) (Fig. 1) testifying to the validity of the Arrhenius

Table 1. Ratio of rate constants $k_{\text{ArOH}}/k_{\text{Ar'OH}}$ of competing reactions between compound **I** and phenols **IIa-IIIi** in the presence of K₂CO₃ in DMF

ArOH-Ar'OH	$k_{\text{ArOH}}/k_{\text{Ar'OH}}^a$			
	-15°C	0°C	20°C	40°C
IIa-IIIb	1.45 ± 0.02	1.45 ± 0.01	1.46 ± 0.03	1.45 ± 0.02
IIb-IIIc	1.31 ± 0.02	1.36 ± 0.01	1.44 ± 0.02	1.51 ± 0.01
IIc-IIId	0.86 ± 0.01	0.90 ± 0.01	0.95 ± 0.01	0.99 ± 0.02
IIe-IIId	5.04 ± 0.11	4.92 ± 0.15	4.77 ± 0.01	4.68 ± 0.09
IIe-IIIf	0.98 ± 0.01	0.94 ± 0.01	0.88 ± 0.05	0.84 ± 0.03
IIg-IIIf	0.97 ± 0.01	0.91 ± 0.02	0.81 ± 0.02	0.74 ± 0.03
IIIh-IIIg	0.53 ± 0.02	0.50 ± 0.01	0.47 ± 0.03	0.45 ± 0.02
IIIi-IIIh	0.55 ± 0.02	0.52 ± 0.01	0.49 ± 0.04	0.47 ± 0.01

^a Average value of no less than two parallel runs.

Table 2. Ratio of rate constants $k_{\text{ArOH}}/k_{\text{PhOH}}$ and difference in the activation parameters of the competing reactions between compound **I** and phenols **IIa-IIIi** in the presence of K₂CO₃ in DMF

Compound no.	$k_{\text{ArOH}}/k_{\text{PhOH}}^a$				$\Delta\Delta H^\ddagger, \text{kJ mol}^{-1b}$	$\Delta\Delta S^\ddagger, \text{J/(mol K)}^{b,c}$
	-15°C	0°C	20°C	40°C		
IIa	1.90 ± 0.02	1.97 ± 0.01	2.10 ± 0.03	2.19 ± 0.02	1.78 ± 0.09	12.2 ± 0.3
IIb	1.31 ± 0.02	1.36 ± 0.01	1.44 ± 0.02	1.51 ± 0.01	1.76 ± 0.07	9.0 ± 0.2
IIc	0.86 ± 0.01	0.90 ± 0.01	0.95 ± 0.01	0.99 ± 0.02	1.73 ± 0.04	5.4 ± 0.1
IIId	1	1	1	1	0	0
IIe	5.04 ± 0.11	4.92 ± 0.15	4.77 ± 0.01	4.68 ± 0.09	-0.92 ± 0.04	9.9 ± 0.2
IIIf	4.94 ± 0.01	4.64 ± 0.01	4.22 ± 0.05	3.93 ± 0.03	-2.83 ± 0.09	2.3 ± 0.3
IIg	4.80 ± 0.01	4.22 ± 0.02	3.43 ± 0.02	2.91 ± 0.03	-6.20 ± 0.25	-10.9 ± 0.7
IIIh	2.54 ± 0.02	2.11 ± 0.01	1.61 ± 0.03	1.31 ± 0.02	-8.20 ± 0.26	-24.0 ± 0.8
IIIi	1.40 ± 0.02	1.10 ± 0.01	0.79 ± 0.04	0.62 ± 0.01	-10.10 ± 0.24	-36.4 ± 0.8

^a Average value of no less than two parallel runs. ^b $\Delta\Delta H^\ddagger = \Delta H^\ddagger_{\text{ArOH}} - \Delta H^\ddagger_{\text{PhOH}}$, $\Delta\Delta S^\ddagger = \Delta S^\ddagger_{\text{ArOH}} - \Delta S^\ddagger_{\text{PhOH}}$. ^c At 20°C.

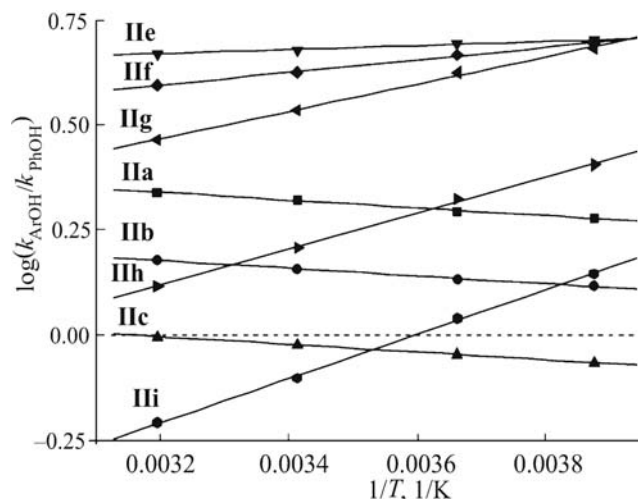


Fig. 1. Dependence of $\log(k_{\text{ArOH}}/k_{\text{PhOH}})$ on $1/T$ for the competing reactions between compound **I** and phenols **IIa–IIIi** in the presence of K_2CO_3 in DMF

equation for each reaction. Using the modified Eyring equations we calculated the differences of the activation parameters $\Delta\Delta H^\ddagger = \Delta\Delta H^\ddagger_{\text{ArOH}} - \Delta\Delta H^\ddagger_{\text{PhOH}}$ and $\Delta\Delta S^\ddagger = \Delta\Delta S^\ddagger_{\text{ArOH}} - \Delta\Delta S^\ddagger_{\text{PhOH}}$ (Table 2).

As seen from Fig. 1, the overall amount of plots $\log(k_{\text{ArOH}}/k_{\text{PhOH}}) - 1/T$ for the competing reactions between compound **I** and phenols **IIa–IIIi** in the presence of K_2CO_3 in DMF can be divided in three groups according to the initial phenols **IIa–IIc**, **IIe–IIg**, and **IIg–IIIi**.

Within each group of the competing reactions in the selected temperature range the relationships of Hammett (Fig. 2) and Brønsted are valid, and for the series **IIa–**

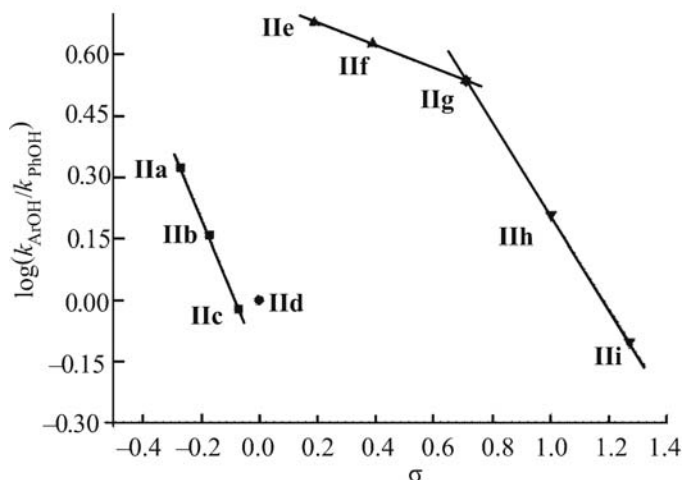


Fig. 2. Dependence of $\lg(k_{\text{ArOH}}/k_{\text{PhOH}})$ on σ for the competing reactions between compound **I** and phenols **IIa–IIIi** in the presence of K_2CO_3 in DMF at 20°C .

IIc the ρ and β_{Nuc} parameters are independent of temperature, but in the phenol series **IIe–IIg** and **IIg–IIIi** these parameters vary with the temperature ((Table 3).

The analysis of plots $\Delta\Delta H^\ddagger - \Delta\Delta S^\ddagger$, $\log(k_{\text{ArOH}}/k_{\text{PhOH}}) - 1/T$, $\rho - 1/T$, and $\beta_{\text{Nuc}} - 1/T$ shows that for each group of the competing reactions an isokinetic equation is valid (Table. 4) and therefore within each series **IIa–IIc**, **IIe–IIg**, and **IIg–IIIi** the condition is fulfilled of the constancy of the reaction mechanism [13].

The positive values of the isokinetic temperature show that at the variation of the reagent's structure the enthalpy and entropy components of the free energy of activation ΔG^\ddagger compensate each other [14, 15]. Evidently the

Table 3. Parameters of Hammett's and Brønsted's equations competing reactions between compound **I** and phenols **IIa–IIIi** in the presence of K_2CO_3 in DMF^a

Compound no.	ρ^b (β_{Nuc}^c)			
	-15°C	0°C	20°C	40°C
IIa–IIc	-1.72 ± 0.06 (0.35 ± 0.10)	-1.71 ± 0.05 (0.35 ± 0.10)	-1.72 ± 0.05 (0.35 ± 0.10)	-1.72 ± 0.06 (0.35 ± 0.10)
IIe–IIg^d	-0.05 ± 0.01 (0.01 ± 0.01)	-0.17 ± 0.02 (0.03 ± 0.01)	-0.36 ± 0.05 (0.06 ± 0.01)	-0.53 ± 0.07 (0.08 ± 0.02)
IIg–IIIi^e	-0.96 ± 0.01 (0.14 ± 0.03)	-1.04 ± 0.01 (0.16 ± 0.03)	-1.14 ± 0.01 (0.17 ± 0.04)	-1.20 ± 0.01 (0.18 ± 0.04)

^a Relative rate constants $k_{\text{ArOH}}/k_{\text{PhOH}}$ are taken from Table. 2; $\sigma_p^- = -0.27$ (4-MeO), -0.17 (4-Me), 0 (H), 0.19 (4-Cl), 0.39 (4-Br), 1.00 (4-CN), 1.27 (4-NO₂), $\sigma_m = -0.07$ (3-Me), 0.71 (3-NO₂) from [10]; pK_a of phenols in DMSO: 19.1 (**IIa**), 18.9 (**IIb**), 18.2 (**IIc**), 18.0 (**IIId**), 16.75 (**IIe**), 16.36 (**IIIf**), 14.4 (**IIg**), 13.2 (**IIH**), 10.8 (**IIIi**) from [11]; pK_a of phenols in DMF correlates with pK_a of phenols in DMSO: $pK_a(\text{DMF}) = 1.56 + 0.96 pK_a(\text{DMSO})$ [12].

^b $r \geq 0.991$.

^c $r \geq 0.960$.

^d $\rho = -2.80 + 712.42/T$ (r 0.997), $\beta_{\text{Nuc}} = 0.42 - 104.96/T$ (r 0.998).

^e $\rho = -2.35 + 358.48/T$ (r 0.997), $\beta_{\text{Nuc}} = 0.36 - 56.60/T$ (r 0.980).

Table 4. Isokinetic temperature β calculated from various relationships

Relationship	β , K		
	IIa–IIc	IIe–IIg	IIg–IIIi
$\Delta\Delta H^\ddagger = f(\Delta\Delta S^\ddagger)$	7	254	152
$\log(k_{\text{ArOH}}/k_{\text{PhOH}}) = f(1/T)$	9	253	153
$\rho = f(1/T)$	0	254	153
$\beta_{\text{Nuc}} = f(1/T)$	0	250	157

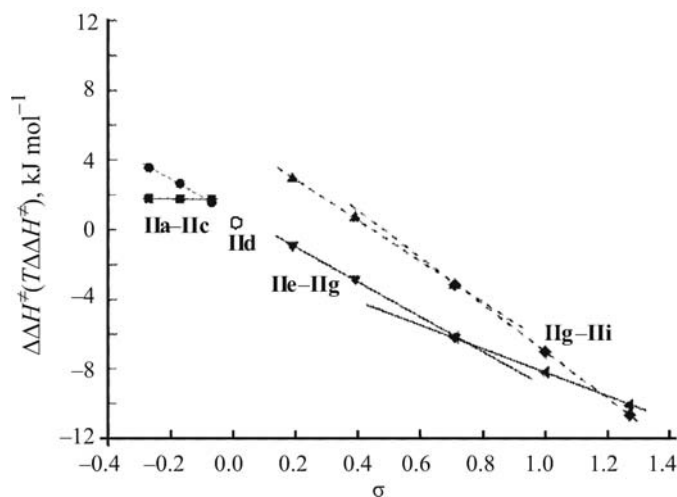
Table 5. Values of parameters $\delta\Delta H^\ddagger$ and $\delta\Delta S^\ddagger$ for isokinetic series of phenols **IIa–IIc**, **IIe–IIg**, and **IIg–IIIi** calculated from relationships $\Delta\Delta H^\ddagger (\Delta\Delta S^\ddagger) - \sigma^a$

Parameter	IIa–IIc	IIe–IIg	IIg–IIIi
$\delta\Delta H^\ddagger$, kJ mol ⁻¹	-0.25 (<i>r</i> 0.993)	-10.19 (<i>r</i> 0.999)	-6.96 (<i>r</i> 0.999)
$\delta\Delta S^\ddagger$, J mol ⁻¹ K ⁻¹	-34 (<i>r</i> 0.999)	-40.12 (<i>r</i> 0.999)	-45.53 (<i>r</i> 0.999)

^a $\Delta\Delta H^\ddagger = \Delta H^\ddagger_{\text{ArOH}} - \Delta H^\ddagger_{\text{PhOH}} = \delta\Delta H^\ddagger\sigma + \text{const}$; $\Delta\Delta S^\ddagger = \Delta S^\ddagger_{\text{ArOH}} - \Delta S^\ddagger_{\text{PhOH}} = \delta\Delta S^\ddagger\sigma + \text{const}$; $\Delta\Delta H^\ddagger$ and $\Delta\Delta S^\ddagger$ values at 293 K were taken from Table 2.

interpretation of the reaction mechanism based on the analysis of the sensitivity of the free energy of activation of the reaction ΔG^\ddagger to the nature of the substituent in the nucleophile expressed through the parameters ρ and β_{Nuc} should be considered very cautiously [16].

Parameters $\delta\Delta H^\ddagger$ and $\delta\Delta S^\ddagger$ computed from the relationships $\Delta\Delta H^\ddagger - \sigma$ and $\Delta\Delta S^\ddagger - \sigma$ respectively are independent of the temperature and reflect the sensitivity

**Fig. 3.** Dependence of $\Delta\Delta H^\ddagger$ (solid lines) and of $T\Delta\Delta S^\ddagger$ (dotted lines) on σ for the competing reactions between compound **I** and phenols **IIa–IIIi** in the presence of K_2CO_3 in DMF at 20°C.

of the variation of enthalpy and entropy of the activation of the reaction as a function of the nature of the substituent in the nucleophile (Table 5, Fig. 3) [14].

As seen from Table 5 for all isokinetic series the values of parameters $\delta\Delta H^\ddagger$ and $\delta\Delta S^\ddagger$ are negative, and for electron-donor substituents (phenols series **IIa–IIc**) the sensitivity of the enthalpy of activation is significantly less than for the electron-acceptor substituents (phenol series **IIe–IIg**).

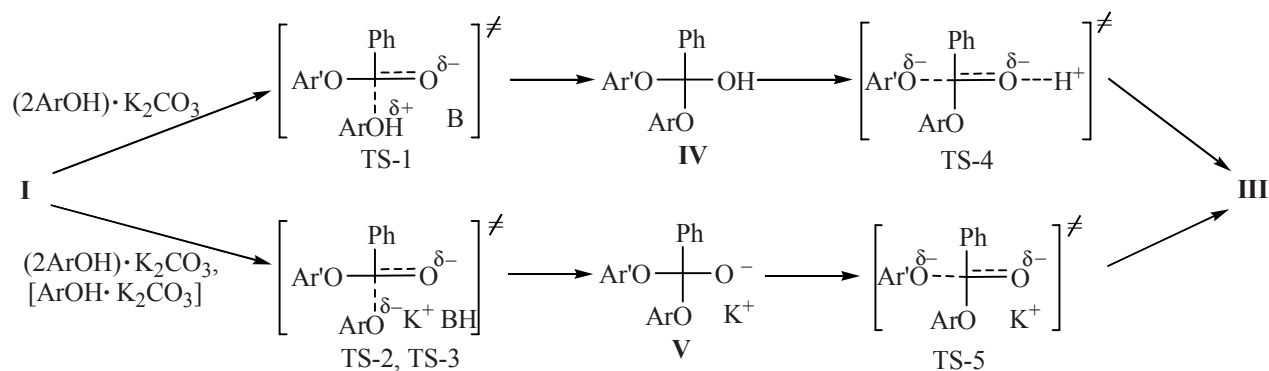
The similarity of parameters $\delta\Delta S^\ddagger$ and $\delta\Delta H^\ddagger$ values for phenol series **IIe–IIg** and **IIg–IIIi** may be regarded as the sign of the analogous structure and energy of the transition states of the respective reactions (Table 5). It was shown before that in substitution reactions of nitro groups in 3,5-dinitrobenzotrifluoride and fluorine atom in the 3-fluoro-5-nitrobenzotrifluoride in the system $\text{ArOH} \cdot \text{K}_2\text{CO}_3$ for phenols with $\text{p}K_a > 14.4$ the acting nucleophile was mainly the complex $(2\text{ArOH}) \cdot \text{K}_2\text{CO}_3$, and for phenols with $\text{p}K_a < 14.4$, the complex $[\text{ArOH} \cdot \text{K}_2\text{CO}_3]$ [17]. This means that the reactions of ester **I** with phenols **IIe–IIg** and **IIg–IIIi** in the presence of potassium carbonate proceed along the common mechanism but involve nucleophiles of different structure

The comparison of the energy parameters $\delta\Delta H^\ddagger$ and $\delta\Delta S^\ddagger$ for the phenols series **IIe–IIg** and **IIa–IIc** suggests that the transition states of the corresponding reactions are similar in the structure but essentially different in the energy (Table 5). It is known that for complex reaction a reversed dependence sometimes occurs for the activation energy of the reaction E_a (activation enthalpy of the reaction ΔH^\ddagger) on the stability of the intermediate product [18]. Proceeding from this knowledge it is presumable that the reactions of ester **I** with phenols **IIe–IIg** and **IIa–IIc** in the presence of potassium carbonate occur via stage mechanism but differ in the stability of the intermediate product. In accordance with the Brønsted–Polanyi relation in event of an isoenthalpy series ($\delta\Delta H^\ddagger = 0$) the first stage should be exothermal [18].

Based on the results obtained and the published data we suggest a kinetic scheme of the reaction of 2,4-dinitrophenyl benzoate (**I**) with complexes $(2\text{ArOH}) \cdot \text{K}_2\text{CO}_3$ and $[\text{ArOH} \cdot \text{K}_2\text{CO}_3]$ formed by phenols with the potassium carbonate (Scheme 3).

In keeping with the scheme the first stage of the transesterification of ester **I** in the system $\text{ArOH} \cdot \text{K}_2\text{CO}_3$ is the nucleophilic attack of complexes $(2\text{ArOH}) \cdot \text{K}_2\text{CO}_3$ and $[\text{ArOH} \cdot \text{K}_2\text{CO}_3]$ characterized by transition states TS-1 (phenol series **IIa–IIc**), TS-2 (phenol series **IIe–**

Scheme 3.



Ar' = 2,4-(NO₂)₂C₆H₃; B = K₂CO₃·ArOH; BH = KHCO₃·ArOH (TS-2), KHCO₃ (TS-3).

IIg), and TS-3 (phenol series **IIg–IIIi**). The formation of a neutral structure of intermediate compound **IV** that is more stable than the anionic structure **V** presumably is caused by the donor effect of the substituents in phenols **IIa–IIc**. The limiting stage of the assumed mechanism is the decomposition of intermediate products **IV** and **V** (transition states TS-4 and TS-5). Thus the rate constant of the reaction k is determined by the equilibrium constant of the first stage K_1 and the rate constant of the second stage k_2 [4]. It should be stressed that the possibility of occurrence of the assumed scheme is due to the proton transfer in the first stage since the considerable reduction of the energy barrier both of the direct and the reverse reactions determines the larger nucleophilicity of complexes $(2\text{ArOH})\cdot\text{K}_2\text{CO}_3$ and $[\text{ArOH}\cdot\text{K}_2\text{CO}_3]$ compared with that of 2,4-dinitrophenolate anion, and also the maintaining of the restriction $k_{-1} \gg k_2$.

The formation of an intermediate product of **IV** type is characteristic of esterification and hydrolysis reactions [19]. The reactions of this type are known to be utterly insensitive to the electronic effects of substituents [20].

In event of intermediate product **V** it is expectable that the electron-acceptor substituents should accelerate the first stage and decelerate the second one [19], therefore the overall effect should be compensated and should give small ρ values (Table 3). Among examples of this type reactions the most often are the condensations of carbonyl compounds, and the isokinetic temperature of these processes is close to the experimental temperature [21].

Hence based on analysis of the established parameters $\delta\Delta H^\ddagger$ and $\delta\Delta S^\ddagger$ we may conclude that the transesterification of 2,4-dinitrophenyl benzoate under the action of phenols in the presence of potassium carbonate in DMF

proceeds by the $A_N + D_N$ mechanism involving the second limiting stage.

EXPERIMENTAL

The reaction mixtures were analyzed by GLC on a chromatograph LKhM-72 (detector catharometer, ramp from 70 to 270°C at a rate 10 deg/min, column 4000 × 4 mm, stationary phase SKTFT-803 (15%) on Chromaton-W, carrier gas helium); the quantitative analysis of mixtures was carried out by absolute calibration with drawing a calibration plot; the identification of the components was performed by adding authentic samples. Commercial DMF was dried by molecular sieves 4 Å and distilled in a vacuum over CaH₂. Commercial phenols were purified by standard procedures. Initial compound **I** was prepared as in [22].

Reaction of phenols **IIa–IIIi** with compound **I** in the presence of potassium carbonate in DMF at 20°C.

General procedure. To a dispersion of 5 mmol of K₂CO₃ and 5 mmol of phenol ArOH in 10 ml of DMF was added 5 mmol of compound **I** and the mixture was dried for 30 min at 20°C. To the reaction mixture 5 ml of water was added, the products were extracted into ethyl ether (3 × 10 ml). The combined extract was dried over MgSO₄, the solvent was distilled off, and the residue was subjected to column chromatography (35 × 150 mm, SiO₂, 100/250μ, CCl₄). Reaction products **IIIa–IIIi** were obtained in a quantitative yield, their physicochemical constants and spectra were consistent with the published data [23]. The product yields on reducing the reaction time to 5 s fall in the range 10–20%.

The competing reactions of each pair of phenols were carried out at their equimolar concentrations that exceeded 5-fold the substrate concentration. The selected

conditions allowed an assumption that the ratio of the concentrations of the formed products was directly proportional to the ratio of the second order rate constants of each reaction [24].

Estimation of relative rate constants of phenols IIa–IIIi reaction with compound I in the presence of potassium carbonate in DMF at 20°C. General procedure. To 2–3 ml of solution of 0.5 mol of phenol ArOH and 0.5 mmol of Ar'OH in DMF 1 mmol of K₂CO₃ was added. The mixture was maintained at constant temperature while stirring. To the dispersion obtained compound I kept at the same temperature were added in one portion in amount of 0.3 ml (0.1 mmol), and 5 s later 3 ml of ethyl ether and 2 ml of water was added to the reaction mixture. The organic layer was separated, the water layer was extracted with ethyl ether (2 × 3 ml). The solvent was distilled off from the combined extracts, the residue was analyzed by GLC. The reaction conditions of the competing reactions and the results are compiled in Table 1.

Estimation of relative reactivity of esters PhCO₂Ar and PhCO₂Ar' with respect to phenols ArOH and Ar'OH in DMF. General procedure. To 2–3 ml of solution of 0.5 mol of phenol ArOH and 0.5 mmol of Ar'OH in DMF 1 mmol of K₂CO₃ was added. To the dispersion obtained 0.3 ml of a solution of 0.05 mmol of ester PhCO₂Ar and 0.05 mmol of PhCO₂Ar' kept at the same temperature were added in one portion, and 5 s later 3 ml of ethyl ether and 2 ml of water were added to the reaction mixture. The organic layer was separated, the water layer was extracted with ethyl ether (2 × 3 ml). The solvent was distilled off from the combined extracts, the residue was analyzed by GLC. Each reaction was performed at –15 and 40°C. In all events the change in the ratio of the molar concentrations of the corresponding esters PhCO₂Ar and PhCO₂Ar' did not exceed 5%.

Reactions of esters IIIb and IIIc with phenols IIb and IIc in the presence of potassium carbonate in DMF. General procedure. To 2–3 ml of solution of 0.5 mol of phenol IIb and 0.5 mmol of phenol IIc in DMF 1 mmol of K₂CO₃ was added. The mixture was stirred for 15 min at 40°C. To the dispersion obtained 0.3 ml (0.1 mmol) of a solution of ester IIIb or IIIc kept at the same temperature was added, and 10 min later 3 ml of ethyl ether and 2 ml of water were added to the reaction mixture. The solvent was distilled off from the combined extracts, the residue was analyzed by GLC. Yield of ester IIIc from IIIb was 15%, of ester IIIb from IIIc 40%. Under similar conditions ester IIIh was

transformed into IIIi in 10% yield, and IIIi into IIIh in 60% yield.

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