

Kinetics of the Reaction of Substituted 4-Nitrophenyl Benzoates with Benzenethiol in the Presence of Potassium Carbonate in Dimethylformamide

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Abstract—The effect of the substituent nature on the rate and activation parameters of transesterification of a series of 4-nitrophenyl benzoates with benzenethiol in dimethylformamide in the presence of potassium carbonate was studied by the competing reaction method. In all cases, change of the Gibbs energy of activation is determined mainly by variation of the enthalpy of activation. 4-Nitrophenyl benzoates having electron-withdrawing substituents in the benzoyl fragment were found to fit an isokinetic relation with an isokinetic temperature β of 318 K. Enthalpy–entropy compensation effect was observed in the reactions with all the examined 4-nitrophenyl benzoates. The relation between the reactivity and polarizability of nucleophilic center in S- and O-nucleophiles is discussed.

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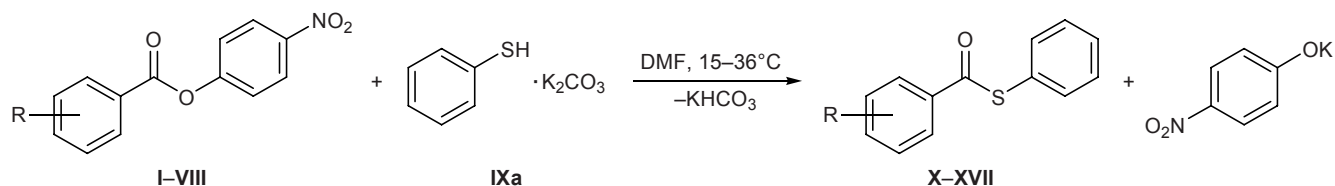
The kinetics of bimolecular nucleophilic reactions at a carbonyl carbon atom were the subject of numerous studies [1–7]. Interest in acyl group transfer reactions originates from both their participation in biological processes [7–9] and applications in organic synthesis [10–13]. Analysis of the kinetic data for these reactions shows that nucleophile nature is an important factor affecting the reactivity of carbonyl carbon atom and reaction mechanism. For example, reactions of substituted phenyl benzoates with anionic nucleophiles (such as hydroxide, cyanide, and phenoxide ions) in aqueous dimethyl sulfoxide (DMSO) include several steps with formation of a tetrahedral intermediate in the rate-determining step [2, 14].

Transesterification reactions with potassium 4-chlorophenoxide as nucleophile also include several steps

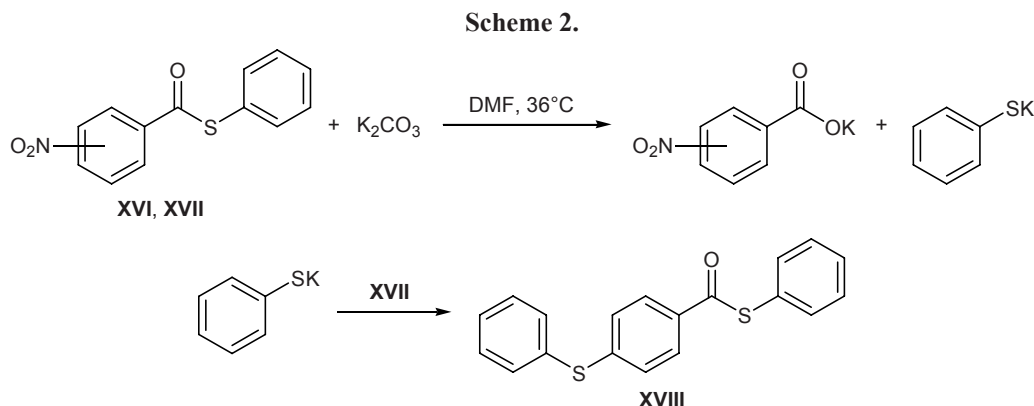
and are characterized by high values of the Yukawa–Tsuno resonance parameter r [15] which reflects resonance demand of the reaction center [16]. However, transesterification of substituted phenyl benzoates with 4-chlorophenol in the presence of potassium carbonate in dimethylformamide (DMF) is characterized by appreciably reduced resonance parameter r , the stepwise reaction mechanism being conserved [17]. In this case, the observed reduction of r may be related to decrease of the resonance demand of the reaction center owing to formation of a cyclic transition state [17].

In order to elucidate how the nucleophile nature affects the transesterification process it was necessary to extend the series of nucleophiles. Therefore, in the present work we examined the kinetics of the reactions of substituted 4-nitrophenyl benzoates **I–VIII** with

Scheme 1.



I, X, R = 4-MeO; **II, XI**, R = 4-Me; **III, XII**, R = H; **IV, XIII**, R = 4-Br; **V, XIV**, R = 3-Br; **VI, XV**, R = 4-F₃C;
VII, XVI, R = 3-O₂N; **VIII, XVII**, R = 4-O₂N.



benzenethiol in DMF in the presence of potassium carbonate. In keeping with our previous data [18], benzenethiol with potassium carbonate in DMF forms nucleophilic complex **IXa** (Scheme 1). The electrophilicity of the ester carbonyl carbon atom depends on the substituent in the benzene ring: electron-donating groups reduce the reactivity, while electron-withdrawing substituents increase it [19]. The electrophilicity of the ester carbonyl carbon atom in molecules **I–VIII** was varied using a set of substituents R characterized by a broad range of Hammett constants σ .

It is known that the reactivity of O- and S-centered anions toward 4-nitrophenyl benzoate is determined by not only their basicity but also polarizability [20]. Therefore, change in the reactivity of nucleophilic species **IXa** toward substituted 4-nitrophenyl benzoates **I–VIII** relative to the reactivity of 4-ClC₆H₄OH·K₂CO₃ (**IXb**) in DMF [17] can also be related to different polarizabilities of the reaction centers in compounds **I–VIII**, **IXa**, and **IXb**.

Benzoates **I–VIII** react with nucleophile **IXa** in dimethylformamide in the temperature range from 15 to 36°C to give substituted S-phenyl benzothioates **X–XVII** (Scheme 1). Compounds **X–XV** are fairly stable under the given conditions. S-Phenyl 3-nitrobenzothioate (**XVI**) was found to react with potassium carbonate in DMF [17, 21] at 36°C to give benzenethiol and the corresponding nitrobenzoic acid, while the reaction of 4-nitrophenyl 4-nitrobenzoate (**VIII**) with benzenethiol was accompanied by replacement of the benzoyl nitro group in the transesterification product, S-phenyl 4-nitrobenzothioate (**XVII**), by phenylsulfanyl group with formation of S-phenyl 4-(phenylsulfanyl)benzothioate (**XVIII**) (Scheme 2). These processes strongly complicated study on the reactivity of esters **VII** and **VIII**; therefore, they were excluded from the set of substrates for kinetic experiments with nucleophile **IXa**.

The relative rate constants for the reactions of esters **I–VI** with nucleophile **IXa** in DMF at different temperatures were determined by the competing reac-

Table 1. Relative rate constants k_{rel} and differences in the activation parameters for the competing reactions of substituted 4-nitrophenyl benzoates **I–VI** with benzenethiol in the presence of potassium carbonate in DMF

Compound no.	k_{rel}^a			$\Delta\Delta H^\ddagger,^b$ kJ/mol	$\Delta\Delta S^\ddagger,^b$ J mol ⁻¹ K ⁻¹	$T\Delta\Delta S^\ddagger,^b,^c$ kJ/mol	$\Delta\Delta G^\ddagger,^b,^c$ kJ/mol
	15°C	26°C	36°C				
I	0.15	0.19	0.25	19.1±2.8	49.9±7.4	14.9	4.2
II	0.40	0.45	0.59	13.5±0.9	38.5±2.7	11.5	2.0
III	1	1	1	0	0	0	0
IV	3.3	2.3	1.6	-25.4±4.6	-78.0±14.0	-23.3	-2.1
V	8.7	2.7	2.0	-52.6±7.9	-167.4±25.1	-50.1	-2.5
VI	14.8	4.4	2.4	-64.7±11.0	-204.2±34.7	-61.1	-3.6

^a Calculated from the data in Table 4 assuming $k_{\text{rel}} = 1$ for compound **III**.

^b The differences $\Delta\Delta H^\ddagger = \Delta H^\ddagger(\text{R}) - \Delta H^\ddagger(\text{H})$, $\Delta\Delta S^\ddagger = \Delta S^\ddagger(\text{R}) - \Delta S^\ddagger(\text{H})$, and $\Delta\Delta G^\ddagger = \Delta G^\ddagger(\text{R}) - \Delta G^\ddagger(\text{H})$ were calculated using the Eyring equation: $\log k_{\text{rel}} = (-\Delta\Delta H^\ddagger/T + \Delta\Delta S^\ddagger)/4.576$ [22].

^c At 26°C.

tion method (Table 1). The rate constants increased in going from electron-donating to electron-withdrawing substituents in substrates **I–VI**, regardless of the reaction temperature. The observed range of variation of the relative rate constants amounts to two orders of magnitude (Table 1); the relative rate constants in analogous transesterification reactions with nucleophile **IXb** changed by three orders of magnitude [17].

Linear relations were found between $\log k_{\text{rel}}$ and $1/T$ for each benzoate: $R = 0.992$ (**I**), 0.992 (**II**), 0.999 (**IV**), 0.970 (**V**), 0.989 (**VI**) (Fig. 1); using these relations we calculated differences in the effective activation parameters $\Delta\Delta H^\ddagger$, $\Delta\Delta S^\ddagger$, and $\Delta\Delta G^\ddagger$, which reflect the reactivity in energy units, by the modified Eyring equation [22] (Table 1). Compounds **III–VI** constitute an isokinetic series with an isokinetic temperature β of 318 K, which was determined as the crossing point of the straight lines in Fig. 1 [23]. Fairly similar values of β were also obtained from the dependences $\Delta\Delta H^\ddagger - \Delta\Delta S^\ddagger$ and $\log k_{\text{rel}}(15^\circ\text{C}) - \log k_{\text{rel}}(36^\circ\text{C})$ (Table 2) [24].

The reactions of compounds **I–VI** with PhSH- K_2CO_3 (**IXa**) showed a common linear kinetic enthalpy–entropy compensation effect (Fig. 2) [23, 25]:

$$\begin{aligned} \Delta\Delta H^\ddagger &= 0.32\Delta\Delta S^\ddagger + 1.18; & (1) \\ R &= 0.999, s = 1.26, n = 6. \end{aligned}$$

The compensation temperature (322 K) is lower than that found for the reactions of substituted 4-nitrophenyl benzoates with nucleophile **IXb** (390 K) [17], and it approaches the experimental temperature range (288–309 K).

As follows from the data in Table 1, increase in the electron-withdrawing power of the substituent in molecules **I–VI** leads to considerable decrease of the differences in the activation parameters ($\Delta\Delta H^\ddagger$, $\Delta\Delta S^\ddagger$, and $\Delta\Delta G^\ddagger$). As in the competing reactions of substituted phenyl benzoates with 4-ClC₆H₄OH·K₂CO₃ (**IXb**) [17], the ranges of variation of $\Delta\Delta H^\ddagger$ and $\Delta\Delta S^\ddagger$ are fairly large, 83.8 kJ/mol and 254.1 J mol⁻¹ K⁻¹, respectively (cf. [26]). The range of variation of $\Delta\Delta G^\ddagger$ for the transesterification of compounds **I–VI** amounts to 7.8 kJ/mol (~1.9 kcal/mol, Table 1), which is typical of reactions of carbonyl compounds with nucleophilic reagents [27, 28]. Change in the Gibbs energy of activation for all reactions is determined mainly by variation of the enthalpy of activation. The relation between $\Delta\Delta H^\ddagger$ and $\Delta\Delta G^\ddagger$ is linear [Eq. (2)].

$$\begin{aligned} \Delta\Delta H^\ddagger &= -14 + 11\Delta\Delta G^\ddagger; & (2) \\ R &= 0.937, s = 14, n = 6. \end{aligned}$$

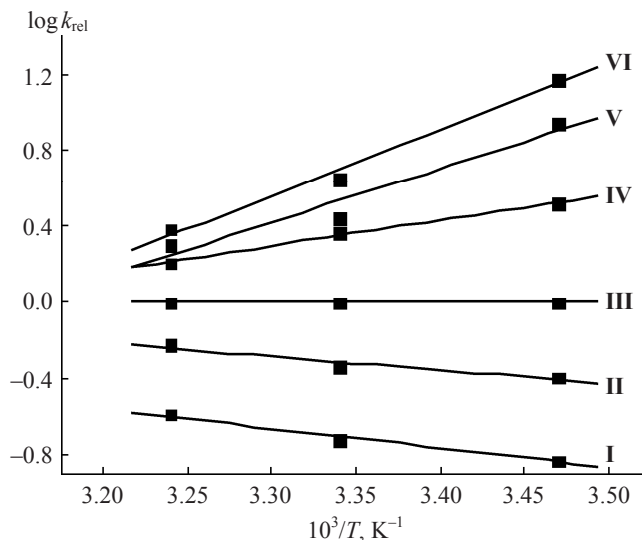


Fig. 1. Semilog plots of the relative rate constants ($\log k_{\text{rel}}$) versus reciprocal temperature ($10^3/T$) for the reactions of substituted 4-nitrophenyl benzoates **I–VI** with benzenethiol in the presence of potassium carbonate in DMF.

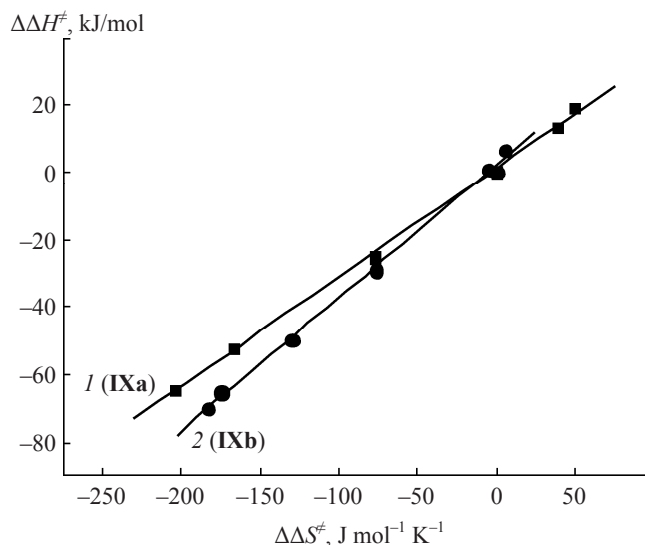


Fig. 2. Plots of the change in the enthalpy of activation $\Delta\Delta H^\ddagger$ versus change in entropy of activation $\Delta\Delta S^\ddagger$ for the reactions of substituted 4-nitrophenyl benzoates with (1) benzenethiol (**IXa**) and (2) 4-chlorophenol (**IXb**) in the presence of potassium carbonate in DMF.

The effect of the substituent R in the benzoyl fragment of esters **I–VI** on the activation parameters can be estimated from the absolute slopes of the corresponding dependences upon substituent constants σ [29, 30]. Table 3 contains the absolute values of ρ for the dependences $a = \rho\sigma + c$ (where a is the activation parameter, $\Delta\Delta H^\ddagger$, $\Delta\Delta S^\ddagger$, $T\Delta\Delta S^\ddagger$, or $\Delta\Delta G^\ddagger$) for transesterification of aryl benzoates with nucleophiles **IXa**

Table 2. Isokinetic temperatures β calculated from different dependences for the transesterification of substituted 4-nitrophenyl benzoates **III–VI**

Dependence	β , K	R	s	n
$\log k_{\text{rel}}-f(1/T)$	318 ± 5	$0.970-0.999$	$0.1-0.01$	4
$\log k_{\text{rel}}(15^\circ\text{C})-\log k_{\text{rel}}(36^\circ\text{C})$	312 ± 25	0.994	0.1	4
$\Delta\Delta H^\ddagger-\Delta\Delta S^\ddagger$	315 ± 3	0.9999	0.5	4

Table 3. Absolute slopes $|\rho|$ of the dependences of activation parameters (a) upon substituent constants σ for transesterification of benzoates, $a = \rho\sigma + c$

Activation parameter a	$ \rho $	
	IXa	IXb^a
$\Delta\Delta H^\ddagger$	108.5 ($c = -5.3$, $R = 0.992$, $s = 5.0$, $n = 6$)	76.4
$\Delta\Delta S^\ddagger$	332 ($c = -20$, $R = 0.987$, $s = 19$, $n = 6$)	192
$T\Delta\Delta S^\ddagger$	99 ($c = -6$, $R = 0.987$, $s = 6$, $n = 6$)	60
$\Delta\Delta G^\ddagger$	9 ($c = 1$, $R = 0.970$, $s = 0.8$, $n = 6$)	16.3

^a Data of [17].

and **IXb** (Fig. 3). The $|\rho|$ values are fairly large, which indicates high sensitivity of the activation parameters to the substituent nature. High sensitivity of the enthalpy of activation is difficult to interpret, for $\Delta\Delta H^\ddagger$ depends on both reactant nature and solvation [30]. As

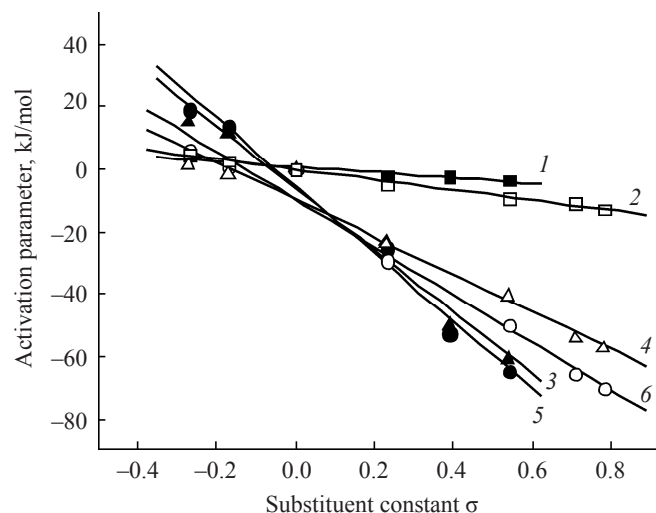


Fig. 3. Plots of (1, 2) $\Delta\Delta G^\ddagger$, (3, 4) $T\Delta\Delta S^\ddagger$, and (5, 6) $\Delta\Delta H^\ddagger$ versus substituent constants σ for the reactions of substituted 4-nitrophenyl benzoates with (1, 3, 5) benzenethiol (**IXa**) and (2, 4, 6) 4-chlorophenol (**IXb**) in the presence of potassium carbonate in DMF.

follows from the data in Table 3, the sensitivity of the entropy of activation to the substituent nature in the transesterification with nucleophile **IXa** is higher than in the reaction with **IXb**. Substituent-related change in the entropy is determined by solvation [31]. Increased sensitivity of the entropy of activation to the substituent nature may result from change in solvation upon formation of transition state. The formation of transition state involves delocalization of charge on the reaction center by the action of electron-withdrawing substituent, which can lead to enhancement of nonspecific solvation of the transition state as compared to solvation of the initial nucleophile. Presumably, the difference in solvation of the initial and transition state in the reaction with S-centered nucleophile **IXa** is larger than in the reaction with O-centered nucleophile **IXb**. The result is that the entropy of activation in the transesterification with S-nucleophile **IXa** decreases to a greater extent than in analogous reaction with O-nucleophile **IXb**. The quantity $\Delta\Delta G^\ddagger$ reflects substituent effect on bond formation. The sensitivity of the energy barrier $\Delta\Delta G^\ddagger$ to the substituent nature is given by the absolute value of the slope of the $\Delta\Delta G^\ddagger-\sigma$ dependence and is interpreted in a way similar to interpretation of the parameter ρ in the Hammett equation [30].

The absolute ρ values found from the Hammett equation (2.4, 1.6, and 1.1 at 15, 26, and 36°C, respectively) are fairly large, which suggests considerable electron density redistribution in the transition state. High absolute values of ρ are typical of reactions following a stepwise mechanism [2]. Positive values of ρ indicate acceleration of the process by electron-withdrawing substituents. It is known that electron-withdrawing substituents accelerate the stage involving nucleophilic attack by increasing the electrophilic demand of the carbonyl carbon atom and decelerate the stage of elimination of leaving group. In our case, the large positive values of ρ indicate that the rate-determining stage precedes formation of tetrahedral intermediate.

The ρ value for the reactions of substituted 4-nitrophenyl benzoates with nucleophile **IXb** at 24°C was found to be 3.43 [17]. The ρ value determined in the present work for the transesterification of substituted 4-nitrophenyl benzoates with PhSH- K_2CO_3 (**IXa**) from the dependence of $\log k_{\text{rel}}$ on σ [32] is considerably lower [Eq. (3)]:

$$\begin{aligned} \log k_{\text{rel}}(26^\circ\text{C}) &= 1.6\sigma - 0.1; \\ R &= 0.972, s = 0.4, n = 6. \end{aligned} \quad (3)$$

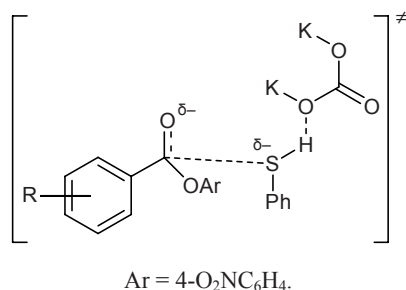
Correlation (3) is appreciably improved when the relative rate constants $\log k_{\text{rel}}(26^\circ\text{C})$ are treated according to the Yukawa–Tsuno equation (4) [16] (Fig. 4):

$$\log k_{\text{rel}}(26^\circ\text{C}) = 1.1\sigma^0 + 0.94(\sigma^+ - \sigma^0) + 0.04; \quad (4)$$

$$R = 0.990, s = 0.07, n = 6.$$

Increase of the correlation coefficient from 0.972 to 0.990 indicates that the use of the Yukawa–Tsuno equation allows us to take into account additional resonance stabilization of the initial state of substrates possessing electron-donating groups in the benzoyl fragment [33].

We previously showed that the kinetics of transesterification of substituted 4-nitrophenyl benzoates with 4-ClC₆H₄OH–K₂CO₃ (**IXb**) [17] are well described by the Yukawa–Tsuno equation [16] with the following parameters: $\rho = 3.45$, $r = 0.17$. The value $r = 0.94$ suggests high degree of resonance interaction between the substituent R in the benzoyl fragment and reaction center in the transition state. Insofar as the resonance demand of the reaction center increases in going from cyclic to acyclic transition state [16], we presumed that the high resonance demand of the reaction center in the reaction under study is related to acyclic structure of the transition state.



The formation of acyclic transition state may be favored by longer distance between the carbonyl carbon atom and nucleophilic center in the reaction with benzenethiol (S-centered nucleophile) as compared to O-centered nucleophile [34], as well as by less effective interaction between the carbonyl carbon atom with soft S-nucleophile as compared to hard O-nucleophile.

Kwon et al. [20] interpreted the ratio of the rate constants for the reactions of 4-nitrophenyl benzoate with benzenethiolate and 4-chlorophenoxide ($k_{\text{O}}/k_{\text{S}} = 1.6$, anhydrous ethanol, 25°C) in terms of different polarizabilities of the substrates and nucleophiles. In our case, the ratio of the rate constants for the reactions of 4-nitrophenyl benzoate with nucleophiles **IXa** and

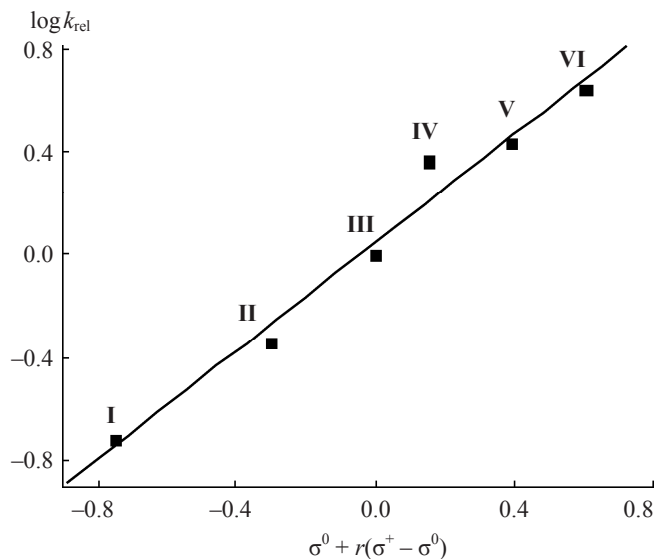


Fig. 4. Semilog plots of the relative rate constants $\log k_{\text{rel}}(26^\circ\text{C})$ for the reactions of substituted 4-nitrophenyl benzoates **I–VI** with benzenethiol in the presence of potassium carbonate in DMF versus the parameter $\sigma^0 + r(\sigma^+ - \sigma^0)$ according to the Yukawa–Tsuno equation; values of σ^0 and σ^+ were taken from [32].

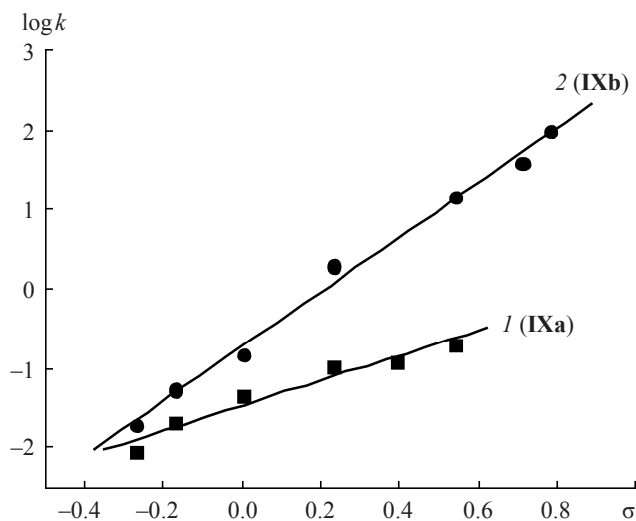


Fig. 5. Semilog plots of the rate constants ($\log k$) for the reactions of substituted 4-nitrophenyl benzoates with (1) benzenethiol (**IXa**) at 26°C and (2) 4-chlorophenol (**IXb**) at 24°C in the presence of potassium carbonate in DMF, calculated from k_{rel} (taken from Table 1 and [17]) and rate constants for the reactions of 4-nitrophenyl benzoate (**III**) with nucleophiles **IXa** and **IXb**, versus substituent constants σ .

IXb ($k_{\text{O}}/k_{\text{S}} = 3.3$; Fig. 5) does not contradict the difference in the nucleophile basicities [35], and it may be related to change of the polarizability of the reaction center in going from O-centered nucleophile to S-centered nucleophile.

Table 4. Relative rate constants for the reactions of substituted 4-nitrophenyl benzoates I–VI with benzenethiol in the presence of potassium carbonate in DMF

Compound no.	k_{rel}^a		
	15°C	26°C	36°C
II/I	2.7±0.4	2.4±0.1	2.3±0.3
III/II	2.5±0.2	2.2±0.2	1.7±0.2
IV/III	3.3±0.6	2.3±0.3	1.6±0.2
VI/IV	4.5±0.7	1.9±0.4	1.5±0.3
VI/V	1.7±0.3	1.6±0.2	1.2±0.1

^a Determined from the results of at least three parallel runs.

Thus the examined transesterification of substituted 4-nitrophenyl benzoates with benzenethiol in the presence of potassium carbonate in DMF is likely to involve several steps with formation of acyclic transition state, and departure of leaving group is not the rate-determining stage. The observed differences in the reactivity of O- and S-nucleophiles are consistent with the difference in their basicity and polarizability of the nucleophilic center.

EXPERIMENTAL

The IR spectra were recorded on a Bruker instrument from 2% solutions in chloroform or KBr pellets (0.25% of a substance). The ¹H and ¹⁹F NMR spectra were measured from solutions in CDCl₃ on Bruker WP-200 SY and AC-200 spectrometers using hexamethyldisiloxane (¹H) and hexafluorobenzene (¹⁹F) as references. The mass spectra (electron impact, 70 eV) were obtained on a Finnigan MAT-8200 mass spectrometer with direct sample admission into the ion source (ion source temperature 220–270°C). The reaction mixtures were analyzed by GLC using Hewlett-Packard HP-5890 and LKhM-72 instruments (thermal conductivity detector; linear oven temperature programming from 50 to 270°C at a rate of 10 deg/min; stationary phase 15% of SKTFT-803, SE-30, or VS-1 on Chromaton W; carrier gas helium, flow rate 60 ml/min); the components were quantitated by the internal normalization technique and were identified by comparing with authentic samples. Gas chromatographic–mass spectrometric analysis was performed on a Hewlett-Packard G 1081A GC–MS system consisting of an HP 5890 Series II chromatograph and an HP-5971 mass-selective detector (electron impact, 70 eV; HP-5 capillary column, 5% of biphenyl and 95% of dimethylsiloxane), 30 m × 0.25 m × 0.25 μm; carrier gas

helium, 1 ml/min; injector temperature 280°C, oven temperature programming from 50 to 280°C). Silica gel KSK (5–40 μ) was used for thin-layer chromatography. Commercial dimethylformamide was dried over phosphoric anhydride, distilled under reduced pressure first over calcium hydride and then over molecular sieves, and stored over molecular sieves under argon. Commercial potassium carbonate was calcined in a muffle furnace and thoroughly ground prior to use. Commercial benzenethiol was distilled under reduced pressure. Commercial thionyl chloride was distilled before use. Commercial 3-bromobenzoic acid was used without additional purification.

Commercial 4-nitrophenol was purified by standard methods. Substituted *p*-nitrophenyl benzoates I–IV and VI–VIII were synthesized according to the procedure described in [17] and were characterized by IR, ¹H and ¹⁹F NMR, and mass spectra.

4-Nitrophenyl 3-bromobenzoate (V). A mixture of 15.8 g (0.08 mol) of 3-bromobenzoic acid, 10.9 g (0.08 mol) of 4-nitrophenol, and 11.5 ml (0.16 mol) of thionyl chloride was heated for 20 h at 80°C. The mixture was cooled to room temperature and poured onto ice, and the precipitate was filtered off, washed with a saturated solution of potassium carbonate and water, and dried. According to the GC–MS data, the product (22.3 g) contained 97% of ester V and 3% of 4-nitrophenol. Recrystallization from ethanol gave 17.3 g (68%) of compound V with mp 121–123°C. IR spectrum, ν , cm⁻¹: 1744 s (C=O); 1347 s, 1524 s (NO₂). ¹H NMR spectrum, δ , ppm: 7.42 m (3H, 2'-H, 6'-H, 5-H), 7.78 m (1H, 4-H, *J* = 8.0 Hz), 8.11 m (1H, 6-H, *J* = 8.0 Hz), 8.32 m (3H, 2-H, 3'-H, 5'-H). Found: $[M]^+$ 320.96372. C₁₃H₈BrNO₄. Calculated: *M* 320.96372.

S-Phenyl benzothioates X–XVII (general procedure). A flask was purged with argon and charged with substituted 4-nitrophenyl benzoate I–VIII, benzenethiol, potassium carbonate, and 10 ml of DMF. The mixture was stirred for 3 h at 20–25°C, diluted with 10 ml of water, and treated with 10% hydrochloric acid until neutral reaction. The precipitate was filtered off, washed with water, and dried.

S-Phenyl 4-methoxybenzothioate (X) was synthesized from 0.96 g (3.52 mmol) of 4-nitrophenyl 4-methoxybenzoate and 0.39 g (3.52 mmol) of benzenethiol using 0.97 g (7.04 mmol) of potassium carbonate. Yield of the crude product 0.8 g (45% according to the GLC data). Recrystallization from hexane gave 0.25 g (29%) of compound X with mp 98–99°C; published data [36]: mp 99°C.

S-Phenyl 4-methylbenzothioate (XI) was synthesized from 1.97 g (7.66 mmol) of 4-nitrophenyl 4-methylbenzoate and 0.84 g (7.66 mmol) of benzenethiol using 2.11 g (15.32 mmol) of potassium carbonate. Yield of the crude product 1.74 g (89%, GLC). Recrystallization from hexane gave 1.3 g (74%) of compound **XI** with mp 91–93°C [37].

S-Phenyl benzothioate (XII) was synthesized from 2.04 g (8.3 mmol) of 4-nitrophenyl benzoate and 0.91 g (8.3 mmol) of benzenethiol using 2.29 g (16.6 mmol) of potassium carbonate. Yield of the crude product 1.52 g (78%, GLC). A 0.35-g portion of the crude product was subjected to vacuum sublimation. Yield 0.26 g (64%), mp 55–56°C; published data [38]: mp 56–57°C.

S-Phenyl 4-bromobenzothioate (XIII) was synthesized from 0.67 g (2.1 mmol) of 4-nitrophenyl 4-bromobenzoate and 0.23 g (2.1 mmol) of benzenethiol using 0.58 g (4.2 mmol) of potassium carbonate. Yield of the crude product 0.4 g (29%, GLC). The crude product was purified by column chromatography on aluminum oxide using chloroform as eluent. Yield 0.15 g (24%), mp 99–100°C [39].

S-Phenyl 3-bromobenzothioate (XIV) was synthesized from 1.7 g (5 mmol) of 4-nitrophenyl 3-bromobenzoate and 0.6 g (5 mmol) of benzenethiol using 1.5 g (10 mmol) of potassium carbonate (reaction time 4 h). Yield of the crude product 1.4 g (85%, GLC). The crude product was purified by thin-layer chromatography on a 20×20-cm plate precoated with silica gel using carbon tetrachloride as eluent. Yield 0.91 g (58%), mp 49–51°C. IR spectrum: ν 1683 cm^{-1} , ν (C=O). ^1H NMR spectrum, δ , ppm: 7.35 m (1H, 5-H, $J = 8.0$ Hz), 7.43–7.50 m (5H, C_6H_5), 7.72 m (1H, 4-H, $J = 8.0$ Hz), 7.94 m (1H, 6-H, $J = 8.0$ Hz), 8.12 m (1H, 2-H). Found: $[M]^+$ 291.95594. $\text{C}_{13}\text{H}_9\text{BrOS}$. Calculated: M 291.95580.

S-Phenyl 4-trifluoromethylbenzothioate (XV) was synthesized from 5.85 g (18.8 mmol) of 4-nitrophenyl 4-trifluoromethylbenzoate and 2.07 g (18.8 mmol) of benzenethiol using 5.19 g (37 mmol) of potassium carbonate in 20 ml of DMF. Yield of the crude product 4.95 g (91%, GLC). A 0.1-g portion of the crude product was purified by vacuum sublimation at 110°C (2–3 mm). Yield 0.09 g (84%), mp 113–114°C; published data [40]: mp 114–115°C.

S-Phenyl 3-nitrobenzothioate (XVI) was synthesized from 0.99 g (3.5 mmol) of 4-nitrophenyl 3-nitrobenzoate and 0.38 g (3.5 mmol) of benzenethiol using 0.96 g (7.4 mmol) of potassium carbonate. Yield

of the crude product 0.71 g (76%, GLC). The crude product was purified by column chromatography on aluminum oxide using chloroform as eluent. Yield 0.58 g (64%), mp 107–109°C. IR spectrum, ν , cm^{-1} : 1680 s (C=O); 1350 s, 1536 s (NO_2). ^1H NMR spectrum, δ , ppm: 7.49 m (5H, C_6H_5), 7.73 m (1H, 5-H), 8.33 m (1H, 6-H, $J = 8.0$ Hz), 8.84 m (1H, 2-H), 8.47 m (1H, 4-H, $J = 8.0$ Hz). Found: $[M]^+$ 259.02866. $\text{C}_{13}\text{H}_9\text{NO}_3\text{S}$. Calculated: M 259.03031.

S-Phenyl 4-nitrobenzothioate (XVII) was synthesized from 0.58 g (2 mmol) of 4-nitrophenyl 4-nitrobenzoate and 0.22 g (4 mmol) of benzenethiol using 0.55 g (2 mmol) of potassium carbonate in 5 ml of DMF. Yield of the crude product 0.47 g (54%, GLC). Purification by column chromatography on aluminum oxide using chloroform as eluent gave 0.18 g (35%) of compound **XVII** with mp 159–161°C; published data [41]: mp 160–162°C.

S-Phenyl 4-(phenylsulfanyl)benzothioate (XVIII). A flask was purged with argon and charged with 0.008 g (0.073 mmol) of benzenethiol, 0.019 g (0.073 mmol) of *S*-phenyl 4-nitrobenzothioate, 0.019 g (0.14 mmol) of potassium carbonate, and 2 ml of DMF. The mixture was stirred for 4 h at 36°C, 5 ml of chloroform and 5 ml of 10% hydrochloric acid were added, the organic layer was separated, and the aqueous layer was extracted with 5 ml of chloroform. The extract was combined with the organic phase, washed with water, dried over CaCl_2 , filtered, and evaporated. According to the GC–MS data, the residue (0.026 g) contained 57% of compound **XVIII**. Purification by thin-layer chromatography on a glass plate precoated with silica gel (5–40 μm) using carbon tetrachloride as eluent gave 0.013 g (53%) of compound **XVIII** with mp 115–117°C. IR spectrum: ν 1674 cm^{-1} , ν (C=O). ^1H NMR spectrum, δ , ppm: 7.21 m (2H, 3-H, 5-H, $J = 9.0$ Hz), 7.38–7.52 m (10H, C_6H_5), 7.87 m (2H, 2-H, 6-H, $J = 9.0$ Hz). Found: $[M]^+$ 322.04853. $\text{C}_{19}\text{H}_{14}\text{OS}_2$. Calculated: M 322.04860.

Reaction of compound XVI with potassium carbonate. A flask was purged with argon and charged with 0.005 g (0.0193 mmol) of compound **XVI**, 0.008 g (0.058 mmol) of potassium carbonate, and 1 ml of DMF. The mixture was kept for 30 min at 36°C, and the reaction was terminated by adding a mixture of 2 ml of chloroform and 2 ml of 5% hydrochloric acid. The organic layer was separated and washed with 2 ml of water. According to the GC–MS data, it contained unreacted compound **XVI** (recovery 88%), 3-nitrobenzoic acid (yield 5%), and benzenethiol (yield 6%).

Reaction of compound XVII with potassium carbonate. A flask was purged with argon and charged with 0.002 g (0.0077 mmol) of compound XVII, 0.004 g (0.029 mmol) of potassium carbonate, and 2 ml of DMF. The mixture was kept for 30 min at 36°C, and the reaction was terminated by adding a mixture of 2 ml of chloroform and 2 ml of 5% hydrochloric acid. The organic layer was separated and washed with 2 ml of water. According to the GC–MS data, it contained unreacted compound XVII (recovery 50%) and *S*-phenyl 4-(phenylsulfanyl)benzothioate (XVIII, yield 15%).

Determination of the relative rate constants of the reactions of compounds I–VI with benzenethiol in dimethylformamide in the presence of potassium carbonate. The reactions were carried out using a large excess of the substrate with respect to the nucleophile to ensure invariance of the relative rate constants during the process. This condition conformed to pseudofirst-order kinetics, so that the substrate ratio may be assumed to be proportional to the ratio of the second-order rate constants for each reaction [42]. A flask was purged with argon and charged with a couple of substrates (I and II or II and III, etc.), benzenethiol, and potassium carbonate at a ratio of 5:5:1:2, and dimethylformamide was added to attain a concentration of I and II of $(6.3\text{--}7.5) \times 10^{-2}$ M. The mixture was kept for a required time (no longer than 30 min) at a specified temperature (15, 26, or 36°C), and the reaction was terminated by adding a mixture of 5 ml of chloroform and 5 ml of 5% hydrochloric acid. The organic layer was separated, washed with 10 ml of water, and dried over CaCl₂, the solvent was removed, and the residue was weighed and analyzed by GLC or GC–MS. The concentrations of compounds I and II were determined taking into account the data for an artificial mixture of these compounds, and the relative rate constants were calculated by the following equation [43]:

$$k_I/k_{II} = (\log[A_I^0] - \log[A_I^\tau]) / (\log[A_{II}^0] - \log[A_{II}^\tau]),$$

where A_I^0 and A_{II}^0 are the initial concentrations of compounds I and II, respectively (M), and A_I^τ and A_{II}^τ are their concentrations at a moment τ (M). The relative rate constants calculated from the results of at least three parallel runs are collected in Table 4.

Determination of the rate constants for the reactions of 4-nitrophenyl benzoate (III) with (1) 4-chlorophenol and (2) benzenethiol in dimethylformamide in the presence of potassium carbonate. A flask was

purged with argon and charged with potassium carbonate and a solution of 4-chlorophenol or benzenethiol in 2 ml of DMF, and the mixture was kept for 30 min at a required temperature. A solution of 4-nitrophenyl benzoate (III) in 2 ml of DMF, maintained at the same temperature, was added, the mixture was kept for a definite time, and a sample was withdrawn, treated with a mixture of chloroform and 5% hydrochloric acid, and analyzed. The concentration of the product was determined on the basis of the GC–MS data (taking into account the results of analysis of an artificial mixture), and the rate constant was determined using the formula for second-order rate constants:

$$k = \{2.303/[\tau(a-b)]\} \log\{[b(a-x)]/[a(b-x)]\},$$

where a and b are the initial reactant concentrations (M), x is the product concentration (M), and τ is the reaction time (s). Each rate constant was determined from the results of at least three parallel runs. Reaction conditions: (1) K₂CO₃, 0.044 g (0.32 mmol); 4-chlorophenol, 0.027 g (0.21 mmol); 4-nitrophenyl benzoate, 0.050 g (0.21 mmol); temperature 24°C; $k = (1.5 \pm 0.2) \times 10^{-1}$ l mol⁻¹ s⁻¹; (2) K₂CO₃, 0.026 g (0.188 mmol); benzenethiol, 0.015 g (0.136 mmol); 4-nitrophenyl benzoate, 0.032 g (0.132 mmol); temperature 26°C; $k = (4.6 \pm 0.3) \times 10^{-2}$ l mol⁻¹ s⁻¹.

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