

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

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Abstract—The effect of the substituent in the benzoyl group on the relative rate and activation parameters of transesterification of substituted 4-nitrophenyl benzoates with 4-chlorophenol in dimethylformamide in the presence of potassium carbonate was studied by the competing reaction technique. The whole series of benzoates showed the enthalpy–entropy compensation effect. 4-Nitrophenyl benzoates having electron-acceptor substituents give rise to isokinetic relationship with an isokinetic temperature β of 382 K. The mechanism of the transesterification process is discussed.

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Transesterification is an important process from the biological viewpoint [1–3]; therefore, interest in studying kinetic relations intrinsic to such reactions continuously increases [4, 5]. All studies performed so far in this line involved variation of several reactivity factors, including electrophilicity of the carbonyl carbon atom, basicity of nucleophile, solvation, etc. [6–13]. The most significant parameter determining the reactivity of such classes of organic compounds as carboxylic acids and their derivatives is the electrophilicity of the carbonyl carbon atom. It is controlled primarily by the nature of substituents in fragments attached to the carbonyl group. Here, donor substituents reduce the reactivity, while electron-withdrawing groups enhance it [14]. The result is that the ρ value in the Hammett [10, 11] or Yukawa–Tsuno [15] correlations for transesterification of substituted phenyl benzoates with phenoxide ions are positive. Neuvonen et al. [16] recently performed correlation analysis of the chemical shifts of the carbonyl carbon atom in the ^{13}C NMR spectra of substituted phenyl benzoates and showed that the high reactivity of compounds having electron-withdrawing groups in transesterification processes originates from weak resonance stabilization of the ground state of the initial esters.

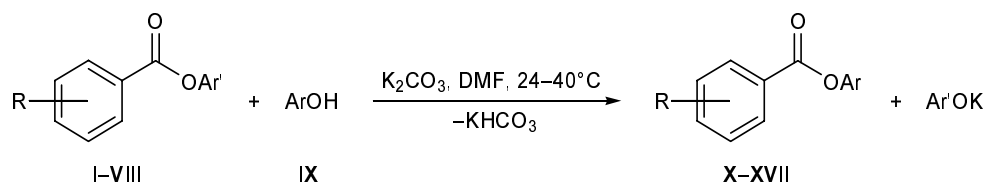
On the other hand, the reactivity of carbonyl compounds can change due to association, especially with proton-donor nucleophiles [17]. We previously showed [18] that the presence of potassium carbonate increases

the reactivity of *meta*-substituted nitrobenzenes in reactions with proton-donor nucleophiles (phenols), which involve replacement of the nitro group or fluorine atom. Presumably, the use of analogous nucleophiles in transesterification should strongly influence the reactivity of the carbonyl carbon atom. The goal of the present work was to examine the effects of the R substituent in the benzoyl fragment and nucleophile nature on the reactivity of *p*-nitrophenyl R-substituted benzoates **I–VIII** in the transesterification process. The set of substituents R was selected in such a way that their Hammett constants σ varied over a wide range to ensure considerable change in the electrophilicity of the carbonyl atom in molecules **I–VIII**.

In the examined temperature range, the reactions of benzoates **I–VII** with the *p*-chlorophenol–potassium carbonate complex (**IX**) smoothly afforded in good yield esters **X–XVI** (Scheme 1) which were stable under the given conditions. However, the most reactive benzoates **VIII** and **XVII** [R = 3,5-(NO₂)₂] readily reacted with K₂CO₃ in DMF at 40°C to give 3,5-dinitrobenzoic acid and 4-nitrophenol or 4-chlorophenol, respectively, in quantitative yield. Therefore, compound **VIII** was excluded from the kinetic study of the transesterification of esters **I–VII** with complex **IX**.

The relative rate constants for the reactions of ester **I–VII** with complex **IX** in DMF at different temperatures were determined by the competing reaction technique (Table 1). The use of this technique is justified,

Scheme 1.



I, X, R = 4-MeO; II, XI, R = 4-Me; III, XII, R = H; IV, XIII, R = 4-Br; V, XIV, R = 4-CF₃; VI, XV, R = 3-NO₂; VII, XVI, R = 4-NO₂; VIII, XVII, R = 3,5-(NO₂)₂; Ar = 4-ClC₆H₄, Ar' = 4-O₂NC₆H₄.

for the overall reaction rate determined in such a way weakly depends on the rates of other stages, namely preliminary chemisorption of the components on the phase boundary of the deprotonating agent and desorption of the products, which are not related directly to the nucleophilic replacement process [19].

The data in Table 1 show that the relative rate constant increases in going from donor substituents R in benzoates **I–VII** to acceptor, regardless of the temperature. The relative rate constants for benzoates **I** and **II** (in which R is a donor group) almost do not change as the temperature rises; by contrast, k_{rel} values for compounds **IV–VII** with an acceptor substituent R appreciably decrease with rise in temperature. Each benzoate gives rise to a linear relation between $\log k_{rel}$ and $1/T$ ($r = 0.988–0.999$ for compounds **I, II**, and **IV–VII** and $r = 0.959$ for benzoate **III**; Fig. 1). On the basis of these relations we calculated the differences $\Delta\Delta H^\ddagger$, $\Delta\Delta S^\ddagger$, and $\Delta\Delta G^\ddagger$ in the apparent activation parameters using a modified Eyring equation [20] (Table 1).

It also follows from the data in Table 1 that increase in the electron-withdrawing power of the R substituent

in **I–VII** leads to a considerable decrease in both enthalpy and entropy components. The ranges of variation of $\Delta\Delta H^\ddagger$ and $\Delta\Delta S^\ddagger$ are unexpectedly large; they are much wider than those found, e.g., for the acylation of aniline in benzene [21]. It should be noted that quite broad ranges of the enthalpies and entropies of activation are typical of complex heterogeneous and enzymatic catalytic reactions [22]. Presumably, the wide range of $\Delta\Delta S^\ddagger$ values ($188.6 \text{ J mol}^{-1} \text{ K}^{-1}$) found in the present work is determined by the mode of complex formation between benzoates **I–VII** and nucleophilic complex **IX**. Decrease in the entropy constituent in going from benzoates **I** and **II** having donor substituents to compounds **IV–VII** substituted by electron-withdrawing groups indicates a harder mode of complex formation of the latter with nucleophile **IX**.

Donor substituents in compounds **I** and **II** stabilize resonance structure **A** and the ground state due to increased contribution of that structure [9, 15, 16].

Probably, stabilization of the ground state leads to a slight increase of the enthalpy component and weakening of the reactivity of compounds **I** and **II** as the electron-donor power of the substituent increases.

Table 1. Relative rate constants k_{rel} and differences in the activation parameters for competing reactions of compounds **I–VII** with complex **IX** in DMF

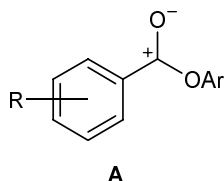
Compound no.	k_{rel}^a			$\Delta\Delta H^\ddagger, ^b \text{ kJ/mol}$	$\Delta\Delta S^\ddagger, ^b \text{ J mol}^{-1} \text{ K}^{-1b}$	$T \Delta\Delta S^\ddagger, ^b, ^c \text{ kJ/mol}$	$\Delta\Delta G^\ddagger, ^b, ^c \text{ kJ/mol}$
	24°C	30°C	40°C				
I	0.13	0.14	0.15	6.4 ± 0.3	4.9 ± 0.2	1.5	4.9
II	0.36	0.36	0.37	0.85 ± 0.02	-5.4 ± 0.1	-1.7	2.6
III	1	1	1	0	0	0	0
IV	12.9	12.0	7.0	-29.2 ± 8.6	-77.0 ± 27.6	-24.1	-5.1
V	98.9	76.7	34.5	-49.9 ± 7.7	-129.9 ± 24.6	-40.7	-9.2
VI	257.2	146.4	62.2	-65.4 ± 0.5	-174.6 ± 1.7	-54.6	-10.8
VII	645.5	367.6	141.7	-70.4 ± 2.0	-183.8 ± 6.4	-57.5	-12.9

^a The relative rate constant was calculated assuming $k_{rel} = 1$ for compound **III** from the data in Table 3.

^b The differences $\Delta\Delta H^\ddagger = \Delta H^\ddagger(R) - \Delta H^\ddagger(H)$, $\Delta\Delta S^\ddagger = \Delta S^\ddagger(R) - \Delta S^\ddagger(H)$, and $\Delta\Delta G^\ddagger = \Delta G^\ddagger(R) - \Delta G^\ddagger(H)$ were calculated by the Eyring equation: $\log k_{rel} = (-\Delta\Delta H^\ddagger/T + \Delta\Delta S^\ddagger)/4.576$ [20].

^c At 40°C.

Enhancement of the electron-withdrawing power of the substituent in compounds **IV–VII** is accompanied by destabilization of the ground state as a result of decreased contribution of resonance structure **A**. Therefore, the enthalpy component considerably decreases, the reactivity increases (Table 1), and transesterification of benzoates **III–VII** is characterized by isokinetic relationship.



Compounds **III–VII** constitute an isokinetic series with an isokinetic temperature β of 382 K, which corresponds to the crossing point of the straight lines in Fig. 1 [23]. Analogous values of β were also calculated from the dependences of $\Delta\Delta H^\ddagger$ upon $\Delta\Delta S^\ddagger$ (Fig. 2) and of $\log k_{\text{rel}}(24^\circ\text{C})$ upon $\log k_{\text{rel}}(40^\circ\text{C})$ (Table 2) [24].

The reactions of all compounds **I–VII** with nucleophile **IX** showed a common linear kinetic enthalpy–entropy compensation effect (Fig. 2) [21, 25].

$$\Delta\Delta H^\ddagger = 0.39\Delta\Delta S^\ddagger + 2.23; R = 0.999, s = 1.67, n = 7.$$

The chemical nature of the observed compensation effect follows from the fact that the compensation temperature (390 K) falls far beyond the experimental temperature range (313–297 K). The range of variation of $\Delta\Delta G^\ddagger$ for the transesterification of compounds **I–VII** is 17.8 kJ/mol (~ 4.3 kcal/mol, Table 1); i.e., it is typical of reactions of carbonyl compounds with nucleophiles [26, 27]. Change in the Gibbs activation energy in all the examined reactions is determined mainly by variation in the enthalpy of activation. The existence of a linear relation between $\Delta\Delta H^\ddagger$ and $\Delta\Delta G^\ddagger$ provides an additional support to the chemical nature of the compensation effect [25]:

$$\Delta\Delta H^\ddagger = -9.49 + 4.64\Delta\Delta S^\ddagger; R = 0.984, s = 6.35, n = 7.$$

In keeping with the above stated, the transesterification process was presumed to follow Scheme 2. In the first stage (fast), complex **IX** is formed [19]. It then reacts with benzoate **I–VII** to give complex **B** (cf. [28]). The subsequent process may be either stepwise or concerted. The stepwise path includes transition state TS-1 which is converted into the final products through tetrahedral intermediate **C**. The concerted path implies formation of the products through transition

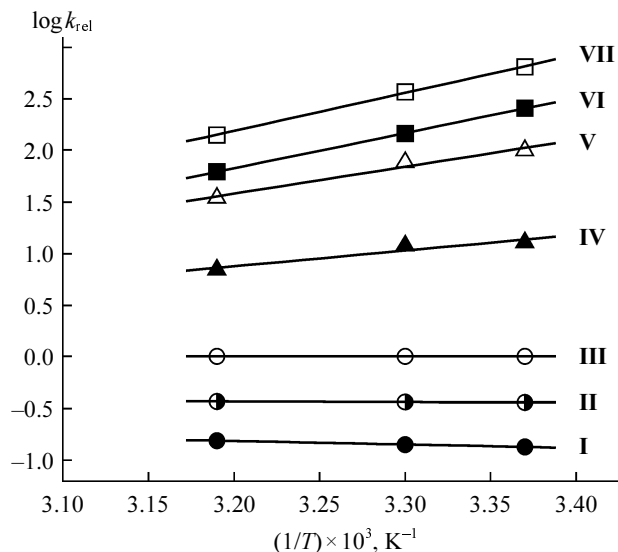


Fig. 1. Semilog plots of the relative rate constants versus reciprocal temperature for the reactions of 4-nitrophenyl benzoates **I–VII** with 4-chlorophenol in DMF in the presence of K_2CO_3 .

state TS-2. Taking into account that the structure of complex **B** is determined by the substrate electrophilicity, an appreciable variation in its geometric parameters within the examined series may be expected (cf. [18]). The transition state structure depends in turn on the geometry of complex **B**, as follows from the high sensitivity of the activation parameters to the substituent. The choice between these two paths (stepwise through intermediate **C** or concerted through transition state TS-2) can be made on the basis of

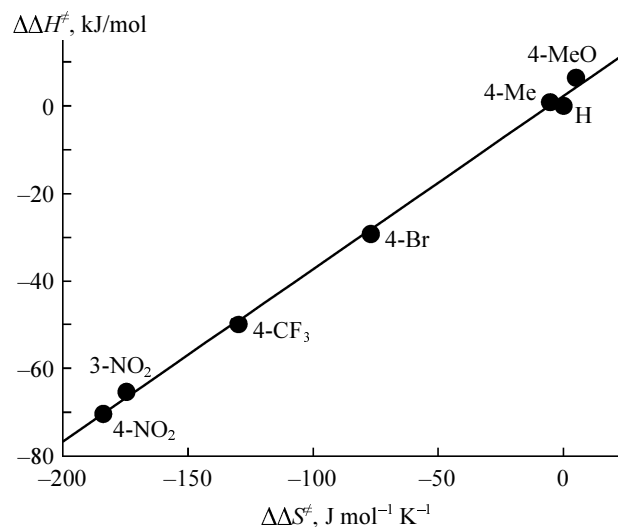
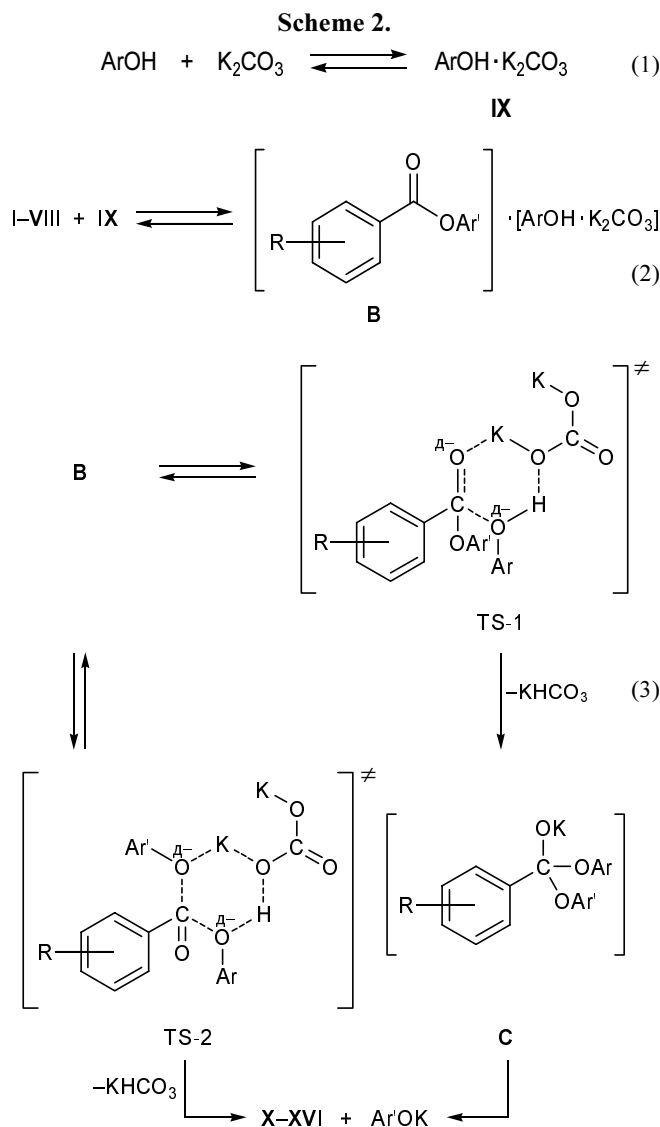


Fig. 2. Plot of the change in the enthalpy of activation versus the change in the entropy of activation for the reactions of 4-nitrophenyl benzoates **I–VII** with 4-chlorophenol in DMF in the presence of K_2CO_3 .



analysis of the ρ value in the Hammett equation [11]. The absolute values of ρ for concerted $\text{S}_{\text{N}}2$ reactions are usually small, for synchronous processes imply relatively small charge variations. For example, the reactions of benzoyl chlorides with aniline and lithium benzenethiolate in EtOH and MeOH are characterized by ρ values of -0.61 and $+0.58$, respectively [29]. Large absolute ρ values are inherent to stepwise proc-

Table 2. Isokinetic temperatures β calculated from different dependences for the transesterification of benzoates **III-VII**

Dependence	β , K	R	s	n
$\log k_{\text{rel}} = f(1/T)$	382 ± 3	$0.960-0.999$	$0.06-0.01$	3
$\log k_{\text{rel}}(24^\circ\text{C}) = f[\log k_{\text{rel}}(40^\circ\text{C})]$	377 ± 1	0.999	0.034	5
$\Delta\Delta H^\ddagger = f(\Delta\Delta S^\ddagger)$	380 ± 1	0.999	0.70	5

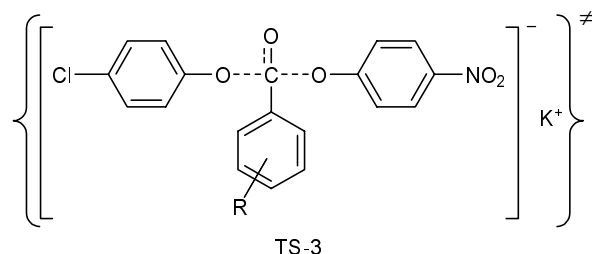
esses; they indicate considerable variation of the electron density distribution in the transition state. For instance, a ρ value of 2.85 was found for the reaction of substituted phenyl benzoates with phenoxide ions [10]. The ρ value determined in the present work from the dependence of $\log k_{\text{rel}}$ upon σ [30] is close to that given in [10]:

$$\log k_{\text{rel}}(24^\circ\text{C}) = 0.11 + 3.43\sigma; \quad R = 0.997, s = 0.13, n = 7. \quad (4)$$

The positive sign of ρ indicates that electron-withdrawing substituents accelerate the reaction. Insofar as electron-withdrawing substituents accelerate the stage of nucleophilic attack due to increase of the electrophilicity of the carbonyl carbon atom and slow down the stage of elimination of the departing group, the large positive ρ value suggests that the formation of transition state **TS-1** is the rate-determining stage. Thus the ρ value found for the transesterification reaction is consistent with the mechanism involving tetrahedral intermediate **C** according to Eq. (3) (Scheme 2).

The kinetics of transesterification of substituted phenyl benzoates with potassium 4-chlorophenoxide in 20% aqueous DMSO were shown [15] to be described by the Yukawa-Tsuno equation [31] with a ρ value of 1.88 and $r = 0.57$. Treatment of the relative rate constants (Table 1) by the same equation gave $\rho = 3.45$ and $r = 0.17$ (Fig. 3). The difference in the Yukawa-Tsuno resonance parameters r determined in the present work and in [15] is related to the reaction constant ρ : the greater the ρ value, the smaller the parameter r [32]. The low value of r (0.17) indicates a weak resonance interaction between the substituent **R** in the benzoyl group and the reaction center in six-membered transition state **TS-1** (Scheme 2). However, increased parameter r for the transesterification of compounds **I-VIII** with $\text{ArO}^- \text{K}^+$ [15] may be determined by the structure of transition state, e.g., **TS-3**, whose stabilization requires enhanced conjugation with the carbocationic center [31].

Proper comparison of ρ implies normalized ρ_n values which are obtained by division of ρ by ρ_0 where



ρ_o is the corresponding parameter for acid ionization of benzoic acids in the same medium ($\rho_o = 2.4$ and 1.3 for the ionization of benzoic acids in DMF [33] and 20% aqueous DMSO [34]). The calculated value for transesterification of benzoates **I–VII** with nucleophile **IX**, $\rho_n = 1.44$, is almost equal to $\rho_n = 1.45$ for analogous reaction with 4-ClC₆H₄O[−] K⁺ as standard nucleophile [15]; these data suggest that the reactions can follow stepwise mechanism through intermediate **C** formed in the rate-determining stage [10, 11, 15].

Thus we showed that transesterification in the presence of K₂CO₃ is characterized by high sensitivity of the activation parameters to the nature of substituent and nucleophile. Analysis of the ρ value and resonance parameter r suggests stepwise mechanism of the process with formation of tetrahedral intermediate through a cyclic transition state in the rate-determining stage

EXPERIMENTAL

The IR spectra were recorded on a Bruker instrument from 2% solutions in CHCl₃ or KBr pellets containing 0.25% of a sample. The ¹H and ¹⁹F NMR spectra were measured on Bruker WP-200 SY and AC-200 spectrometers; the chemical shifts were measured relative to HMDS and hexafluorobenzene, respectively. The mass spectra (electron impact, 70 eV) were run on a Finnigan MAT-8200 mass spectrometer (ion source temperature 100–200°C). The reaction mixtures were analyzed by GLC on HP 5890 and LKhM-7A instruments [heat conductivity detector, oven temperature programming from 50 to 270°C at a rate of 10 deg/min; stationary phases SKTFT-803, SE-30, and VS-1 (15%) 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. All reagents and solvents were commercial products. Dimethylformamide was dried over phosphoric anhydride and was distilled over calcium hydride; potassium carbonate was calcined in an oven and finely ground prior to use; thionyl chloride and benzoyl chloride were distilled; substituted benzoic acids were used without additional purification; 4-nitrophenol and 4-chlorophenol were purified by standard procedures. The products were characterized by the IR, ¹H and ¹⁹F NMR, and mass spectra.

4-Nitrophenyl benzoates **I**, **II**, **IV**, and **VI–VIII**.

A mixture of 0.2 mol of thionyl chloride, 0.1 mol of 4-nitrophenol, and 0.1 mol of the corresponding substituted benzoic acid was heated at the boiling point

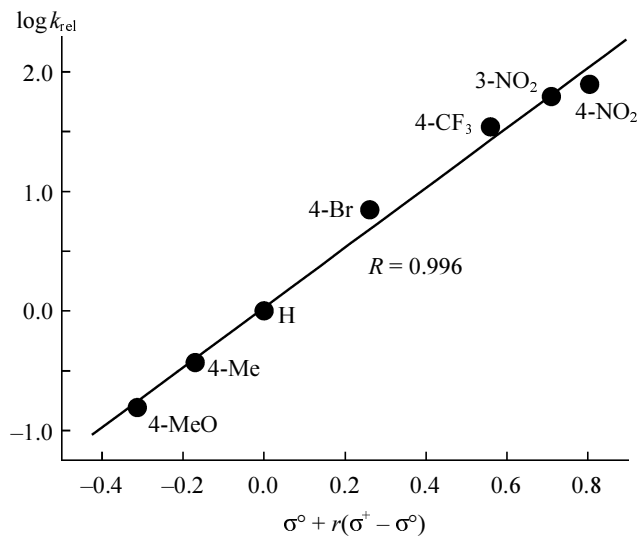


Fig. 3. Correlation of the logarithms of the relative rate constants $\log k_{rel}(24^\circ\text{C})$ for the reactions of 4-nitrophenyl benzoates **I–VII** with 4-chlorophenol in DMF in the presence of K₂CO₃ with the parameter $[\sigma^o + r(\sigma^+ - \sigma^o)]$ according to the Yukawa–Tsuno equation: $\log k_{rel}(24^\circ\text{C}) = \rho[\sigma^o + r(\sigma^+ - \sigma^o)]$; $\rho = 3.45$, $r = 0.17$; $R = 0.999$, $s = 0.09$, $n = 7$; the σ^o and σ^+ values were taken from [30].

until it became homogeneous. Excess thionyl chloride was distilled off, the residue was cooled to room temperature and poured onto ice, and the precipitate was filtered off, washed with water, dried, and analyzed by gas–liquid chromatography.

4-Nitrophenyl 4-methoxybenzoate (I). Reaction time 27.7 h, yield 85% (yield of the isolated product 81%), mp 166–167°C (from hexane–benzene, 4:1); published data [35]: mp 166°C.

4-Nitrophenyl 4-methylbenzoate (II). Reaction time 30.5 h, yield 82% (65%), mp 122–123°C (from CH₂Cl₂); published data [36]: 120.3–121.3°C.

4-Nitrophenyl 4-bromobenzoate (IV). Reaction time 13.3 h, yield 98% (67%), mp 162–164°C (from acetone). IR spectrum (KBr), ν , cm^{−1}: 1340 s and 1520 s (NO₂), 1741 s (C=O). ¹H NMR spectrum (CDCl₃), δ , ppm: 7.39 m (2H, 3-H, 5-H, $J = 8.0$ Hz), 7.65 m (2H, 2'-H, 6'-H, $J = 9.0$ Hz), 8.03 m (2H, 2-H, 6-H, $J = 8.0$ Hz), 8.29 m (2H, 3'-H, 5'-H, $J = 9.0$ Hz). Found: M 320.96309. C₁₃H₈BrNO₄. Calculated: M 320.96372.

4-Nitrophenyl 3-nitrobenzoate (VI). Reaction time 31.5 h, yield 86% (67%), mp 139–141°C (from benzene). IR spectrum (CHCl₃), ν , cm^{−1}: 1350 s and 1531 s (NO₂), 1755.0 s (C=O). ¹H NMR spectrum (DMSO-*d*₆), δ , ppm: 7.64 m (2H, 2'-H, 6'-H, $J = 9.0$ Hz), 7.90 m (1H, 3-H, $J = 8.0$ Hz), 8.35 m (2H, 3'-H, 5'-H, $J = 9.0$ Hz), 8.55 m (2H, 2-H, 4-H, $J =$

9.0 Hz), 8.77 m (1H, 6-H). Found: M 288.03796. $C_{13}H_8N_2O_6$. Calculated: M 288.03823.

4-Nitrophenyl 4-nitrobenzoate (VII). Reaction time 30.6 h, yield 80% (43%), mp 157–159°C (from hexane–benzene, 4:1); published data [36]: mp 158–159°C.

4-Nitrophenyl 3,5-dinitrobenzoate (VIII). Reaction time 22 h, yield 98% (86%), mp 188–190°C (from EtOH); published data [35]: mp 188°C.

4-Nitrophenyl benzoates III and V. Benzoyl chloride or 4-trifluoromethylbenzoyl fluoride, 0.1 mol, was added dropwise over a period of 30 min to a mixture of 0.1 mol of 4-nitrophenol and 0.1 mol of triethylamine in 10 ml of toluene. The mixture was kept for 4 h at 20–25°C and poured onto ice. The precipitate was filtered off, washed with water, dried, and analyzed by GLC.

4-Nitrophenyl benzoate (III). Yield 84% (71%), mp 146–147°C (from $CHCl_3$); published data [35]: mp 142–143°C.

4-Nitrophenyl 4-trifluoromethylbenzoate (V). Yield 82% (64%), mp 85–86°C (from hexane– $CHCl_3$, 4:1). IR spectrum (KBr), ν , cm^{-1} : 1351 s and 1520 s (NO_2), 1759 s (C=O). 1H NMR spectrum ($CDCl_3$), δ , ppm: 7.40 m (2H, 3-H, 5-H, $J = 8.0$ Hz), 7.65 m (2H, 2'-H, 6-H, $J = 9.0$ Hz), 8.25 m (2H, 2-H, 6-H, $J = 8.0$ Hz), 8.30 m (2H, 3'-H, 5'-H, $J = 9.0$ Hz). ^{19}F NMR spectrum ($CDCl_3$): δ_F 98.67 ppm, s (3F, CF_3). Found: M 311.04090. $C_{14}H_8F_3NO_4$. Calculated: M 311.04053.

4-Chlorophenyl benzoates X–XVII. A flask was purged with argon and charged with 0.01 mol of 4-chlorophenol, 0.02 mol of potassium carbonate, and 0.01 mol of 4-nitrophenyl benzoate I–VIII. Dimethylformamide, 10 ml, was added, the mixture was stirred for 3 h at 60°C and poured into water, and the precipitate was filtered off, washed with water, dried, and analyzed by GLC.

Table 3. Relative rate constants for competing reactions of compounds I–VII with complex IX in DMF at 24–40°C

Substrates	k_{rel}^a		
	24°C	30°C	40°C
II/I	2.7±0.2	2.57±0.02	2.38±0.05
III/II	2.77±0.05	2.8±0.5	2.72±0.03
IV/III	12.9±1.7	12.0±1.9	7.0±0.4
V/IV	7.7±1.1	6.4±1.3	4.9±0.2
VI/V	2.6±0.3	1.9±0.1	1.8±0.3
VII/V	2.5±0.6	2.5±0.5	2.3±0.2

^a Average values calculated from the results of at least three runs.

itate was filtered off, washed with water, dried, and analyzed by GLC.

4-Chlorophenyl 4-methoxybenzoate (X). Yield 90% (77%), mp 94–95°C (from hexane–benzene, 4:1). IR spectrum ($CHCl_3$): $\nu(C=O)$ 1733 cm^{-1} , s. 1H NMR spectrum (DMSO- d_6), δ , ppm: 7.11 m (2H, 2'-H, 6'-H, $J = 9.0$ Hz), 7.28 m (2H, 3-H, 5-H, $J = 9.0$ Hz), 7.50 m (2H, 3'-H, 5'-H, $J = 9.0$ Hz), 8.06 m (2H, 2-H, 6-H, $J = 9.0$ Hz). Found: M 262.03961. $C_{14}H_{11}ClO_3$. Calculated: M 262.03967.

4-Chlorophenyl 4-methylbenzoate (XI). Yield 85% (73%), mp 92–93°C (Al_2O_3 , eluent hexane); published data [36]: mp 89.2–90.7°C.

4-Chlorophenyl benzoate (XII). Yield 98% (85%), mp 82–83°C (from hexane–benzene); published data [36]: mp 88–89°C.

4-Chlorophenyl 4-bromobenzoate (XIII). Yield 85% (71%), mp 84–85°C (from hexane–benzene, 4:1). IR spectrum ($CHCl_3$): $\nu(C=O)$ 1733 cm^{-1} , s. 1H NMR spectrum (DMSO- d_6), δ , ppm: 7.34 m (2H, 2'-H, 6'-H, $J = 9.0$ Hz), 7.81 m (2H, 3-H, 5-H, $J = 8.0$ Hz), 7.52 m (2H, 3'-H, 5'-H, $J = 9.0$ Hz), 8.03 m (2H, 2-H, 6-H, $J = 8.0$ Hz). Found: M 309.93930. $C_{13}H_8ClBrO_2$. Calculated: M 309.93967.

4-Chlorophenyl 4-trifluoromethylbenzoate (XIV). Yield 86% (72%), mp 89–90°C (from hexane–benzene, 4:1). IR spectrum ($CHCl_3$): $\nu(C=O)$ 1745 cm^{-1} , s. 1H NMR spectrum (DMSO- d_6), δ , ppm: 7.37 m (2H, 2'-H, 6'-H, $J = 9.0$ Hz), 7.54 m (2H, 3'-H, 5'-H, $J = 9.0$ Hz), 7.96 m (2H, 3-H, 5-H, $J = 8.0$ Hz), 8.31 m (2H, 2-H, 6-H, $J = 8.0$ Hz). ^{19}F NMR spectrum ($CDCl_3$): δ_F 110.71 ppm, s (3F, CF_3). The elemental composition and the molecular weight were determined from the high-resolution mass spectrum. Found: M 300.01596. $C_{14}H_8ClF_3O_2$. Calculated: M 300.01648.

4-Chlorophenyl 3-nitrobenzoate (XV). Yield 65% (47%), mp 127–128°C (hexane– CH_2Cl_2 , 4:1). IR spectrum ($CHCl_3$), ν , cm^{-1} : 1352 s and 1537 s (NO_2), 1748 s (C=O). 1H NMR spectrum (DMSO- d_6), δ , ppm: 7.38 m (2H, 2'-H, 6'-H, $J = 9.0$ Hz), 7.55 m (2H, 3'-H, 5'-H, $J = 9.0$ Hz), 7.90 m (1H, 3-H, $J = 8.0$ Hz), 8.53 m (2H, 2-H, 4-H, $J = 8.0$ Hz), 8.77 m (1H, 6-H). Found: M 277.01450. $C_{13}H_8ClNO_4$. Calculated: M 277.01418.

4-Chlorophenyl 4-nitrobenzoate (XVI). Yield 80% (37%), mp 177–178°C (from hexane– CH_2Cl_2 , 4:1); published data [36]: mp 171–172°C.

4-Chlorophenyl 3,5-dinitrobenzoate (XVII). Yield 35% (27%), mp 174–175°C (from EtOH). IR spectrum ($CHCl_3$), ν , cm^{-1} : 1349 s and 1544 s (NO_2),

1749 s (C=O). ^1H NMR spectrum (DMSO- d_6), δ , ppm: 7.40 m (2H, 2'-H, 6'-H, $J = 9.0$ Hz), 7.56 m (2H, 3'-H, 5'-H, $J = 9.0$ Hz), 9.07 m (2H, 2-H, 6-H, $J = 9.0$ Hz), 9.11 m (1H, 4-H). Found: M 321.99930. $\text{C}_{13}\text{H}_7\text{ClN}_2\text{O}_6$. Calculated: M 321.99926.

Test of compounds VIII and XVII for stability under the transesterification conditions. A flask was purged with argon and charged with 0.48 mmol of compound VIII or 0.04 mmol of compound XVII, 1.45 or 0.11 mmol of K_2CO_3 , and 3 or 1.3 ml of DMF, respectively. The mixture was kept for 3 h at 40°C , and the reaction was terminated by adding a mixture of 5 ml of chloroform and 5 ml of 5% hydrochloric acid. The organic phase was separated, the aqueous phase was extracted with chloroform (2×5 ml), and the extracts were combined with the organic phase, washed with 10 ml of water, dried over CaCl_2 , and evaporated. According to the ^1H NMR data (DMSO- d_6), the residue contained equimolar amounts of 3,5-dinitrobenzoic acid and 4-nitrophenol (from compound VIII) or 3,5-dinitrobenzoic acid and 4-chlorophenol (from compound XVII).

Determination of the relative rate constants of the reactions of compounds I–VII with 4-chlorophenol in DMF in the presence of K_2CO_3 . A flask was purged with argon and charged with a couple of competing benzoates (I/II or II/III, etc.), 4-chlorophenol, and K_2CO_3 at a ratio of 10:10:1:2, and DMF was added to attain a concentration of I and II of about 10^{-1} M. The mixture was kept for a required time (no longer than 60 min) at a specified temperature (24, 30, or 40°C), and the reaction was terminated by adding a mixture of 5 ml of chloroform and 5 ml of 5% hydrochloric acid. The organic phase was separated, washed with 10 ml of water, dried over CaCl_2 , and evaporated, and the residue was analyzed by GLC. The relative rate constants were calculated by the following equation [37]:

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

where A_{I}^0 and A_{II}^0 are the initial concentrations of compounds I and II, mol/l, and A_{I}^τ and A_{II}^τ are their concentrations at a time τ . The values calculated from the results of at least three runs, are given in Table 3.

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