

Inverse phase transfer catalysis. Kinetics of the pyridine 1-oxide-catalyzed reaction of chlorobenzoyl chloride and chlorobenzoate ion

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Abstract

The substitution reactions of 2-, 3- or 4-chlorobenzoyl chloride (2-, 3- or 4-ClC₆H₄COCl) and 2-, 3- or 4-chlorobenzoate ion (2-, 3- or 4-ClC₆H₄COO⁻) in a two-phase H₂O/CH₂Cl₂ medium using pyridine 1-oxide (PNO) as an inverse phase-transfer catalyst were investigated. Experimental results strongly support that the reaction of ClC₆H₄COCl and PNO in organic phase to produce the intermediate, 1-(chlorobenzoyloxy)pyridinium chloride (ClC₆H₄COONP⁺Cl⁻) is the rate-determining step and that the equilibrium distribution of PNO between H₂O and CH₂Cl₂ phases is always maintained. The order of reactivities of benzoyl chlorides toward reaction with PNO is 2-ClC₆H₄COCl > 3-ClC₆H₄COCl > 4-ClC₆H₄COCl > PhCOCl. The order of reactivities of benzoate ions toward reaction with PhCOONP⁺ ion is (3-, 4-ClC₆H₄COO⁻) > 2-ClC₆H₄COO⁻ > PhCOO⁻.

Keywords: Chlorobenzoyl chloride; Chlorobenzoate ion; Pyridine 1-oxide; Inverse phase-transfer catalysis; Kinetics

1. Introduction

Phase transfer catalysis (PTC) has been widely recognized as a versatile and effective technique in organic synthesis utilizing a two-phase solvent medium [1–7]. In normal phase-transfer catalysis (NPTC), the anionic reactant is continuously transported with a cationic phase-transfer catalyst from the aqueous to the organic phase for reaction [1,3,4]. Reverse phase-transfer catalysis (RPTC) involves continuous transport of the cationic reactant with an anionic phase-transfer catalyst from aqueous

phase to organic phase for reaction [8–10]. In contrast, inverse phase-transfer catalysis (IPTC) as named by Mathius and Vaidya [11] involves the conversion of reactant in organic phase by a phase-transfer catalyst to an ionic intermediate, which is transported into the aqueous phase for reaction. The IPTC technique has been applied to the synthesis of acid anhydrides [12–14] and ketones [15]. Jwo et al. studied the kinetics and mechanism of the pyridine 1-oxide-catalyzed IPTC reaction of benzoyl chloride with carboxylate and dicarboxylate ions [14,16–19]. Carboxylic acid anhydrides are important intermediates for synthesis of esters, amides, and peptides. The PTC technique provides an effective

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method [12–14,20–24] for synthesizing acid anhydrides. In this work, we study the IPTC reaction of 2-, 3- or 4-chlorobenzoyl chloride with 2-, 3-, or 4-chlorobenzoate ion in a two-phase medium catalyzed by pyridine 1-oxide. The effects of reactants, pyridine 1-oxide, organic solvent, and temperature were investigated and the experimental results rationalized.

2. Experimental section

2.1. Materials

2-, 3-, and 4-Chlorobenzoyl chlorides (2-, 3-, and 4-ClC₆H₄COCl; 95%, 97%, and 99% purities) (Aldrich); pyridine 1-oxide (PNO, C₅H₅NO, 95%), and naphthalene (C₁₀H₈, 99%) (Merck); sodium benzoate (PhCOONa, 99%), 2-, 3-, and 4-chlorobenzoic acid (2-, 3-, and 4-ClC₆H₄COOH; 98%, 99%, and 99%) (Ferak); and dichloromethane (99%) (Wako) were used. Other chemicals used were of the highest reagent grade commercially available. Due to the hygroscopic property of PNO, (PNOH⁺Cl⁻) crystals (mp. 179–181°C) were used instead. These crystals were prepared by adding dropwise 4 ml of concentrated HCl to 20 ml of aqueous solution containing 10 g of PNO [14]. Deionized water was obtained from reverse osmosis (Millipore Milli-RO 20).

2.2. Procedures

2.2.1. Synthesis of symmetric chlorobenzoyl anhydrides

A 50 ml CH₂Cl₂ solution containing chlorobenzoyl chloride (0.2 M) was mixed with a 50 ml aqueous solution containing chlorobenzoate ion (0.5 M) and PNO (0.02 M) in a 200 ml three-necked Pyrex flask. The reaction was carried out under agitation at 1200 rpm. After the reaction was complete, the CH₂Cl₂ solution was separated and washed with NaOH solution (0.02 M) to remove chlorobenzoic acid. It was then washed twice with deionized water and

dried with anhydrous MgSO₄. Product chlorobenzoyl anhydride ((ClC₆H₄CO)₂O) was obtained after concentrating the CH₂Cl₂ solution with a rotatory evaporator. The HPLC analysis of the product showed only one peak. The elemental analysis showed that the purity of the product was at least 98%, e.g. for (4-ClC₆H₄CO)₂O: Anal. Calcd. for C₁₄H₈Cl₂O₃: C, 56.97; H, 2.71; Cl, 24.04. Found: C, 56.80; H, 2.70; Cl, 23.80.

2.2.2. Kinetic experiments

The kinetic experiments were run in a 200-ml three-necked Pyrex flask fitted with a flat-bladed stirring paddle. The reactor was submerged in a thermostated water bath. Both reactant solutions were thermostated at the desired temperature (within ±0.2°C) for at least 20 min. The kinetic run was started by adding 40 ml of aqueous solution (containing a known amount of RCOONa and PNOH⁺Cl⁻ to 40 ml of organic phase solution (containing a known amount of RCOCl and naphthalene) in the flask. The reaction was carried out under a constant rate of agitation. During the reaction, an aliquot (0.2 ml) was withdrawn at a chosen time, immediately put into the extraction sample bottle which contained 0.2 ml of n-hexane and 0.7 ml of H₂O and kept cold in an ice-water bath. The extract bottle was shaken vigorously for at least 30 s and allowed to stand for several minutes to allow the two phases to separate.

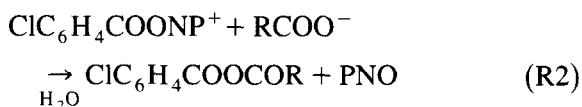
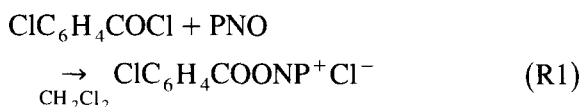
The organic phase was analyzed by HPLC (Hitachi L-6200 series) using the internal standard method; HPLC analysis conditions: column, Lichrospher 100 RP18 (5 m); wavelength, 254 nm (UV detector); (i) eluent, CH₃CN/H₂O = 58/42; flow rate, 1.5 ml/min, elution time (min): 2-ClC₆H₄COOH (0.78), 2-ClC₆H₄COCl (7.41), (2-ClC₆H₄CO)₂O (11.4), C₁₀H₈ (8.54); (ii) eluent, CH₃CN/H₂O = 62/38; flow rate, 1.5 ml/min, elution time (min): 3-ClC₆H₄COOH (0.74), 3-ClC₆H₄COCl (7.56), (3-ClC₆H₄CO)₂O (14.0), 4-ClC₆H₄COOH (0.76), 4-ClC₆H₄COCl (7.40), (4-ClC₆H₄CO)₂O (14.0), C₁₀H₈ (6.60); (iii) elu-

ent, $\text{CH}_3\text{CN}/\text{H}_2\text{O} = 62/38$, flow rate, 1.3 ml/min, elution time (min): PhCOCl (6.25), $(\text{PhCO})_2\text{O}$ (7.44), $4\text{-ClC}_6\text{H}_4\text{COCl}$ (9.36), $4\text{-ClC}_6\text{H}_4\text{COOCOPh}$ (11.7), C_{10}H_8 (8.41); (iv) eluent, $\text{CH}_3\text{CN}/\text{H}_2\text{O} = 62/38$, flow rate, 1.4 ml/min, elution time (min): PhCOCl (5.31), $(\text{PhCO})_2\text{O}$ (6.14), $3\text{-ClC}_6\text{H}_4\text{COCl}$ (8.00), $3\text{-ClC}_6\text{H}_4\text{COOCOPh}$ (9.39), C_{10}H_8 (8.00). The response factor f was calibrated using $C_r/C_{is} = f(S_r/S_{is})$ (C , concentration; S , peak area; is , internal standard; r , unknown compound). The values of f measured were 0.685 ± 0.003 , 0.435 ± 0.002 , 0.204 ± 0.002 , 0.245 ± 0.003 , and 0.172 ± 0.004 for $2\text{-ClC}_6\text{H}_4\text{COCl}$, $3\text{-ClC}_6\text{H}_4\text{COCl}$, $4\text{-ClC}_6\text{H}_4\text{COCl}$, $(2\text{-ClC}_6\text{H}_4\text{CO})_2\text{O}$, and $(\text{PhCO})_2\text{O}$ (0.00200–0.0200) M, respectively with $[\text{C}_{10}\text{H}_8] = (0.0100\text{--}0.0200)$ M.

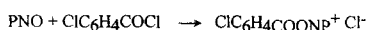
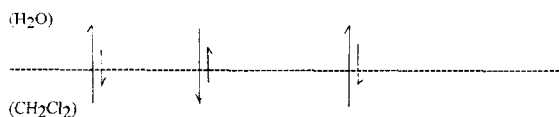
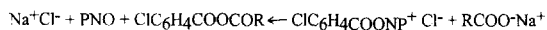
3. Kinetics

The PNO-catalyzed reaction of chlorobenzoyl chloride ($\text{ClC}_6\text{H}_4\text{COCl}$) and benzoate ion (RCOO^- , $\text{R} = \text{Ph}$ or ClC_6H_4) in $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$ medium can be simplified as depicted in Scheme 1.

Two main reaction processes are shown in reactions R1 and R2.



The intermediate product, 1-(chlorobenzoyloxy)-pyridinium chloride ($\text{ClC}_6\text{H}_4\text{COONP}^+\text{Cl}^-$)



Scheme 1.

produced in the organic phase (reaction R1) will transfer to the aqueous phase and react with RCOO^- ion to generate the acid anhydride ($\text{ClC}_6\text{H}_4\text{COOCOR}$) (reaction R2). Reaction R2 is essentially irreversible, since $\text{ClC}_6\text{H}_4\text{COOCOR}$ is extracted into the CH_2Cl_2 phase rapidly. Reaction R1 is considerably slower than reaction R2 and is the rate-determining step. If the distribution of PNO between H_2O and CH_2Cl_2 phases is very rapid and remains at equilibrium, then the rate of reaction can be expressed by a pseudo-first-order rate equation (Eq. 1). The observed pseudo-first-order rate constant (k_{obs}) was determined by the linear-least-squares (LLS) fit of the plot of $\ln[\text{ClC}_6\text{H}_4\text{COCl}]_{\text{org}}$ vs. time.

$$-\frac{d[\text{ClC}_6\text{H}_4\text{COCl}]_{\text{org}}}{dt} = k_{\text{obs}}[\text{ClC}_6\text{H}_4\text{COCl}]_{\text{org}} \quad (1)$$

4. Results and discussion

The study of the two-phase reactions between chlorobenzoyl chlorides ($\text{ClC}_6\text{H}_4\text{COCl}$) and chlorobenzoate ($\text{ClC}_6\text{H}_4\text{COO}^-$) ions showed that the rate of reaction depended on the amounts of reactants and catalyst, the organic solvent, the ionic strength of the aqueous solution, the agitation rate, and the temperature. This reaction produced both the substitution product ($(\text{ClC}_6\text{H}_4\text{CO})_2\text{O}$) and the hydrolysis product ($\text{ClC}_6\text{H}_4\text{COOH}$).

4.1. Effect of agitation

Without agitation, the rate of reaction was slow whereas it increased asymptotically with increasing rate of agitation. For $[2\text{-ClC}_6\text{H}_4\text{COCl}]_{\text{org}} = 0.0100$ M, $[2\text{-ClC}_6\text{H}_4\text{COONa}]_{\text{aq}} = 0.500$ M, $[\text{PNO}]_{\text{aq}} = 6.00 \times 10^{-4}$ M in 40 ml of H_2O and 40 ml of CH_2Cl_2 , the values of k_{obs} at 22°C were (1.63, 2.77, 3.82, 4.63, and 4.60) $\times 10^{-3} \text{ s}^{-1}$ at the agitation rates of (500, 700, 1000, 1100, and 1200) rpm, respectively. When the agitation rate was

greater than 1100 rpm, it appeared that the two phases exhibited uniform mixing, i.e. the rate of reaction was independent of the agitation rate. Therefore, most of the kinetic experiments were run at 1100–1200 rpm.

4.2. Solvent effect

Both polar and non-polar organic solvents were used to study the solvent effects. For $[2\text{-ClC}_6\text{H}_4\text{COCl}]_{\text{org}} = 0.0100$ M, $[\text{PNO}]_{\text{aq}} = 2.00 \times 10^{-4}$ M, $[2\text{-ClC}_6\text{H}_4\text{COO}^-]_{\text{aq}} = 0.500$ M, the values of k_{obs} at 22°C were (1.67, 1.20, and 0.123) $\times 10^{-3}$ s⁻¹ in H₂O/CH₂Cl₂, n-C₆H₁₄/H₂O, and C₆H₆/H₂O medium, respectively. The yield of (2-ClC₆H₄CO)₂O was 96% in H₂O/CH₂Cl₂, which was considerably higher than those of 14% in C₆H₆/H₂O and 9.5% in n-C₆H₁₄/H₂O. The low yields of (2-ClC₆H₄CO)₂O in the latter two media were mainly due to the hydrolysis of 2-ClC₆H₄COCl and (2-ClC₆H₄CO)₂O itself, which produced 2-ClC₆H₄COOH. In this work, most experi-

ments were therefore run in H₂O/CH₂Cl₂ medium.

4.3. Uncatalyzed reaction

In the absence of the phase-transfer catalyst PNO, ClC₆H₄COCl reacted with ClC₆H₄COO⁻ ion in a two-phase medium to produce (ClC₆H₄CO)₂O and ClC₆H₄COOH with the latter being the major product. The observed rate constant k_{obs} or k_{h} depended on the ionic strength (μ) in the aqueous phase. For example, for $[2\text{-ClC}_6\text{H}_4\text{COCl}]_{\text{org}} = 0.0100$ M in H₂O/CH₂Cl₂, the values of k_{h} at 22°C were (0.833, 1.08, and 1.23) $\times 10^{-4}$ s⁻¹ with $\mu = 0$ M, 0.5 M (adjusted with NaNO₃), and 0.5 M (adjusted with 2-ClC₆H₄COONa), respectively. In most experiments, the ionic strength in the aqueous phase was kept constant at 0.5 M (adjusted with ClC₆H₄COONa or PhCOONa). Under similar conditions, the relative rate of hydrolysis was 3-ClC₆H₄COCl > (2-ClC₆H₄COCl, 4-ClC₆H₄COCl).

Table 1

Effects of PNO on the rate constants of the reactions of chlorobenzoyl chlorides and chlorobenzoate ions in H₂O/CH₂Cl₂ medium at various temperatures

T/°C	[PNO] _{aq} /10 ⁻⁴ M	k _{obs} /10 ⁻⁴ s ⁻¹		
		2-ClC ₆ H ₄ COCl	3-ClC ₆ H ₄ COCl	4-ClC ₆ H ₄ COCl
10	0.00	0.633	1.12	0.617
	0.50	—	3.67	—
	1.00	7.52	6.30	4.85
	2.00	14.8	11.4	9.15
	3.00	21.3	16.2	12.5
	4.00	27.2	—	16.7
22	0.00	1.23	1.47	1.23
	0.50	—	5.37	—
	1.00	9.57	8.27	6.82
	2.00	18.7	14.5	12.5
	3.00	26.0	21.5	18.2
	4.00	32.5	—	22.8
36	0.00	1.68	2.10	1.57
	0.50	11.3	6.83	—
	1.00	20.0	13.8	10.2
	2.00	27.7	22.2	16.5
	3.00	38.0	32.5	24.0
	4.00	49.8	—	31.8

$[\text{ClC}_6\text{H}_4\text{COCl}]_{\text{org}} = 0.0100$ M, $[\text{ClC}_6\text{H}_4\text{COO}]_{\text{aq}} = 0.500$ M.

The temperature dependence of k_h is shown in Table 1. The apparent activation energies (E_a) obtained by the LLS fits of the plots of $\ln k_h$ vs. $1/T$ were $(27.7 \pm 0.4, 17.7 \pm 0.1, \text{ and } 26.0 \pm 0.8) \text{ kJ mol}^{-1}$ for 2- $\text{ClC}_6\text{H}_4\text{COCl}$, 3- $\text{ClC}_6\text{H}_4\text{COCl}$, and 4- $\text{ClC}_6\text{H}_4\text{COCl}$, respectively. The values of k_h at 22°C for 2- $\text{ClC}_6\text{H}_4\text{COCl}$ were $(5.95, 1.08, \text{ and } 0.917) \times 10^{-4} \text{ s}^{-1}$ in ($n\text{-C}_6\text{H}_{14}/\text{H}_2\text{O}$, $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$, and $\text{C}_6\text{H}_6/\text{H}_2\text{O}$), respectively.

4.4. PNO-catalyzed reaction

In the presence of PNO as the phase-transfer catalyst, $\text{ClC}_6\text{H}_4\text{COCl}$ reacted quite rapidly with $\text{ClC}_6\text{H}_4\text{COO}^-$ ion in $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$ medium to produce mainly $(\text{ClC}_6\text{H}_4\text{CO})_2\text{O}$ and a small amount of $\text{ClC}_6\text{H}_4\text{COOH}$. Typical kinetic results are shown in Fig. 1. When both $[\text{ClC}_6\text{H}_4\text{COONa}]$ and the ionic strength in the aqueous phase were not constant, the value of k_{obs} first increased with increasing

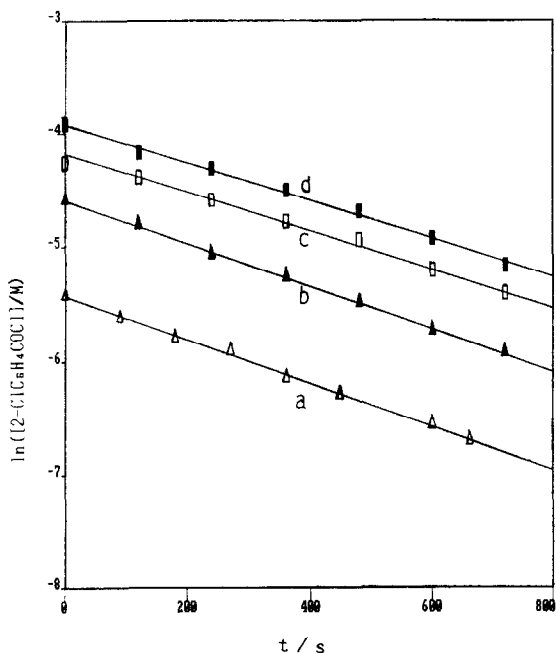


Fig. 1. Plots of $\ln[2\text{-ClC}_6\text{H}_4\text{COCl}]$ vs. time for the PNO-catalyzed reaction of 2-chlorobenzoyl chloride and 2-chlorobenzoate ion in $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$ medium. $[2\text{-ClC}_6\text{H}_4\text{COCl}]_{\text{org}} = (\text{a}) 5.00 \times 10^{-3} \text{ M}$, (b) 0.0100 M , (c) 0.0150 M , (d) 0.0200 M ; $[\text{PNO}]_{\text{aq}} = 2.00 \times 10^{-4} \text{ M}$, $[2\text{-ClC}_6\text{H}_4\text{COO}^-]_{\text{aq}} = 0.500 \text{ M}$, 22°C , 40 ml of H_2O and 40 ml of CH_2Cl_2 .

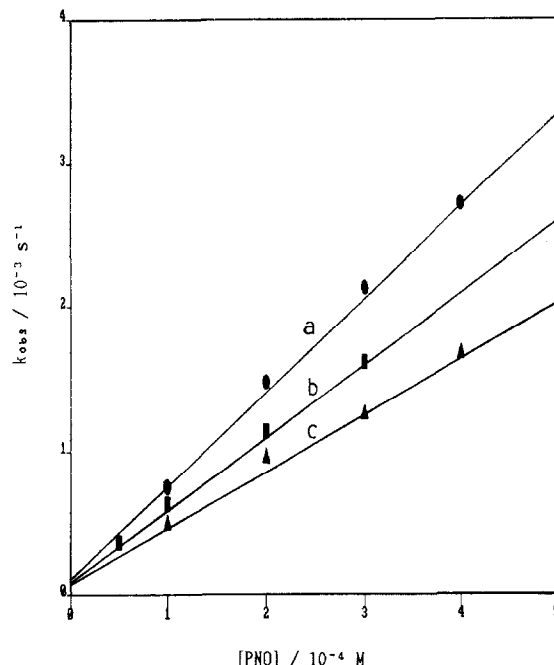


Fig. 2. Effect of PNO on the observed rate constant of the reaction of chlorobenzoyl chloride and chlorobenzoate ion in $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$ medium. $[\text{ClC}_6\text{H}_4\text{COCl}]_{\text{org}} = 0.0100 \text{ M}$, $[\text{ClC}_6\text{H}_4\text{COO}^-]_{\text{aq}} = 0.500 \text{ M}$, 22°C , 40 ml of H_2O and 40 ml of CH_2Cl_2 . (a) 2- $\text{ClC}_6\text{H}_4\text{COCl}$, (b) 3- $\text{ClC}_6\text{H}_4\text{COCl}$, (c) 4- $\text{ClC}_6\text{H}_4\text{COCl}$.

$[\text{ClC}_6\text{H}_4\text{COONa}]$ up to about 0.3 M and then decreased with further increase in $[\text{ClC}_6\text{H}_4\text{COONa}]$. When the ionic strength was kept constant at 0.5 M , the value of k_{obs} increased asymptotically with $[\text{ClC}_6\text{H}_4\text{COONa}]$ to a limit value. In most experiments, the ionic strength in the aqueous phase was kept constant at 0.5 M . Typical results are shown in Table 1. The plot of k_{obs} vs. $[\text{PNO}]_{\text{aq}}$ is linear (Fig. 2), implying that this reaction is also first-order with respect to PNO. The value of k_{obs} at the intercept is in good agreement with that of k_h of the corresponding uncatalyzed reaction. Thus, similar to the PNO-catalyzed reaction of PhCOCl and PhCOO^- ion in $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$ [14], the rate law of this PNO-catalyzed reaction can generally be expressed by Eq. 2.

$$\begin{aligned} -d[\text{ClC}_6\text{H}_4\text{COCl}]_{\text{org}}/dt \\ = k_{\text{obs}}[\text{ClC}_6\text{H}_4\text{COCl}]_{\text{org}} \\ = (k_h + k_c[\text{PNO}]_{\text{aq}})[\text{ClC}_6\text{H}_4\text{COCl}]_{\text{org}} \end{aligned} \quad (2)$$

Table 2
Temperature dependence of k_c of the PNO-catalyzed reaction of chlorobenzoyl chloride and chlorobenzoate ion in H_2O/CH_2Cl_2 medium

$T/^\circ C$	$k_c/M^{-1} s^{-1}$		
	2-ClC ₆ H ₄ COCl	3-ClC ₆ H ₄ COCl	4-ClC ₆ H ₄ COCl
10	6.46	5.08	3.88
22	8.10	6.43	5.37
36	11.6	9.95	7.03
$E_a/kJ mol^{-1}$	15.8 ± 2.3	18.9 ± 2.9	16.6 ± 1.2

where $k_{obs} = k_h + k_c[PNO]_{iaq}$ and k_h and k_c are the uncatalyzed and catalyzed rate constants, respectively. Both k_h and k_c are complicated and depend on the concentration of chlorobenzoate ion, ionic strength, and temperature. The values of k_c calculated at various temperatures by the LLS fits of the plots of k_{obs} vs. $[PNO]$ and the apparent activation energies (E_a) obtained by the LLS fits of the Arrhenius plots ($\ln k_c$ vs. $1/T$) are shown in Table 2. These results imply that the order of reactivity toward

Table 3
Effects of PNO on the rate constants of the reactions of mixed benzoyl chlorides and benzoate ion in H_2O/CH_2Cl_2 medium

$[PNO]_{iaq}/10^{-4} M$	$k_{obs}/10^{-4} s^{-1}$				$k_c/M^{-1} s^{-1}$
	1.00	2.00	3.00	4.00	
PhCOCl + 3-ClC ₆ H ₄ COCl + PhCOO ⁻ reaction					
PhCOCl	6.17	10.0	13.5	17.2	3.67
3-ClC ₆ H ₄ COCl	8.83	15.2	21.3	28.0	6.37
PhCOCl + 4-ClC ₆ H ₄ COCl + PhCOO ⁻ reaction					
PhCOCl	5.67	9.17	13.0	16.0	3.62
4-ClC ₆ H ₄ COCl	7.83	13.0	18.5	23.3	5.22

$[PhCOCl]_{iorg} = [3-ClC_6H_4COCl]_{iorg} = [4-ClC_6H_4COCl]_{iorg} = 0.0100 M$; $[PhCOO^-]_{iaq} = 0.500 M$, $22^\circ C$.

Table 4
Effects of PNO and benzoate ions on the rate constants of reactions of benzoyl chlorides and benzoate ions in H_2O/CH_2Cl_2 medium

$[PNO]_{iaq}/10^{-4} M$	$k_{obs}/10^{-4} s^{-1}$								$k_c/M^{-1} s^{-1}$
	0.600	1.00	1.20	1.60	2.00	2.60	3.00	4.00	
Reaction of PhCOCl									
2-CIBA	—	6.00	—	—	9.67	—	13.3	16.8	3.58
3-CIBA	—	6.00	—	—	9.50	—	13.3	16.7	3.60
4-CIBA	—	5.83	—	—	9.50	—	13.2	16.3	3.50
Reaction of 2-ClC ₆ H ₄ COCl									
BA	8.00	—	13.7	—	21.8	—	32.0	—	10.1
3-CIBA	8.00	—	13.3	—	21.3	27.0	—	—	9.60
4-CIBA	8.67	—	14.7	—	21.3	—	32.0	—	9.63
Reaction of 3-ClC ₆ H ₄ COCl									
BA	—	8.83	—	—	15.0	—	21.7	28.0	6.37
4-CIBA	—	9.17	—	—	15.0	—	21.3	27.7	6.18
Reaction of 4-ClC ₆ H ₄ COCl									
BA	—	7.50	—	—	12.8	—	18.5	23.3	5.43
2-CIBA	—	7.83	—	—	13.0	—	18.3	23.2	5.15
3-CIBA	6.33	—	—	10.8	13.0	—	—	23.3	5.17

BA = PhCOO⁻; 2-CIBA = 2-ClC₆H₄COO⁻; 3-CIBA = 3-ClC₆H₄COO⁻; 4-CIBA = 4-ClC₆H₄COO⁻; $[BA]_{iaq} = [2-CIBA]_{iaq} = [3-CIBA]_{iaq} = [4-CIBA]_{iaq} = 0.500 M$; $[PhCOCl]_{iorg} = [2-ClC_6H_4COCl]_{iorg} = [3-ClC_6H_4COCl]_{iorg} = [4-ClC_6H_4COCl]_{iorg} = 0.0100 M$; $22^\circ C$.

reaction with PNO is $2\text{-ClC}_6\text{H}_4\text{COCl} > 3\text{-ClC}_6\text{H}_4\text{COCl} > 4\text{-ClC}_6\text{H}_4\text{COCl} > \text{PhCOCl}$.

4.5. Effect of mixed benzoyl chlorides

The above kinetic results imply that for these reactions the rate-determining step is the reaction of $\text{ClC}_6\text{H}_4\text{COCl}$ and PNO in the organic phase (reaction R1). This argument is further supported by studying the PNO-catalyzed two-phase reaction of benzoate ion with mixed benzoyl chlorides. Typical results are shown in Table 3. The values of k_c for PhCOCl , $3\text{-ClC}_6\text{H}_4\text{COCl}$, and $4\text{-ClC}_6\text{H}_4\text{COCl}$ are similar to those measured independently (Table 2). These results imply that these benzoyl chlorides react independently with PNO in organic phase despite the significant differences in their reactivities. These results also strongly support the assumption that the equilibrium distribution of PNO between H_2O and CH_2Cl_2 phases is always maintained.

4.6. Effects and reactivities of benzoate ions

The effects of various benzoate ions on the reactions of benzoyl chlorides with PNO in CH_2Cl_2 are shown in Table 4. Since the ionic reaction of the intermediate ($\text{ClC}_6\text{H}_4\text{COONP}^+\text{Cl}^-$) with carboxylate ion (RCOO^-) (reaction R2) is very rapid, a similar value of k_c is expected for various benzoate ions under the same reaction conditions. The results in Table 4 indicate that the value of k_c depends somewhat on the benzoate ion used. This result can be explained by the effect of carboxylate ion on the distribution of PNO between H_2O and CH_2Cl_2 phases [18].

Since reaction R2 is very rapid, the direct measurement of its rate is not feasible. However, it can be deduced from studying the effects of mixed benzoate ions on the relative yields of acid anhydrides. Typical results are shown in Figs. 3 and 4. Fig. 3 shows that PhCOO^- ion competes with 2-, 3- or 4- $\text{ClC}_6\text{H}_4\text{COO}^-$ ion for reaction with

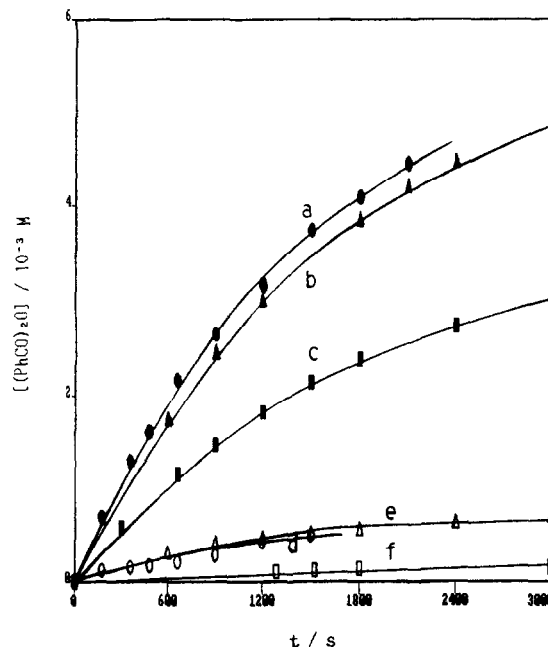


Fig. 3. Effects of chlorobenzoate ions on the yield of benzoic anhydride in the PNO-catalyzed reaction of benzoyl chloride and benzoate ion in $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$ medium. $[\text{PhCOCl}]_{\text{org}} = 0.0100$ M, $[\text{PNO}]_{\text{aq}} = 1.00 \times 10^{-4}$ M, $[\text{PhCOO}^-]_{\text{aq}} + [\text{RCOO}^-]_{\text{aq}} = 0.500$ M, 22°C , $[\text{PhCOO}^-]_{\text{aq}} : [\text{RCOO}^-]_{\text{aq}} = (\text{a, b, c}) 7:1$; $(\text{d, e, f}) 1:7$, $\text{RCOO}^- = (\text{a, d}) 4\text{-ClC}_6\text{H}_4\text{COO}^-$, $(\text{b, e}) 2\text{-ClC}_6\text{H}_4\text{COO}^-$, $(\text{c, f}) 3\text{-ClC}_6\text{H}_4\text{COO}^-$.

PhCOONP^+ ion to produce $(\text{PhCO})_2\text{O}$ and 2-, 3- or 4- $\text{ClC}_6\text{H}_4\text{COOCOPh}$, respectively. The relative reactivities of PhCOO^- and 2-, 3-, and 4- $\text{ClC}_6\text{H}_4\text{COO}^-$ ions can be deduced from the ratios of $(\text{PhCO})_2\text{O}$ yields of parallel runs. The ratios of a/d, b/e, and c/f in Fig. 3 imply that the order of relative reactivities of these benzoate ions is $3\text{-ClC}_6\text{H}_4\text{COO}^- > 4\text{-ClC}_6\text{H}_4\text{COO}^- > 2\text{-ClC}_6\text{H}_4\text{COO}^- > \text{PhCOO}^-$. Similar results are obtained by comparing the ratios of yields of 4- $\text{ClC}_6\text{H}_4\text{COOCOPh}$, 2- $\text{ClC}_6\text{H}_4\text{COOCOPh}$, and 3- $\text{ClC}_6\text{H}_4\text{COOCOPh}$ of a/d, b/e, and c/f, respectively. Fig. 4 shows that 2- $\text{ClC}_6\text{H}_4\text{COO}^-$ ion competes with PhCOO^- , 3- or 4- $\text{ClC}_6\text{H}_4\text{COO}^-$ ion for reaction with 2- $\text{ClC}_6\text{H}_4\text{COONP}^+$ ion to produce $(2\text{-ClC}_6\text{H}_4\text{CO})_2\text{O}$ and 2- or 4- $\text{ClC}_6\text{H}_4\text{COOCOPh}$, respectively. The order of relative reactivities of these benzoate ions is $4\text{-ClC}_6\text{H}_4\text{COO}^- \geq 3\text{-ClC}_6\text{H}_4\text{COO}^- > 2\text{-ClC}_6\text{H}_4\text{COO}^-$.

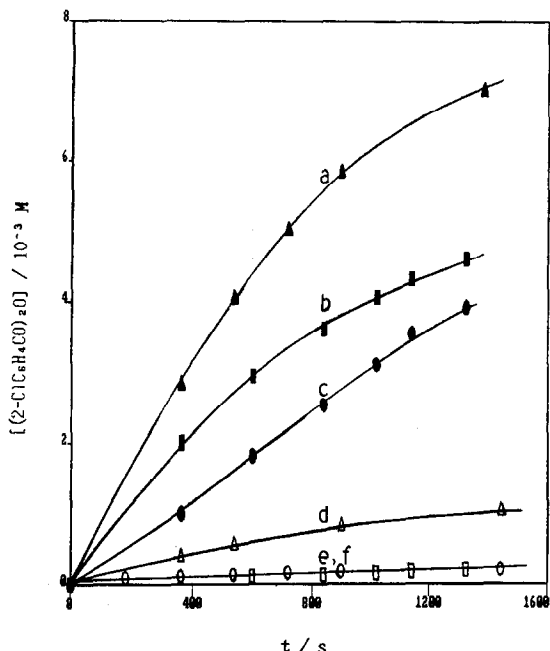


Fig. 4. Effects of carboxylate ions on the yield of chlorobenzoyl anhydride in the PNO-catalyzed reaction of 2-chlorobenzoyl chloride and 2-chlorobenzoate ion in $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$ medium. $[\text{2-ClC}_6\text{H}_4\text{COCl}]_{\text{org}} = 0.0100 \text{ M}$, $[\text{PNO}]_{\text{org}} = 1.00 \times 10^{-4} \text{ M}$, $[\text{2-ClC}_6\text{H}_4\text{COO}^-]_{\text{aq}} + [\text{RCOO}^-]_{\text{aq}} = 0.500 \text{ M}$, 22°C . $[\text{2-ClC}_6\text{H}_4\text{COO}^-]_{\text{aq}} : [\text{RCOO}^-]_{\text{aq}} = (\text{a, b, c}) 7:1$; $(\text{d, e, f}) 1:7$; $\text{RCOO}^- = (\text{a, d}) \text{PhCOO}^-$, $(\text{b, e}) 3\text{-ClC}_6\text{H}_4\text{COO}^-$, $(\text{c, f}) 4\text{-ClC}_6\text{H}_4\text{COO}^-$.

$\text{ClC}_6\text{H}_4\text{COO}^- > \text{PhCOO}^-$. The values of $\text{p}K_{\text{b}}$ at 25°C are 9.81, 10.0, 10.2, and 11.1 for PhCOO^- , 4-, 3-, and 2- $\text{ClC}_6\text{H}_4\text{COO}^-$ ions, respectively [25]. The order of reactivities of benzoate ions mentioned above correlates quite well for 2-, 3-, and 4- $\text{ClC}_6\text{H}_4\text{COO}^-$ ions. The lower reactivity of PhCOO^- ion is not quite consistent with the simple inverse phase transfer mechanism. This result can be rationalized by invoking that acyl transfer occurs in both the aqueous phase and organic phases [13] and that the reaction at the interface is also operating [19].

5. Conclusion

The reaction of chlorobenzoyl chloride and chlorobenzoate ion in a two-phase $\text{H}_2\text{O}/$

CH_2Cl_2 medium with pyridine 1-oxide (PNO) as inverse phase-transfer catalyst was investigated. The main conclusions were:

(a) The kinetics of the reaction follows a pseudo-first-order rate law. The observed rate constant is a linear function of the initial concentration of PNO in the aqueous phase.

(b) The reaction of chlorobenzoyl chloride with PNO in the organic phase to produce the intermediate, 1-(chlorobenzoyloxy)-pyridinium ion, is the rate determining step. The equilibrium distribution of PNO between H_2O and CH_2Cl_2 phases is always maintained.

(c) The order of reactivities of benzoyl chlorides toward reaction with PNO is $2\text{-ClC}_6\text{H}_4\text{-COCl} > 3\text{-ClC}_6\text{H}_4\text{-COCl} > 4\text{-ClC}_6\text{H}_4\text{-COCl} > \text{PhCOCl}$.

(d) The order of reactivities of benzoate ions toward reaction with 1-(benzoyloxy)-pyridinium ion is $(3\text{-, } 4\text{-ClC}_6\text{H}_4\text{COO}^-) > 2\text{-ClC}_6\text{H}_4\text{COO}^- > \text{PhCOO}^-$.

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