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Inverse phase transfer catalysis. Kinetics of the pyridine 1-oxide-catalyzed reactions of dichlorobenzoyl chlorides and benzoate ions

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Abstract

The substitution reactions of 2,3-, 2,4-, 3,4-, or 3,5-dichlorobenzoyl chloride ($Cl_2C_6H_3COCl$) and 2,3-, 2,4-, 3,4-, or 3,5-dichlorobenzoate ion ($Cl_2C_6H_5COO^-$) or benzoate ion ($C_6H_5COO^-$) in a two-phase H_2O/CH_2Cl_2 medium using pyridine 1-oxide (PNO) as an inverse phase transfer catalyst were investigated. The reaction of $Cl_2C_6H_3COCl$ and PNO in CH_2Cl_2 to produce the ionic intermediate, 1-(dichlorobenzoyloxy)-pyridinium chloride ($Cl_2C_6H_3COONP^+Cl^-$) is the rate-determining step. In the PNO-catalyzed two-phase reaction of $Cl_2C_6H_3COCl$ and C_6H_5COONa, the order of reactivities of $Cl_2C_6H_3COCl$ toward reaction with PNO is (2,3-, 2,4-) > 3,5- > 3,4- ≫ 2,6-$Cl_2C_6H_3COCl$, whereas it is 3,5- > (2,3-, 3,4-) > 2,4-$Cl_2C_6H_3COCl$ in the PNO-catalyzed two-phase reaction of $Cl_2C_6H_3COCl$ and the corresponding $Cl_2C_6H_3COONa$. The order of reactivities of $Cl_2C_6H_3COO^-$ ions towards the reaction with 1-(benzoyloxy)-pyridinium ($C_6H_5COONP^+$) ion is (3,4-, 3,5-) > (2,3-, 2,4-$Cl_2C_6H_3COO^-$).

Keywords: Dichlorobenzoyl chlorides; Dichlorobenzoate ions; Pyridine 1-oxide; Dichlorobenzoic anhydrides; Inverse phase transfer catalysis

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1. Introduction

Phase transfer catalysis (PTC) has versatile applications in organic reactions such as substitution, alkylation, and redox reactions via two-phase media [1–7]. The PTC technique is generally classified as normal (NPTC) [1], reverse (RPTC) [8,9], and inverse (IPTC) [10]. The NPTC reactions have been studied extensively, which involve transport of an anionic reactant with a cationic phase transfer catalyst from the water phase into the organic phase for reaction [1–7]. In contrast, the IPTC reaction involves the conversion of a reactant in the organic phase by a phase transfer catalyst to an ionic intermediate, the transportation of the intermediate for reaction with the reactant in the water phase, and then the regeneration of the catalyst. The IPTC technique has been applied successfully to the synthesis of acid anhydrides [11–13] and ketones [14]. Carboxylic acid anhydrides are important intermediates for the synthesis of esters, amides, and peptides. Conventionally, acid anhydrides are synthesized under anhydrous

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conditions [15]. However, it is widely recognized that the PTC technique provides an effective and versatile method for synthesizing acid anhydrides [11–13,16–20]. Kuo and Jwo [21], Wang et al. [22–25,28], Ou et al. [26], Liou et al. [27] and Hung and Jwo [29] have studied the kinetics and mechanism of the pyridine 1-oxide (PNO)-catalyzed IPTC reaction of benzoyl chlorides with carboxylate and dicarboxylate ions. In this article, the kinetics of the PNO-catalyzed IPTC reactions of 2,3-, 2,4-, 3,4-, 3,5-, or 2,6-dichlorobenzoyl chloride with the corresponding dichlorobenzoate or benzoate ion in a two-phase medium were studied. The effects of substituent, catalyst, organic solvent, pH value and temperature were investigated. Both symmetric dichlorobenzoic anhydrides and mixed benzoic dichlorobenzoic anhydrides were synthesized. The experimental results are rationalized.

2. Experimental

2.1. Materials

PNO; 2,4-, 2,6-, and 3,4-dichlorobenzoyl chlorides; 2,4-, 2,6-, 3,4-, and 3,5-dichlorobenzoic acids (Aldrich); 2,3- and 3,5-dichlorobenzoyl chlorides; and 2,3-benzoic acid (Lancaster); sodium benzoate (Ferak); and naphthalene (Merck) were used. Deionized water was obtained from reverse osmosis. Due to the hygroscopic property of PNO, $(PNO)H^+ Cl^-$ crystals (anal. calcd. for C_5H_6ClNO: C, 45.62; H, 4.60; N, 10.65; Cl, 26.96; found: C, 45.43; H, 4.56; N, 10.46; Cl, 26.90) prepared according to the literature method [21] were used instead.

2.2. Procedures

2.2.1. Synthesis of symmetric and mixed dichlorobenzoic anhydrides

Under agitation at 1200 rpm, a 50-ml CH_2Cl_2 solution of dichlorobenzoyl chloride (0.2 M) was mixed with a 50-ml aqueous solution containing the desired dichlorobenzoate or benzoate ion (0.5 M) and PNO (0.02 M) in a 250-ml three-necked Pyrex flask. After the reaction was complete, the CH_2Cl_2 layer was separated and washed with NaOH solution (0.02 M) to remove dichlorobenzoic or benzoic acid. It was then washed twice with deionized water and dehydrated with anhydrous $MgSO_4$. The symmetric dichlorobenzoic anhydrides were obtained after concentrating the CH_2Cl_2 solution with a rotatory evaporator in a hot water bath, whereas the mixed benzoicdichlorobenzoic anhydrides were obtained in an ice-water bath instead to avoid the disproportionation reaction [13]. The HPLC analysis of the product showed only one peak. Anal. calcd. for $C_{14}H_6Cl_4O_3$: C, 46.15; H, 1.65; Cl, 39.01; found: C, 46.22; H, 1.72; Cl, 38.95 ($(2,3\text{-}Cl_2C_6H_3CO)_2O$); C, 46.14; H, 1.59; Cl, 38.81 ($(2,4\text{-}Cl_2C_6H_3CO)_2O$); C, 46.10; H, 1.66; Cl, 38.94 ($(3,4\text{-}Cl_2C_6H_3CO)_2O$); and C, 46.04; H, 1.71; Cl, 38.89 ($(3,5\text{-}Cl_2C_6H_3CO)_2O$). Calcd. for $C_{14}H_8Cl_2O_3$: C, 56.97; H, 2.71; Cl, 24.04; found: C, 59.96; H, 2.73; Cl, 24.08 ($2,3\text{-}Cl_2C_6H_3COOCOC_6H_5$); C, 45.92; H, 2.70; Cl, 24.01 ($2,4\text{-}Cl_2C_6H_3COOCOC_6H_5$); C, 56.93; H, 2.75; Cl, 24.05 ($3,4\text{-}Cl_2C_6H_3COOCOC_6H_5$); and C, 56.94; H, 2.80; Cl, 24.11 ($3,5\text{-}Cl_2C_6H_3COOCOC_6H_5$). Mass (EI-MS) spectral data indicate that the base peak is $m/e = (175, 173)$ ($Cl_2C_6H_3CO^+$ fragment) for symmetric dichlorobenzoic anhydrides ($(Cl_2C_6H_3CO)_2O$), and it is $m/e = 105$ ($C_6H_5CO^+$ fragment) for the mixed benzoic-dichlorobenzoic anhydrides ($Cl_2C_6H_3COOCOC_6H_5$).

2.2.2. Kinetic experiment

The kinetic experiments were run in a 250-ml three-necked Pyrex flask fitted with a flat-bladed stirring paddle and submerged in a thermostated water bath. Both organic and aqueous solutions of reactants were thermostated at the desired temperature (within ± 0.2°C) for at least 30 min. The kinetic run was started by adding 50 ml of aqueous solution (containing known amounts of $Cl_2C_6H_3COONa$ (or C_6H_5COONa) and $(PNO)H^+ Cl^-$) to 50 ml of organic solution (containing known amounts of $Cl_2C_6H_3COCl$ and internal standard (naphthalene)) in the reactor under 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 H_2O and was kept cold in an ice-water bath. The extraction bottle was shaken vigorously for at least 40 s to quench the reaction. The organic phase was analyzed by HPLC (Hitachi L-6200 series) using the internal standard method; HPLC analysis conditions: column, Lichrospher 100 RP18 (5 μm); wavelength, 254 nm (UV detector); (i) eluent, $CH_3CN/H_2O = 68/32$ by volume; flow rate: 1.5 ml/min; elution time (min): $C_{10}H_8$ (4.89), 2,3-$Cl_2C_6H_3COCl$ (5.87), 2,4-$Cl_2C_6H_3COCl$ (6.45), 3,4-$Cl_2C_6H_3COCl$ (7.58), 3,5-$Cl_2C_6H_3COCl$ (8.51), (2,3-$Cl_2C_6H_3CO)_2$ (11.0), (2,4-$Cl_2C_6H_3CO)_2$ (14.3), (3,4-$Cl_2C_6H_3CO)_2$ (18.1), and (3,5-$Cl_2C_6H_3CO)_2$ (22.7); (ii) eluent, $CH_3CN/H_2O = 65/35$; flow rate: 1.5 ml/min; elution time (min): $C_{10}H_8$ (5.36), 2,3-$Cl_2C_6H_3COCl$ (6.60), 2,4-$Cl_2C_6H_3COCl$ (7.22), 3,4-$Cl_2C_6H_3COCl$ (8.09), 3,5-$Cl_2C_6H_3COCl$ (9.76), 2,3-$Cl_2C_6H_3COOCOC_6H_5$ (7.78), 2,4-$Cl_2C_6H_3COOCOC_6H_5$ (8.78), 3,4-$Cl_2C_6H_3COOCOC_6H_5$ (9.36), and 3,5-$Cl_2C_6H_3COOCOC_6H_5$ (12.4); (iii) eluent, $CH_3CN/H_2O = 58/42$; flow rate: 1.5 ml/min; elution time (min): C_6H_5COCl (6.07), $C_{10}H_8$ (8.18), 4-$ClC_6H_4COOCOC_6H_5$ (12.2), 2,3-$Cl_2C_6H_3COOCOC_6H_5$ (15.5), 2,4-$Cl_2C_6H_3COOCOC_6H_5$ (18.1), 3,4-$Cl_2C_6H_3COOCOC_6H_5$ (18.7), and 3,5-$Cl_2C_6H_3COOCOC_6H_5$ (21.3). The response factor f was calibrated using $C_x/C_{is} = f(S_x/S_{is})$ (C, concentration; S, peak area; x, unknown; is, internal standard). The values of f measured with $[C_{10}H_8] = (0.0100–0.0200)$ M are 0.545 (2,3-$Cl_2C_6H_3COCl$), 0.444 (2,4-$Cl_2C_6H_3COCl$), 0.420 (3,4-$Cl_2C_6H_3COCl$), 0.970 (3,5-$Cl_2C_6H_3COCl$), 0.228 ((2,3-$Cl_2C_6H_3CO)_2$), 0.111 ((2,4-$Cl_2C_6H_3CO)_2$), 0.0895 ((3,4-$Cl_2C_6H_3CO)_2$), 0.207 ((3,5-$Cl_2C_6H_3CO)_2$), 0.210 (2,3-$Cl_2C_6H_3COOCOC_6H_5$), 0.138 (2,4-$Cl_2C_6H_3COOCOC_6H_5$), 0.119 (3,4-$Cl_2C_6H_3COOCOC_6H_5$), 0.192 (3,5-$Cl_2C_6H_3COOCOC_6H_5$), and 0.0999 (4-$ClC_6H_4COOCOC_6H_5$). The pseudo-first-order rate constant (k_{obs}) was determined by the linear-least-squares (LLS) fit of the plot of $\ln[Cl_2C_6H_3COCl]$ vs. time.

3. Results and discussion

The PNO-catalyzed two-phase reaction of $Cl_2C_6H_3COCl$ and $RCOO^-$ ($R = Cl_2C_6H_3$ or C_6H_5) in H_2O/CH_2Cl_2 medium can be simplified as shown in the following two main reaction processes (R1 and R2):

$$Cl_2C_6H_3COCl + PNO \xrightarrow[CH_2Cl_2]{} Cl_2C_6H_3COONP^+Cl^- \tag{R1}$$

$$Cl_2C_6H_3COONP^+ + RCOO^- \xrightarrow[H_2O]{} Cl_2C_6H_3COOCOR + PNO \tag{R2}$$

$$Cl_2C_6H_3COONP^+ + H_2O \xrightarrow[H_2O]{} Cl_2C_6H_3COOH + PNOH^+ \tag{R3}$$

The intermediate, 1-(dichlorobenzoyloxy)-pyridinium ($Cl_2C_6H_3COONP^+$) ion produced in the organic phase (reaction R1) will transfer quickly to the aqueous phase and reacts with $RCOO^-$ ion (reaction R2) to produce the substitution product, $Cl_2C_6H_3COOCOR$ or reacts with H_2O to produce the hydrolysis product, $Cl_2C_6H_3COOH$ (reaction R3). The acid anhydride is rapidly extracted into the organic phase and the PNO catalyst regenerated in reactions R2 and R3 can catalyze the reaction further. All three reactions (R1–R3) are essentially irreversible. In general, R1 is considerably slower than reactions R2 and R3 and is the rate-determining step. Furthermore, if the distribution of the PNO catalyst between H_2O and CH_2Cl_2 phases is established very rapidly and remains at equilibrium, then the reaction follows a pseudo-first-order kinetics. Preliminary study of this reaction showed that the rate of reaction depended on the amounts of reactants and catalyst, the organic solvent, the rate of agitation, the pH value, and the temperature. The PNO-catalyzed reaction produced mainly the substitution product, the acid anhydride ($Cl_2C_6H_3COOCOR$), whereas the uncatalyzed reaction produced mainly the hydrolysis product ($Cl_2C_6H_3COOH$). Similar to the previous results [21,26,27,29], without agitation, the rate of reaction was slow, whereas it increased asymptotically with increased rate of agitation and appeared to be independent of the agitation rate beyond 1100 rpm. Therefore, most of the kinetic experiments were run at 1200 rpm. The reaction took place more favorably in polar organic solvent than in the nonpolar organic solvent. For example, with $[3,4\text{-}Cl_2C_6H_3COCl]_{iorg} = 0.0100$ M, $[PNO]_{iaq} = 2.00 \times 10^{-4}$ M, $[C_6H_5COONa]_{iaq} = 0.500$ M, the values of k_{obs} at 20°C were $(25.3, 0.670, \text{and } 0.061) \times 10^{-4}$ s^{-1} in H_2O/CH_2Cl_2, $n\text{-}C_6H_{14}/H_2O$, and C_6H_6/H_2O media, respectively. In this work, most kinetic experiments were run in H_2O/CH_2Cl_2 medium, with the ionic strength and the pH value of the aqueous phase being kept at 0.5 M and 7.5, respectively.

3.1. Uncatalyzed reaction

The uncatalyzed two-phase reaction of $Cl_2C_6H_3COCl$ and C_6H_5COONa produced mainly the hydrolysis product, $Cl_2C_6H_3COOH$. For $[Cl_2C_6H_3COCl]_{iorg} = 0.0100$ M and $[C_6H_5COONa]_{iaq} = 0.500$ M in H_2O/CH_2Cl_2 medium, the values of k_{obs} or k_h at 22°C are $(1.88, 2.17, 1.67 \text{ and } 3.13) \times 10^{-5}$ s^{-1} for 2,3-, 2,4-, 3,4-, and 3,5-$Cl_2C_6H_3COCl$, respectively. The values of k_h at 22°C for the uncatalyzed reactions of ClC_6H_4COCl in H_2O/CH_2Cl_2 medium are $(1.23, 1.47, \text{and } 1.23) \times 10^{-4}$ s^{-1} for 2-, 3-, and 4-ClC_6H_4COCl, respectively [26]. Therefore, the rates of hydrolysis of the dichloro-substituted benzoyl chlorides are considerably slower than those of the monochloro-substituted benzoyl chlorides. This is in part due to the lower solubility of $Cl_2C_6H_3COCl$ in the aqueous phase than that of ClC_6H_4COCl.

3.2. PNO-catalyzed reaction

3.2.1. Symmetric dichlorobenzoic anhydrides

The PNO-catalyzed reaction of $Cl_2C_6H_3COCl$ and the corresponding $Cl_2C_6H_3COONa$ in H_2O/CH_2Cl_2 medium produced rapidly the symmetric dichlorobenzoic anhydride, $(Cl_2C_6H_3CO)_2O$ (> 95% yield) and a trace amount of $Cl_2C_6H_3COOH$. The rate of reaction depends linearly on $[PNO]_{iaq}$. Typical kinetic results are shown in Fig. 1. The plots of k_{obs} vs. $[PNO]_{iaq}$ are linear (Fig. 2), which implies that the reaction is first-order with respect to PNO. Similar to the PNO-catalyzed reaction of benzoyl chloride and benzoate ion in H_2O/CH_2Cl_2 medium [21], the rate law of this

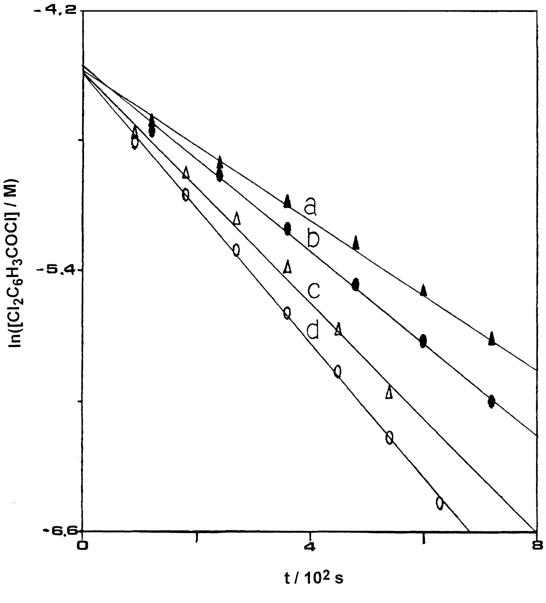

Fig. 1. Plots of $\ln[Cl_2C_6H_3COCl]$ vs. time for the PNO-catalyzed reactions of $Cl_2C_6H_3COCl$ and the corresponding $Cl_2C_6H_3COONa$ in 50 ml H_2O/50 ml CH_2Cl_2 medium. $[Cl_2C_6H_3COCl]_{iorg} = 0.0100$ M, $[Cl_2C_6H_3COONa]_{iaq} = 0.500$ M, $[PNO]_{iaq} =$ (a, b, c) 1.00×10^{-4} M, (d) 5.00×10^{-5} M, 22°C, pH = 7.5. (a) 2,3-$Cl_2C_6H_3COCl$, (b) 2,4-$Cl_2C_6H_3COCl$, (c) 3,4-$Cl_2C_6H_3COCl$, (d) 3,5-$Cl_2C_6H_3COCl$.

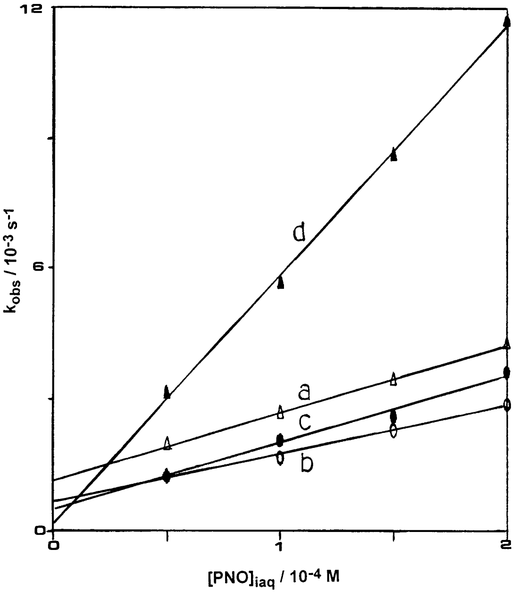

Fig. 2. Plots of k_{obs} vs. $[PNO]_{iaq}$ for the PNO-catalyzed reactions of $Cl_2C_6H_3COCl$ and the corresponding $Cl_2C_6H_3COONa$ in 50 ml $H_2O/50$ ml CH_2Cl_2 medium. $[Cl_2C_6H_3COCl]_{iorg} = 0.0100$ M, $[Cl_2C_6H_3COONa]_{iaq} = 0.500$ M, 22°C, pH = 7.5. (a) 2,3-$Cl_2C_6H_3COCl$, (b) 2,4-$Cl_2C_6H_3COCl$, (c) 3,4-$Cl_2C_6H_3COCl$, (d) 3,5-$Cl_2C_6H_3COCl$.

PNO-catalyzed reaction can be expressed by Eq. (1).

$$\begin{aligned} -\mathrm{d}[Cl_2C_6H_3COCl]_{org}/\mathrm{d}t &= k_{obs}[Cl_2C_6H_3COCl]_{org} \\ &= \left(k_h + k_c[PNO]_{iaq}\right)[Cl_2C_6H_3COCl]_{org} \end{aligned} \quad (1)$$

In Eq. (1), $k_{obs} = k_h + k_c$ $[PNO]_{iaq}$, where k_h and k_c are the uncatalyzed (hydrolysis) and the catalyzed rate constants, respectively. The values of (k_h, k_c) at 22°C obtained from the LLS fits of the plots of k_{obs} vs. $[PNO]_{iaq}$ (Fig. 2) are $(1.13 \times 10^{-3}$ s^{-1}, 15.6 M^{-1} $s^{-1})$, $(6.35 \times 10^{-4}$ s^{-1}, 1.08 M^{-1} $s^{-1})$, $(4.55 \times 10^{-4}$ s^{-1}, 15.4 M^{-1} $s^{-1})$, and $(9.50 \times 10^{-5}$ s^{-1}, 57.3 M^{-1} $s^{-1})$ for 2,3-, 2,4-, 3,4- and 3,5-$Cl_2C_6H_3COCl$, respectively. These results indicate that the order of reactivity towards the reaction with PNO is 3,5- > (2,3-, 3,4-) > 2,4-$Cl_2C_6H_3COCl$. The values of k_h of PNO-catalyzed reactions are larger than those of the corresponding uncatalyzed reactions, which implies that the presence of PNO also catalyzes the hydrolysis of $Cl_2C_6H_3COCl$ (reaction R3). For the case of 2,6-$Cl_2C_6H_3COCl$, the reaction was slow even for $[PNO]_{iaq} = 0.01$ M and no significant amount of $(2,6\text{-}Cl_2C_6H_3CO)_2O$ was observed.

3.2.2. Mixed benzoicchlorobenzoic anhydrides

The PNO-catalyzed reaction of $Cl_2C_6H_3$-COCl and C_6H_5COONa in H_2O/CH_2Cl_2 medium produced mainly the mixed benzoicchlorobenzoic anhydride ($Cl_2C_6H_3COO$-COC_6H_5) (> 90% yield) and small amounts of $Cl_2C_6H_3COOH$ and C_6H_5COOH. Typical kinetic results are shown in Fig. 3. The values of k_c obtained from the LLS fits of the plots of k_{obs} vs. $[PNO]_{iaq}$ (Figs. 4–7) are shown in Table 1. The apparent activation energies (E_a) obtained from LLS fits of the Arrhenius plots of ln k_c vs. $1/T$ are also shown in Table 1. In contrast to the result in Section 3.2.1, these results indicate that the order of reactivity to-

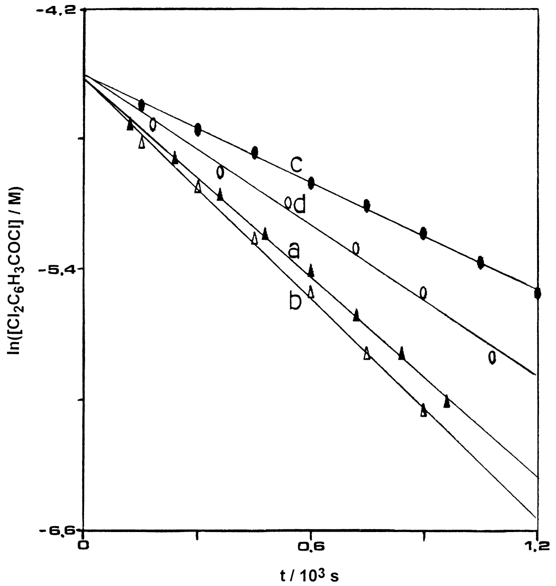

Fig. 3. Plots of $\ln[Cl_2C_6H_3COCl]$ vs. time for the PNO-catalyzed reactions of $Cl_2C_6H_3COCl$ and C_6H_5COONa in 50 ml $H_2O/50$ ml CH_2Cl_2 medium. $[Cl_2C_6H_3COCl]_{iorg} = 0.0100$ M, $[C_6H_5COONa]_{iaq} = 0.500$ M, $[PNO]_{iaq}$ = (a, b) 1.50×10^{-4} M, (c, d) 1.00×10^{-4} M, 10°C, pH = 7.5. (a) 2,3-$Cl_2C_6H_3COCl$, (b) 2,4-$Cl_2C_6H_3COCl$, (c) 3,4-$Cl_2C_6H_3COCl$, (d) 3,5-$Cl_2C_6H_3COCl$.

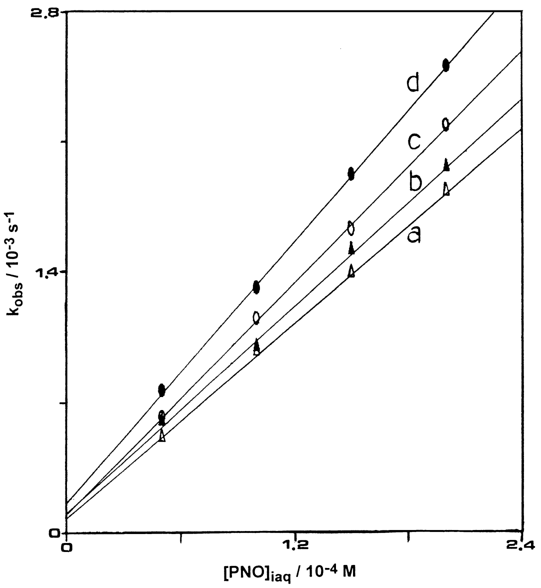

Fig. 4. Plots of k_{obs} vs. $[PNO]_{iaq}$ for the PNO-catalyzed reactions of 2,3-$Cl_2C_6H_3COCl$ and C_6H_5COONa in 50 ml H_2O/50 ml CH_2Cl_2 medium at various temperatures. $[2,3\text{-}Cl_2C_6H_3COCl]_{iorg} = 0.0100$ M, $[C_6H_5COONa]_{iaq} = 0.500$ M, pH = 7.5. (a) 5°C, (b) 10°C, (c) 15°C, (d) 22°C.

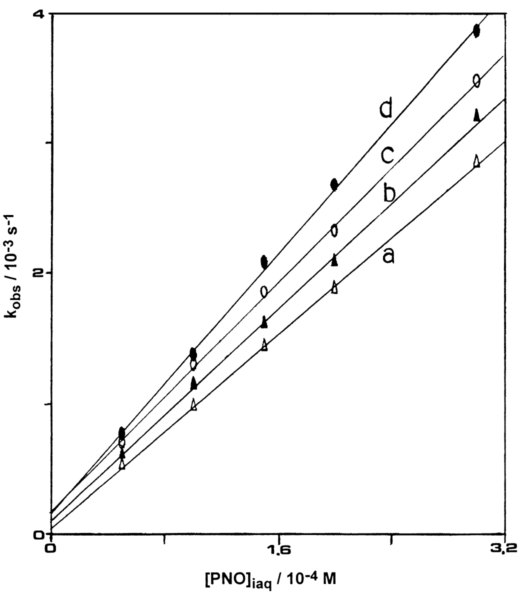

Fig. 5. Plots of k_{obs} vs. $[PNO]_{iaq}$ for the PNO-catalyzed reactions of 2,4-$Cl_2C_6H_3COCl$ and C_6H_5COONa in 50 ml H_2O/50 ml CH_2Cl_2 medium at various temperatures. $[2,4\text{-}Cl_2C_6H_3COCl]_{iorg} = 0.0100$ M, $[C_6H_5COONa]_{iaq} = 0.500$ M, pH = 7.5. (a) 5°C, (b) 10°C, (c) 15°C, (d) 20°C.

wards the reaction with PNO is (2,4-, 2,3-) > 3,5- > 3,4-$Cl_2C_6H_3COCl$.

It was observed that the reaction rate depends on the pH value of the aqueous phase. The 2,4-$Cl_2C_6H_3COCl$ system was chosen for studying the pH effect. For $[2,4\text{-}Cl_2C_6H_3COCl]_{iorg} = 0.0100$ M, $[C_6H_5COONa]_{iaq} = 0.500$ M, and at 22°C, the values of k_c obtained from the LLS fits of the plots of k_{obs} vs. $[PNO]_{iaq}$ (Fig. 8) are (22.3, 12.8, 11.0 and 9.42) M^{-1} s^{-1} for pH = 5.4, 6.1, 7.5 and 12.0, respectively. For $[2,4\text{-}Cl_2C_6H_3COCl]_{iorg} = 0.0100$ M, $[2,4\text{-}Cl_2C_6H_3COONa]_{iaq} = 0.500$ M, and at 22°C, the values of k_c are (19.2, 11.4, and 11.9) M^{-1} s^{-1} for pH = 5.6, 7.4, and 12.0, respectively. The value of k_c decreases with increased pH value for pH < 12, which can be rationalized partly by invoking that the increase in the acidity of the aqueous phase increases the distribution of benzoic acids in the organic phase, which in turn increases the distribution of PNO in the organic phase, and thus promotes the reaction [28].

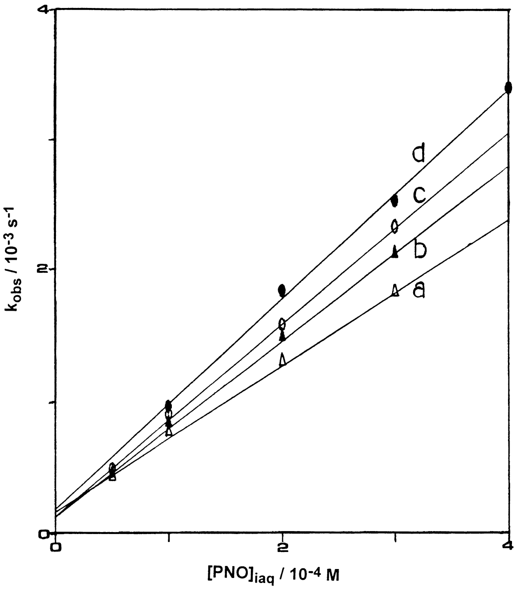

Fig. 6. Plots of k_{obs} vs. $[PNO]_{iaq}$ for the PNO-catalyzed reactions of 3,4-$Cl_2C_6H_3COCl$ and C_6H_5COONa in 50 ml H_2O/50 ml CH_2Cl_2 medium at various temperatures. $[3,4\text{-}Cl_2C_6H_3COCl]_{iorg} = 0.0100$ M, $[C_6H_5COONa]_{iaq} = 0.500$ M, pH = 7.5. (a) 5°C, (b) 10°C, (c) 15°C, (d) 20°C.

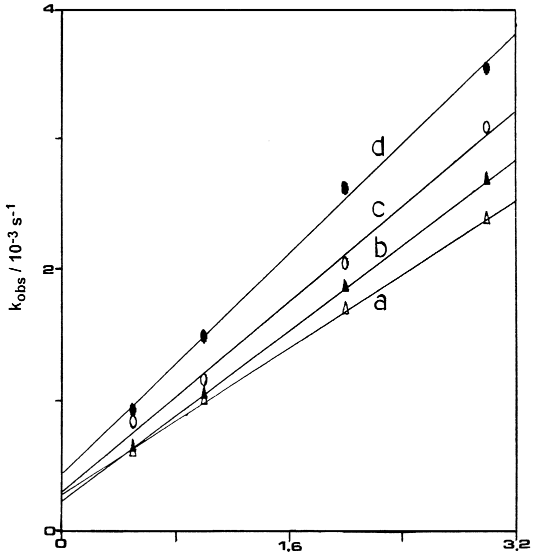

Fig. 7. Plots of k_{obs} vs. $[PNO]_{iaq}$ for the PNO-catalyzed reactions of 3,5-$Cl_2C_6H_3COCl$ and C_6H_5COONa in 50 ml H_2O/50 ml CH_2Cl_2 medium at various temperatures. $[3,5\text{-}Cl_2C_6H_3COCl]_{iorg} = 0.0100$ M, $[C_6H_5COONa]_{iaq} = 0.500$ M, pH = 7.5. (a) 5°C, (b) 10°C, (c) 15°C, (d) 22°C.

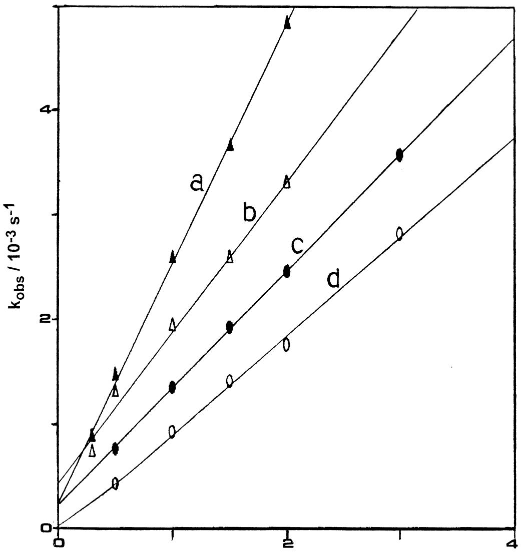

Fig. 8. Plots of k_{obs} vs. $[PNO]_{iaq}$ for the PNO-catalyzed reactions of 2,4-$Cl_2C_6H_3COCl$ and C_6H_5COONa in 50 ml H_2O/50 ml CH_2Cl_2 medium at various pH values. $[2,4\text{-}Cl_2C_6H_3COCl]_{iorg} = 0.0100$ M, $[C_6H_5COONa]_{iaq} = 0.500$ M, 20°C, pH = (a) 5.4, (b) 6.1, (c) 7.5, (d) 12.0.

3.2.3. Reactivities of benzoate ions

Since the ionic reaction of the intermediate ($Cl_2C_6H_3COONP^+$) ion with the carboxylate ($RCOO^-$) ion (reaction R2) is very rapid, the direct measurement of its rate is not feasible.

Table 1
Temperature dependence of the PNO-catalyzed rate constant (k_c) of the two-phase reaction of dichlorobenzoyl chloride and benzoate ion. $[Cl_2C_6H_3COCl]_{iorg} = 0.0100$ M, $[C_6H_5COONa]_{iaq} = 0.500$ M, 50 ml H_2O/50 ml CH_2Cl_2, pH = 7.5, 1200 rpm, DCBC = $Cl_2C_6H_3COCl$

T (°C)	k_c (M^{-1} s^{-1})			
	2,3-DCBC	2,4-DCBC	3,4-DCBC	3,5-DCBC
5	8.68	9.28	5.57	7.07
10	9.12	10.2	6.66	8.17
15	10.2	11.0	7.30	9.12
20	–	12.4	7.98	–
22	11.6	–	–	10.5
E_a (kJ mol^{-1})	12.0 ± 1.2	12.8 ± 0.9	15.9 ± 1.9	15.7 ± 0.8
22	(15.6)[a]	(11.1)[b]	(15.4)[c]	(57.3)[d]

[a] $[2,3\text{-}Cl_2C_6H_3COONa]_{iaq} = 0.500$ M.
[b] $[2,4\text{-}Cl_2C_6H_3COONa]_{iaq} = 0.500$ M.
[c] $[3,4\text{-}Cl_2C_6H_3COONa]_{iaq} = 0.500$ M.
[d] $[3,5\text{-}Cl_2C_6H_3COONa]_{iaq} = 0.500$ M.

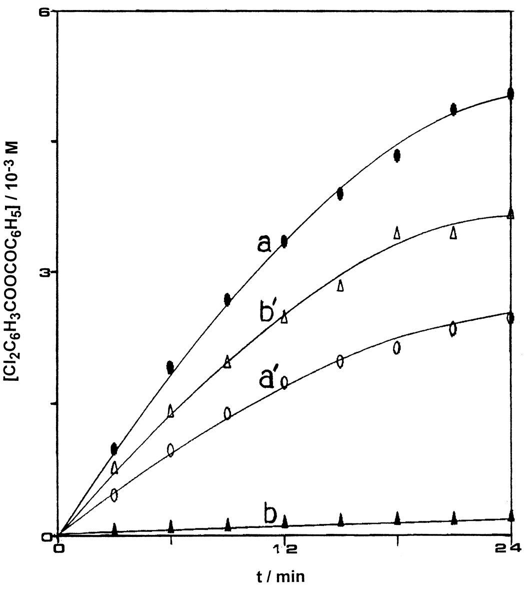

Fig. 9. $[Cl_2C_6H_3COOCOC_6H_5]$ vs. time for the PNO-catalyzed reaction of C_6H_5COCl and mixed 2,4- and 3,5-$Cl_2C_6H_3COO^-$ ions in 50 ml H_2O/50 ml CH_2Cl_2 medium. $[C_6H_5COCl]_{iorg} = 0.0100$ M, $[PNO]_{iaq} = 2.00 \times 10^{-4}$ M, 22°C, pH = 7.5, $[3,5\text{-}Cl_2C_6H_3COO^-]_{iaq}$ = (a) 0.4375 M, (a′) 0.0625 M, $[2,4\text{-}Cl_2C_6H_3COO^-]_{iaq}$ = (b) 0.0625 M, (b′) 0.4375 M. (a, a′): 3,5-$Cl_2C_6H_3COOCOC_6H_5$, (b, b′): 2,4-$Cl_2C_6H_3COOCOC_6H_5$.

However, the relative reactivities of various benzoate ions can be deduced from studying the competitive effects of mixed benzoate ions on the relative rates (or yields) of the production of mixed acid anhydrides. For example, assuming other things being equal and $[\text{mixed benzoate}]_{iaq} \gg [C_6H_5COCl]_{iorg}$, the relative reactivities of $XC_6H_4COO^-$ and $YC_6H_4COO^-$ ions toward the reaction with $C_6H_5COONP^+$ ion can be deduced from the expression of $\Delta[XC_6H_4COOCOC_6H_5]_{org} / \Delta[YC_6H_4COOC_6H_5]_{org} = k_X[XC_6H_4COONa]_{iaq} / k_Y[YC_6H_4COONa]_{iaq}$. Typical results are shown in Fig. 9. For $[C_6H_5COCl]_{iorg} = 0.0100$ M, $[PNO]_{iaq} = 2.00 \times 10^{-4}$ M, $[\text{mixed benzoate}]_{iaq} = 0.500$ M, 22°C, $Cl_2C_6H_3COOCOC_6H_5$ = DCBBA, $ClC_6H_4COOCOC_6H_5$ = CBBA, $Cl_2C_6H_3COONa$ = SDCB, and ClC_6H_4COONa = SCB, the results are summarized as follows.

(i) Δ[2,4-DCBBA]/Δ[2,3-DCBBA] = $(13.0 \pm 1.8)/1.0$ and $1.0/(4.6 \pm 0.9)$ for [2,4-SDCB]/[2,3-SDCB] = 7/1 and 1/7, respectively.

(ii) Δ[2,4-DCBBA]/Δ[3,5-DCBBA] = $(1.45 \pm 0.06)/1.0$ and $1.0/(28.4 \pm 1.8)$ for [2,4-SDCB]/[3,5-SDCB] = 7/1 and 1/7, respectively.

(iii) Δ[2,4-DCBBA]/Δ[4-CBBA] = $(8.1 \pm 0.1)/1.0$ and $1.0/(6.6 \pm 0.5)$ for [2,4-SDCB]/[4-SCB] = 7/1 and 1/7, respectively.

(iv) Δ[2,3-DCBBA]/Δ[3,4-DCBBA] = $(1.2 \pm 0.1)/1.0$, $1.0/(20.8 \pm 5.2)/1.0$, and $1.0/(5.3 \pm 0.5)$ for [2,3-SDCB]/[3,4-SDCB] = 7/1, 1/7, and 1/1, respectively.

(v) Δ[3,4-DCBBA]/Δ[3,5-DCBBA] = $(6.3 \pm 0.2)/1.0$, $1.0/(11.5 \pm 1.1)/1.0$, and $1.0/(1.3 \pm 0.2)$ for [3,4-SDCB]/[3,5-SDCB] = 7/1, 1/7, and 1/1, respectively.

(vi) Δ[3,4-DCBBA]/Δ[4-CBBA] = $1.0/(1.6 \pm 0.1)$ and $(34.5 \pm 4.1)/1.0$ for [3,4-SDCB]/[4-SCB] = 7/1 and 1/7, respectively.

(vii) The rates of the reactions in (i)–(vi) are quite insensitive to the change of the mixed benzoate ions. The average value of k_{obs} calculated from 18 kinetic runs is $(8.57 \pm 0.87) \times 10^{-4}\ s^{-1}$.

These results, combined with the previous results [26], indicate that the order of relative reactivities of benzoate ions towards the reaction with 1-(benzoyloxy)-pyridinium (C_6H_5CO-ONP^+) ion is (3,4-, 3,5-$Cl_2C_6H_3COO^-$) > (2,3-, 2,4-$Cl_2C_6H_3COO^-$; 3-, 4-$ClC_6H_4COO^-$) > 2-$ClC_6H_4COO^-$ > $C_6H_5COO^-$. Thus, it can be concluded that the electrowithdrawing chloro-substituent increases the reactivity of benzoate ion and that the meta-substituent exhibits a greater effect on promoting the reactivity.

3.3. Discussion

The above kinetic results, combined with the previous results [21,26], indicate that the order of reactivity of benzoyl chlorides towards the reaction with PNO is (2,4-, 2,3-$Cl_2C_6H_3COCl$) > 3,5-$Cl_2C_6H_3COCl$ > (3,4-$Cl_2C_6H_3COCl$, 2-ClC_6H_4COCl) > 3-ClC_6H_4COCl4ClC_6H_4COCl > C_6H_5COCl ≫ 2,6-$Cl_2C_6H_3COCl$. The effect of chloro-substituent implies that the inductive effect predominates over the resonance effect during the formation of the activated complex of chloro-substituted benzoyl chloride and PNO. The *ortho*-substituent may also facilitate the reaction by stabilizing the transition state via complexing with the positively charged nitrogen atom of the pyridinium moiety. Furthermore, the considerably lower reactivity of 2,6-$Cl_2C_6H_3COCl$ can be rationalized by invoking the steric effect, i.e. the presence of the second chloro-substituent at the *ortho*-position hinders the formation of the activated complex. The above kinetic results imply that the reaction of $Cl_2C_6H_3COCl$ and PNO in the organic phase (reaction R1) is the rate-determining step for these reactions. This argument is further supported by studying the PNO-catalyzed reaction of benzoate ion with mixed dichlorobenzoyl chlorides. For example, with $[2,3\text{-}Cl_2C_6H_3COCl]_{iorg}$ = [3,5-$Cl_2C_6H_3$-

$COCl]_{iorg} = 5.00 \times 10^{-3}$ M, $[C_6H_5COONa]_{iaq} = 0.500$ M, and $[PNO]_{iaq} = 2.00 \times 10^{-4}$ M, the values of k_{obs} at 22°C are $(2.43$ and $2.65) \times 10^{-3}$ s^{-1} for 2,3- and 3,5-$Cl_2C_6H_3COCl$, respectively, which are similar to the values of $(2.50$ and $2.62) \times 10^{-3}$ s^{-1} measured independently (Figs. 4 and 7). These results indicate that both 2,3- and 3,5-$Cl_2C_6H_3COCl$ react independently with PNO in the organic phase and also strongly support the assumption that the equilibrium distribution of PNO between H_2O and CH_2Cl_2 phases is always maintained. It is worth noting that in the PNO-catalyzed two-phase reaction of $Cl_2C_6H_3COCl$ and C_6H_5COONa, the order of reactivities of $Cl_2C_6H_3COCl$ towards the reaction with PNO is (2,3-, 2,4-) > 3,5- > 3,4- > 2,6-$Cl_2C_6H_3COCl$, whereas it is 3,5- > (2,3-, 3,4-) > 2,4$Cl_2C_6H_3COCl$ in the PNO-catalyzed two-phase reaction of $Cl_2C_6H_3COCl$ and $Cl_2C_6H_3COONa$ (Table 1). These results may be rationalized by invoking the reaction of $Cl_2C_6H_3COCl$ and $Cl_2C_6H_3COONa$ (reaction R4) at the interface or in the intermediate phase, in some sense similar to the tri-liquid-phase catalysis observed in the reaction of benzyl chloride and bromide ion in toluene/water medium [30]. This argument is also supported by the higher reactivity of 3,4- and 3,5-$Cl_2C_6H_3COO^-$ ion mentioned above.

$$Cl_2C_6H_3COCl(org) + PNO(aq) \rightarrow Cl_2C_6H_3CONP^+Cl^-(aq) \qquad (R4)$$

4. Conclusion

The reaction of dichlorobenzoyl chloride and benzoate or dichlorobenzoate ion in a two-phase H_2O/CH_2Cl_2 medium using PNO as an inverse phase-transfer catalyst was investigated. The main conclusions are:

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

(b) The reaction of dichlorobenzoyl chloride with PNO in CH_2Cl_2 phase to produce the intermediate, 1-(dichlorobenzoyloxy)-pyridinium ion, is the rate-determining step.

(c) In the PNO-catalyzed reaction of dichlorobenzoyl chloride and $C_6H_5COO^-$ ion in H_2O/CH_2Cl_2 medium, the order of reactivities of dichlorobenzoyl chlorides towards the reaction with PNO is (2,3-, 2,4-) > 3,5- > 3,4- ≫ 2,6-$Cl_2C_6H_3COCl$.

(d) In the PNO-catalyzed reaction of dichlorobenzoyl chloride and the corresponding $Cl_2C_6H_3COO^-$ ion in H_2O/CH_2Cl_2 medium, the order of reactivities of dichlorobenzoyl chlorides towards the reaction with PNO is 3,5- > (2,3-, 3,4-) > 2,4-$Cl_2C_6H_3COCl$.

(e) The order of reactivities of dichlorobenzoate ions towards the reaction with 1-(benzoyloxy)-pyridinium ($C_6H_5COONP^+$) ion is (3,4-, 3,5-) > (2,3-, 2,4-$Cl_2C_6H_3COO^-$).

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