

# Inverse phase transfer catalysis: kinetics of the pyridine-1-oxide-catalyzed two-phase reactions of methyl-, methoxy-, iodo-, and nitro-benzoyl chlorides and benzoate ions

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## Abstract

The substitution reactions of  $\text{XC}_6\text{H}_4\text{COCl}$  [ $\text{X} = 2\text{-}, 3\text{-}, \text{or } 4\text{-CH}_3; 2\text{-}, 3\text{-}, \text{or } 4\text{-CH}_3\text{O}; 2\text{-}, \text{ or } 4\text{-I}; \text{ or } 2\text{-}, 3\text{-}, \text{ or } 4\text{-NO}_2$ ] and  $\text{YC}_6\text{H}_4\text{COONa}$  [ $\text{Y} = 2\text{-}, 3\text{-}, \text{ or } 4\text{-CH}_3; 2\text{-}, 3\text{-}, \text{ or } 4\text{-CH}_3\text{O}; 2\text{-I}; 4\text{-NO}_2; \text{ or H}$ ] in a two-phase  $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$  medium using pyridine-1-oxide (PNO) as an inverse phase transfer catalyst were investigated. In general, the kinetics of the reaction follows a pseudo-first-order rate law, with the observed rate constant being a linear function of the concentration of PNO in the water phase. In contrast to other analogous reactions, the hydrolysis reaction of 2-, 3-, or 4- $\text{NO}_2\text{C}_6\text{H}_4\text{COCl}$  in  $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$  medium is catalyzed considerably by PNO and reaches an equilibrium. In the PNO-catalyzed reaction of  $\text{XC}_6\text{H}_4\text{COCl}$  and  $\text{XC}_6\text{H}_4\text{COONa}$  in  $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$  medium, the order of reactivities of  $\text{XC}_6\text{H}_4\text{COCl}$  toward reaction with PNO in  $\text{CH}_2\text{Cl}_2$  is  $2\text{-IC}_6\text{H}_4\text{COCl} > 4\text{-IC}_6\text{H}_4\text{COCl} > (\text{C}_6\text{H}_5\text{COCl}, 3\text{-CH}_3\text{OC}_6\text{H}_4\text{COCl}) > 3\text{-CH}_3\text{C}_6\text{H}_4\text{COCl} > (2\text{-CH}_3\text{C}_6\text{H}_4\text{COCl}, 4\text{-CH}_3\text{C}_6\text{H}_4\text{COCl}) > 4\text{-CH}_3\text{OC}_6\text{H}_4\text{COCl} > 2\text{-CH}_3\text{OC}_6\text{H}_4\text{COCl}$ . Combined with the results of other analogous reactions, good Hammett correlations with positive reaction constant were obtained for the *meta*- and *para*-substituents, which supports that the  $\text{XC}_6\text{H}_4\text{COCl}$ -PNO reaction in  $\text{CH}_2\text{Cl}_2$  is a nucleophilic substitution reaction. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Methyl-, methoxy-, iodo-, and nitro-benzoyl chlorides; Benzoate ions; Pyridine-1-oxide; Inverse phase transfer catalysis

## 1. Introduction

In the past three decades, the study of the phase transfer catalysis (PTC) has grown to become an important area of research in chemistry and chemical engineering. Numerous interfacial organic synthetic reactions were made feasible by utilizing the PTC technique. Extensive PTC reactions have been studied focusing on the normal phase transfer catalysis

(NPTC), in which the anionic reactant is continuously transported with a cationic phase transfer catalyst from the water phase into the organic phase for reaction with a second reactant [1–7]. In contrast, the inverse phase transfer catalysis (IPTC), as named by Mathias and Vaidya [8], involves the conversion of a reactant in the organic phase by a phase transfer catalyst to an ionic intermediate, which is transported into the water phase for reaction. The IPTC technique provides one of the most attractive methods for synthesizing acid anhydrides [9–16], which are important intermediates for the synthesis of esters, amides, and peptides. Kuo and Jwo [17], Wang et al. [18–24], Ou et al. [25], Liou

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and Jwo [26], Hung and Jwo [27], and Chang and Jwo [28] have studied the kinetics and mechanism of the two-phase substitution reactions of benzoyl chlorides with carboxylate and dicarboxylate ions using pyridine-1-oxide (PNO) as an inverse phase transfer catalyst. In this paper, the PNO-catalyzed IPTC reactions of methyl-, methoxy-, iodo-, and nitro-benzoyl chlorides with benzoate ions in a two-phase medium were studied. Both symmetric and mixed benzoic anhydrides were synthesized. The correlations of the effects of substituents on this reaction series are presented and the results are rationalized.

## 2. Experimental

### 2.1. Materials

Pyridine-1-oxide (Aldrich); biphenyl (Ferak); 2-, 3- and 4-toluoyl chlorides, 2-, 3- and 4-toluic acids, 2-, 3- and 4-methoxybenzoyl chlorides, 3- and 4-methoxybenzoic acids, 2- and 4-iodobenzoyl chlorides, 2-iodobenzoic acid, 2- and 4-nitrobenzoyl chlorides, and 4-nitrobenzoic acid (Lancaster); 4-anisoyl chloride (Acros); 3-nitrobenzoyl chloride (TCI); anthracene ( $C_{14}H_{10}$ ) and biphenyl ( $C_{12}H_{10}$ ) (Ferak); naphthalene ( $C_{10}H_8$ ) and tetra-*n*-butylammonium hydroxide (Merck) were used. Deionized water was obtained from reverse osmosis (Millipore Milli-RO 20). Due to the hygroscopic property of pyridine-1-oxide (PNO), (PNO) $H^+Cl^-$  crystals (Anal. Calcd. for  $C_5H_6ClNO$ : C, 45.60; H, 4.56; N, 10.64; Cl, 26.99. Found: C, 45.65; H, 4.71; N, 10.62; Cl, 26.89) were used instead [17].

### 2.2. Procedures

#### 2.2.1. Synthesis of symmetric and mixed benzoic anhydrides

Under agitation at 1200 rpm, a 50 ml  $CH_2Cl_2$  solution of  $XC_6H_4COCl$  ( $X = CH_3, CH_3O, \text{ or } I$ ) (0.2 M) was mixed with a 50 ml aqueous solution containing the desired benzoate salt  $YC_6H_4COONa$  ( $Y = H, CH_3, CH_3O, \text{ or } I$ ) (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 benzoic acids. It was then washed twice with deion-

ized water and dried with anhydrous  $MgSO_4$ . The symmetric benzoic anhydrides were obtained after concentrating the  $CH_2Cl_2$  solution with a rotatory evaporator in a hot water bath, whereas the mixed benzoic anhydrides were obtained in an ice water bath instead to avoid its disproportionation reaction [16]. Anal. Calcd. for  $C_{16}H_{14}O_3$ : C, 75.59; H, 5.51. Found: C, 75.65; H, 5.60 [(2- $CH_3C_6H_4CO$ ) $_2O$ ]; C, 75.57; H, 5.53 [(3- $CH_3C_6H_4CO$ ) $_2O$ ]; C, 75.49; H, 5.54 [(4- $CH_3C_6H_4CO$ ) $_2O$ ]. Calcd. for  $C_{16}H_{14}O_5$ : C, 67.13; H, 4.90. Found: C, 67.08; H, 4.90 [(3- $CH_3OC_6H_4CO$ ) $_2O$ ]; C, 67.11; H, 4.97 [(4- $CH_3OC_6H_4CO$ ) $_2O$ ]. Calcd. for  $C_{14}H_8I_2O_3$ : C, 35.14; H, 1.67. Found: C, 35.06, H, 1.70 [(2- $IC_6H_4CO$ ) $_2O$ ]. Calcd. for  $C_{14}H_9IO_3$ : C, 47.86; H, 2.27. Found: C, 47.84; H, 2.39 (4- $IC_6H_4COOCOC_6H_5$ ).

#### 2.2.2. Kinetic experiment

The kinetic runs were carried out 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  $\pm 0.2^\circ C$ ) for at least 30 min. The kinetic run was started by adding 50 ml of aqueous solution (containing known amounts of  $YC_6H_4COONa$  and (PNO) $H^+Cl^-$ ) to 50 ml of organic solution (containing known amounts of  $XC_6H_4COCl$  and internal standard) under constant 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 then analyzed by HPLC using the internal standard method. HPLC analysis conditions and data — column, Lichrospher 100 RP-18 (5  $\mu m$ ); wavelength, 254 nm:

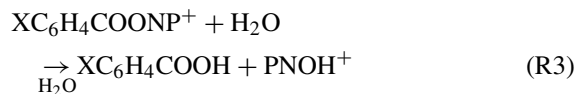
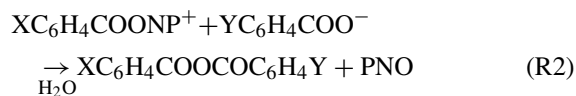
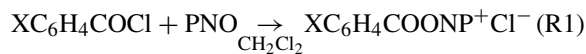
1. eluent,  $CH_3CN/H_2O = 85/15$  by volume; flow rate, 0.5 ml/min; elution time (min): 4- $CH_3C_6H_4COCl$  (8.40), 3- $CH_3C_6H_4COCl$  (8.66), (4- $CH_3C_6H_4CO$ ) $_2O$  (9.40), (3- $CH_3C_6H_4CO$ ) $_2O$  (9.85), and  $C_{14}H_{10}$  (12.32);
2. eluent,  $CH_3CN/H_2O = 70/30$  by volume; flow rate, 1.0 ml/min; elution time (min): 4- $CH_3OC_6H_4COCl$  (2.11), (4- $CH_3OC_6H_4CO$ ) $_2O$  (4.97), and  $C_{12}H_{10}$  (7.65);

3. eluent, CH<sub>3</sub>CN/H<sub>2</sub>O = 65/35 by volume; flow rate, 1.0 ml/min; elution time (min): 3-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>-COCl (7.38), (3-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>CO)<sub>2</sub>O (8.76), and C<sub>12</sub>H<sub>10</sub> (11.38);
4. eluent, CH<sub>3</sub>CN/H<sub>2</sub>O = 62/38 by volume; flow rate, 1.2 ml/min; elution time (min): C<sub>10</sub>H<sub>8</sub> (8.48), 2-IC<sub>6</sub>H<sub>4</sub>COCl (8.66), 2-IC<sub>6</sub>H<sub>4</sub>COOCOC<sub>6</sub>H<sub>5</sub> (10.69), C<sub>12</sub>H<sub>10</sub> (11.62), 4-IC<sub>6</sub>H<sub>4</sub>COCl (12.28), 4-IC<sub>6</sub>H<sub>4</sub>COOCOC<sub>6</sub>H<sub>5</sub> (14.62), (2-IC<sub>6</sub>H<sub>4</sub>CO)<sub>2</sub>O (15.48), C<sub>14</sub>H<sub>10</sub> (17.63);
5. eluent, CH<sub>3</sub>CN/H<sub>2</sub>O = 100/0 by volume; flow rate, 0.5 ml/min; elution time (min): 2-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-COCl (4.66), 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>COCl (4.80), 3-NO<sub>2</sub>C<sub>6</sub>-H<sub>4</sub>COCl (4.84), 2-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>COCl (5.04), C<sub>12</sub>H<sub>10</sub> (6.06).

The response factor  $f$  was calibrated using  $C_x/C_{IS} = f(A_x/A_{IS})$  ( $C$ , concentration;  $A$ , peak area;  $x$ , unknown compound;  $IS$ , internal standard). The values of  $f$  are (i) 8.60 (2-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>COCl), 9.46 (3-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>COCl), 8.76 (4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>COCl), 7.37 [(2-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CO)<sub>2</sub>O], 5.49 [(3-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CO)<sub>2</sub>O], 3.44 [(4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CO)<sub>2</sub>O], 33.4 (2-IC<sub>6</sub>H<sub>4</sub>COCl), and 7.91 (2-IC<sub>6</sub>H<sub>4</sub>COOCOC<sub>6</sub>H<sub>5</sub>) (versus  $IS = C_{14}H_{10}$ ); (ii) 2.39 (2-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>COCl), 2.43 (3-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>COCl), 1.25 (4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>COCl), 1.09 [(3-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>CO)<sub>2</sub>O], 1.07 [(4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>-CO)<sub>2</sub>O], 2.75 (2-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>COCl), 2.42 (3-NO<sub>2</sub>C<sub>6</sub>-H<sub>4</sub>COCl), 1.34 (4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>COCl), 4.93 (2-IC<sub>6</sub>H<sub>4</sub>-COCl), and 1.41 [(2-IC<sub>6</sub>H<sub>4</sub>CO)<sub>2</sub>O] (versus  $IS = C_{12}H_{10}$ ); (iii) 0.621 (4-IC<sub>6</sub>H<sub>4</sub>COCl), 0.170 (4-IC<sub>6</sub>H<sub>4</sub>-COOCOC<sub>6</sub>H<sub>5</sub>) (versus  $IS = C_{10}H_8$ ).

### 3. Results and discussion

The reaction scheme of the PNO-catalyzed reaction of XC<sub>6</sub>H<sub>4</sub>COCl and YC<sub>6</sub>H<sub>4</sub>COONa in H<sub>2</sub>O/CH<sub>2</sub>Cl<sub>2</sub> medium can be simplified as shown in the following reaction processes (R1), (R2), and (R3):



The intermediate, XC<sub>6</sub>H<sub>4</sub>COONP<sup>+</sup>Cl<sup>-</sup>, produced in the organic phase (reaction (R1)) will transfer quickly to the water phase and reacts with YC<sub>6</sub>H<sub>4</sub>COO<sup>-</sup> ion to generate the substitution product, benzoic anhydride (XC<sub>6</sub>H<sub>4</sub>COOCOC<sub>6</sub>H<sub>4</sub>Y) (reaction (R2)) or reacts with H<sub>2</sub>O to produce the hydrolysis product, benzoic acid (XC<sub>6</sub>H<sub>4</sub>COOH) (reaction (R3)). Under suitable reaction condition, all three reactions are essentially irreversible. In general, reaction (R1) is considerably slower than reactions (R2) and (R3) and is the rate-determining step. Then, if the distribution of PNO catalyst between water and organic phases is very rapid and remains at equilibrium during the reaction, the rate of reaction can be expressed by a pseudo-first-order rate equation (Eq. (1)):

$$-\frac{d[XC_6H_4COCl]_{org}}{dt} = k_{obs}[XC_6H_4COCl]_{org} \quad (1)$$

The pseudo-first-order rate constant ( $k_{obs}$ ) was determined by the linear-least-square (LLS) fit of the plot of  $\ln[XC_6H_4COCl]$  versus time. Similar to previous studies [17–28], most kinetic experiments were run in H<sub>2</sub>O/CH<sub>2</sub>Cl<sub>2</sub> medium at 1200 rpm, pH = 7.5, and with ionic strength in the water phase being 0.5 M.

#### 3.1. Uncatalyzed reaction

In the absence of PNO catalyst, XC<sub>6</sub>H<sub>4</sub>COCl reacted with YC<sub>6</sub>H<sub>4</sub>COONa in H<sub>2</sub>O/CH<sub>2</sub>Cl<sub>2</sub> medium to produce mainly the hydrolysis product, XC<sub>6</sub>H<sub>4</sub>COOH (reaction (R3)). Typical kinetic results for CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>-COCl are shown in Fig. 1a, c and e. The values of the observed rate constants ( $k_{obs}$ ) or the hydrolysis rate constant ( $k_h$ ) are shown in Table 1. Under similar conditions, the relative rate of hydrolysis is 2-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>COCl > 4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>COCl > 2-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>COCl ≫ (2-NO<sub>2</sub>-, 4-CH<sub>3</sub>-, 3-CH<sub>3</sub>O-, 3-CH<sub>3</sub>-)C<sub>6</sub>H<sub>4</sub>COCl ≫ (2-I-, 3-NO<sub>2</sub>-, 4-NO<sub>2</sub>-, 4-I-)C<sub>6</sub>H<sub>4</sub>COCl. For [2-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>COCl]<sub>iorg</sub> = 0.0100 M, [2-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>COONa]<sub>iaq</sub> = 0.500 M in 50 ml H<sub>2</sub>O/50 ml CH<sub>2</sub>Cl<sub>2</sub>, the values of  $k_{obs}$  or  $k_h$  are (2.65, 3.53, 5.85, 7.28, and 10.6) × 10<sup>-4</sup> s<sup>-1</sup> at 10, 15, 20, 25, and 30°C, respectively. For [2-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>COCl]<sub>iorg</sub> = 0.0100 M, [NaNO<sub>3</sub>]<sub>iaq</sub> = 0.500 M in 50 ml H<sub>2</sub>O/50 ml CH<sub>2</sub>Cl<sub>2</sub>, the values of  $k_h$  are (1.04, 1.63, 2.00, and 2.27) × 10<sup>-3</sup> s<sup>-1</sup> at 5, 7, 10, and 12°C, respectively. The apparent activation energies ( $E_a$ ) obtained by the LLS fits of the

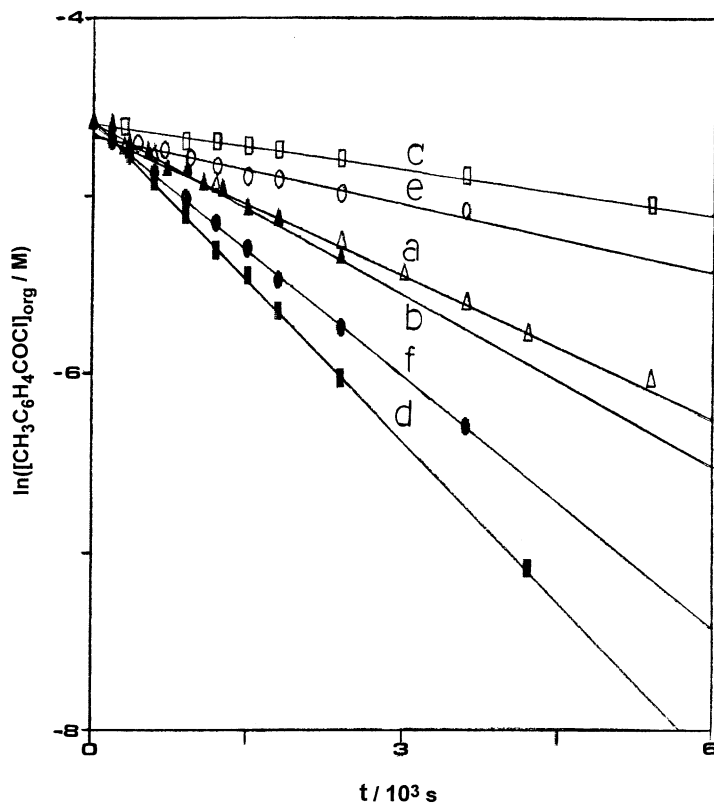


Fig. 1. Plots of  $\ln[\text{CH}_3\text{C}_6\text{H}_4\text{COCl}]_{\text{org}}$  vs. time for the PNO-catalyzed reactions of  $\text{CH}_3\text{C}_6\text{H}_4\text{COCl}$  and  $\text{CH}_3\text{C}_6\text{H}_4\text{COONa}$  in 50 ml  $\text{H}_2\text{O}/50$  ml  $\text{CH}_2\text{Cl}_2$  medium at  $\text{pH} = 7.5$ .  $[\text{CH}_3\text{C}_6\text{H}_4\text{COCl}]_{\text{org}} = 0.0100$  M,  $[\text{CH}_3\text{C}_6\text{H}_4\text{COONa}]_{\text{aq}} = 0.500$  M,  $[\text{PNO}]_{\text{aq}} = 0$  M (a, c, e);  $2.00 \times 10^{-4}$  M (b, d, f);  $10^\circ\text{C}$  (a, b);  $20^\circ\text{C}$  (c–f); 2- $\text{CH}_3\text{C}_6\text{H}_4\text{COCl}$  (a, b); 3- $\text{CH}_3\text{C}_6\text{H}_4\text{COCl}$  (c, d); 4- $\text{CH}_3\text{C}_6\text{H}_4\text{COCl}$  (e, f).

Table 1

The observed rate constants ( $k_{\text{obs}}$ ) or the hydrolysis rate constants ( $k_{\text{h}}$ ) of the uncatalyzed reactions of  $\text{XC}_6\text{H}_4\text{COCl}$  and  $\text{XC}_6\text{H}_4\text{COONa}$  in 50 ml  $\text{H}_2\text{O}/50$  ml  $\text{CH}_2\text{Cl}_2$  medium<sup>a</sup>

$\text{XC}_6\text{H}_4\text{COCl}$	$k_{\text{obs}}$ or $k_{\text{h}}$ ( $10^{-4} \text{ s}^{-1}$ )	$\text{XC}_6\text{H}_4\text{COCl}$	$k_{\text{obs}}$ or $k_{\text{h}}$ ( $10^{-4} \text{ s}^{-1}$ )
2- $\text{CH}_3\text{C}_6\text{H}_4\text{COCl}$	2.65 <sup>b</sup>	2- $\text{IC}_6\text{H}_4\text{COCl}$	1.10
3- $\text{CH}_3\text{C}_6\text{H}_4\text{COCl}$	0.850	2- $\text{IC}_6\text{H}_4\text{COCl}$	1.02 <sup>c</sup>
4- $\text{CH}_3\text{C}_6\text{H}_4\text{COCl}$	1.23	4- $\text{IC}_6\text{H}_4\text{COCl}$	0.183 <sup>c</sup>
2- $\text{CH}_3\text{OC}_6\text{H}_4\text{COCl}$	20.0 <sup>b,d</sup>	2- $\text{NO}_2\text{C}_6\text{H}_4\text{COCl}$	2.02 <sup>d</sup>
3- $\text{CH}_3\text{OC}_6\text{H}_4\text{COCl}$	0.517	3- $\text{NO}_2\text{C}_6\text{H}_4\text{COCl}$	0.215 <sup>d</sup>
4- $\text{CH}_3\text{OC}_6\text{H}_4\text{COCl}$	11.4	4- $\text{NO}_2\text{C}_6\text{H}_4\text{COCl}$	0.123 <sup>d</sup>
3- $\text{CH}_3\text{OC}_6\text{H}_4\text{COCl}$	0.678 <sup>c</sup>		
4- $\text{CH}_3\text{OC}_6\text{H}_4\text{COCl}$	7.82 <sup>c</sup>		

<sup>a</sup>  $[\text{XC}_6\text{H}_4\text{COCl}]_0 = 0.0100$  M;  $[\text{XC}_6\text{H}_4\text{COONa}]_0 = 0.500$  M, and  $20^\circ\text{C}$ .

<sup>b</sup>  $[\text{XC}_6\text{H}_4\text{COCl}]_0 = 0.0100$  M;  $[\text{XC}_6\text{H}_4\text{COONa}]_0 = 0.500$  M, and  $10^\circ\text{C}$ .

<sup>c</sup>  $[\text{C}_6\text{H}_5\text{COONa}]_0 = 0.500$  M.

<sup>d</sup>  $[\text{NaNO}_3]_0 = 0.500$  M.

Table 2

The observed rate constant ( $k_{\text{obs}}$ ) and the yield of benzoic anhydride ( $\text{XC}_6\text{H}_4\text{COOCOC}_6\text{H}_4\text{Y}$ ) for the PNO-catalyzed reaction of benzoyl chloride ( $\text{XC}_6\text{H}_4\text{COCl}$ ) and benzoate ion ( $\text{YC}_6\text{H}_4\text{COONa}$ ) in 50 ml  $\text{H}_2\text{O}/50$  ml  $\text{CH}_2\text{Cl}_2$  medium<sup>a</sup>

[PNO] <sub>0</sub> = 1.00 M		$k_{\text{obs}}$ ( $10^{-4}$ s <sup>-1</sup> )								
X	Y	1.00	2.00	3.00	3.20	4.00	5.00	6.00	8.00	16.0
2-CH <sub>3</sub> <sup>b</sup>	2-CH <sub>3</sub>	4.15 (39.3)	5.72 (55.1)	6.87 (63.4)	–	–	10.2 (76.0)	–	–	–
3-CH <sub>3</sub>	3-CH <sub>3</sub>	–	5.93 (75.6)	–	9.23 (89.6)	11.7 (89.2)	–	15.8 (89.7)	24.8 (>95)	–
4-CH <sub>3</sub>	4-CH <sub>3</sub>	–	4.68 (37.1)	–	6.45 (69.4)	7.60 (57.9)	–	10.7 (57.1)	13.6 (55.5)	–
3-CH <sub>3</sub> O	3-CH <sub>3</sub> O	4.17 (60.5)	8.52 (81.3)	–	–	16.3 (84.8)	–	–	29.3 (93.5)	55.8 (84.8)
4-CH <sub>3</sub> O	4-CH <sub>3</sub> O	11.6 (7.54)	12.9 (11.8)	–	–	14.1 (17.3)	–	15.3 (19.8)	16.6 (23.8)	–
3-CH <sub>3</sub> O	H	–	3.98	–	–	8.05	–	11.9	15.0	–
4-CH <sub>3</sub> O	H	–	7.98	–	–	9.47	10.1	–	10.5	–
2-I	2-I	17.7 (88.7)	32.0 (>95)	52.3 (>95)	–	70.8 (>95)	–	–	–	–
2-I	H	11.6 (84.4)	21.2 (>95)	31.5 (>95)	–	45.5 (>95)	–	–	–	–
4-I	H	7.40 (70.7)	13.0 (69.7)	20.5 (81.9)	–	27.8 (88.7)	–	–	–	–

<sup>a</sup> The values in parentheses is the yield (%) of the corresponding benzoic anhydride.  $[\text{XC}_6\text{H}_4\text{COCl}]_0 = 0.0100$  M;  $[\text{YC}_6\text{H}_4\text{COONa}]_0 = 0.500$  M, and 20°C.

<sup>b</sup>  $[\text{XC}_6\text{H}_4\text{COCl}]_0 = 0.0100$  M;  $[\text{YC}_6\text{H}_4\text{COONa}]_0 = 0.500$  M, and 10°C.

Arrhenius plots of  $\ln k_{\text{h}}$  versus  $1/T$  are  $49.9 \pm 3.0$  and  $69.3 \pm 15.5$  kJ mol<sup>-1</sup> for 2-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>COCl and 2-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>COCl, respectively.

### 3.2. PNO-catalyzed reaction

In the presence of PNO,  $\text{XC}_6\text{H}_4\text{COCl}$  reacted with  $\text{YC}_6\text{H}_4\text{COONa}$  in  $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$  medium to produce mainly the substitution product,  $\text{XC}_6\text{H}_4\text{COOCOC}_6\text{H}_4\text{Y}$  (reaction (R2)). Typical kinetic results for  $\text{CH}_3\text{C}_6\text{H}_4\text{COCl}$  are shown in Fig. 1b, d, and f. The values of  $k_{\text{obs}}$  are shown in Table 2. The plots of  $k_{\text{obs}}$  versus  $[\text{PNO}]_{\text{iaq}}$  are linear, implying that the reaction is also first order with respect to PNO. The value of  $k_{\text{obs}}$  at the intercept is generally in good agreement with that of the corresponding uncatalyzed reaction. Thus, similar to the PNO-catalyzed reaction of  $\text{C}_6\text{H}_5\text{COCl}$  and  $\text{C}_6\text{H}_5\text{COONa}$  in  $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$  [17], the rate law of this PNO-catalyzed reaction can generally be expressed by Eq. (2).

$$\begin{aligned} & \frac{d[\text{XC}_6\text{H}_4\text{COCl}]_{\text{org}}}{dt} \\ &= k_{\text{obs}}[\text{XC}_6\text{H}_4\text{COCl}]_{\text{org}} \\ &= (k_{\text{h}} + k_{\text{c}}[\text{PNO}]_{\text{iaq}})[\text{XC}_6\text{H}_4\text{COCl}]_{\text{org}} \end{aligned} \quad (2)$$

where  $k_{\text{obs}} = k_{\text{h}} + k_{\text{c}}[\text{PNO}]_{\text{iaq}}$  and  $k_{\text{h}}$  and  $k_{\text{c}}$  are the uncatalyzed (hydrolysis) and catalyzed rate constants, respectively. The values of  $k_{\text{c}}$  are shown in Table 3.

Combined with the previous results [17,22,23,27,28], in the PNO-catalyzed reaction of  $\text{XC}_6\text{H}_4\text{COCl}$  and  $\text{C}_6\text{H}_5\text{COONa}$  in  $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$ , the order of reactivities of  $\text{XC}_6\text{H}_4\text{COCl}$  toward reaction with PNO in  $\text{CH}_2\text{Cl}_2$  is (2,3-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>COCl, 2, 4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>COCl) > (2-IC<sub>6</sub>H<sub>4</sub>COCl, 2-FC<sub>6</sub>H<sub>4</sub>COCl, 2-ClC<sub>6</sub>H<sub>4</sub>COCl, 3,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>COCl) > (3,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>COCl, 2-BrC<sub>6</sub>H<sub>4</sub>COCl) > (4-IC<sub>6</sub>H<sub>4</sub>COCl, 3-FC<sub>6</sub>H<sub>4</sub>COCl, 3-BrC<sub>6</sub>H<sub>4</sub>COCl, 3-ClC<sub>6</sub>H<sub>4</sub>COCl) > (4-BrC<sub>6</sub>H<sub>4</sub>COCl, 4-ClC<sub>6</sub>H<sub>4</sub>COCl) > 4-FC<sub>6</sub>H<sub>4</sub>COCl >  $\text{C}_6\text{H}_5\text{COCl}$  > (3-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>COCl, 4-(CH<sub>3</sub>)<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>COCl) > 4-CH<sub>3</sub>-OC<sub>6</sub>H<sub>4</sub>COCl  $\gg$  2,6-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>COCl. In contrast, in the PNO-catalyzed reactions of  $\text{XC}_6\text{H}_4\text{COCl}$  and  $\text{XC}_6\text{H}_4\text{COONa}$  in  $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$ , it is 3,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>COCl > 2-IC<sub>6</sub>H<sub>4</sub>COCl > (2,3-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>COCl, 3,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>COCl) > 2,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>COCl > 2-FC<sub>6</sub>H<sub>4</sub>COCl > (2-BrC<sub>6</sub>H<sub>4</sub>COCl, 2-ClC<sub>6</sub>H<sub>4</sub>COCl) > (3-FC<sub>6</sub>H<sub>4</sub>COCl, 3-BrC<sub>6</sub>H<sub>4</sub>COCl, 3-ClC<sub>6</sub>H<sub>4</sub>COCl) > 4-BrC<sub>6</sub>H<sub>4</sub>COCl > 4-ClC<sub>6</sub>H<sub>4</sub>COCl > 4-FC<sub>6</sub>H<sub>4</sub>COCl > ( $\text{C}_6\text{H}_5\text{COCl}$ , 3-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>COCl) > (2-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>COCl, 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>COCl) > 4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>COCl > (2-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>COCl, 2,6-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>COCl).

As shown in Table 2, the yield of benzoic anhydride,  $\text{XC}_6\text{H}_4\text{COOCOC}_6\text{H}_4\text{Y}$ , depends on the relative rates of PNO-catalyzed and uncatalyzed paths (i.e.  $k_{\text{c}}[\text{PNO}]_{\text{iaq}}$  versus  $k_{\text{h}}$ ). For example, the yields (%) of benzoic anhydrides are 55.1 ( $[\text{PNO}]_{\text{iaq}} = 2.00 \times 10^{-4}$  M) and 81.2 ( $8.00 \times 10^{-4}$  M) for

Table 3

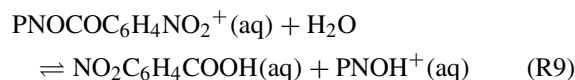
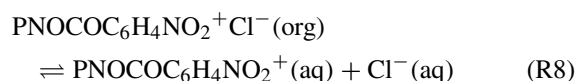
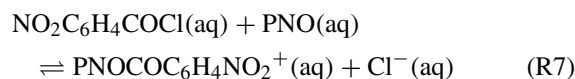
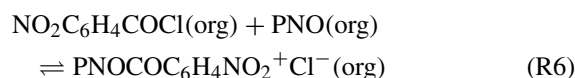
The catalyzed rate constant ( $k_c$ ) for the PNO-catalyzed reaction of benzoyl chloride ( $\text{XC}_6\text{H}_4\text{COCl}$ ) and benzoate ion ( $\text{YC}_6\text{H}_4\text{COONa}$ ) in  $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$  medium. a: this work

X	Y	$k_c$ ( $\text{M}^{-1} \text{s}^{-1}$ )	$T$ ( $^\circ\text{C}$ )	Reference
H	H	3.60	22	[17]
2-CH <sub>3</sub>	2-CH <sub>3</sub>	1.49	10	a
3-CH <sub>3</sub>	3-CH <sub>3</sub>	2.53	20	a
4-CH <sub>3</sub>	4-CH <sub>3</sub>	1.53	20	a
4-(CH <sub>3</sub> ) <sub>3</sub>	H	1.87	20	[27]
3-CH <sub>3</sub> O	3-CH <sub>3</sub> O	3.40	20	a
3-CH <sub>3</sub> O	H	1.83	20	a
4-CH <sub>3</sub> O	4-CH <sub>3</sub> O	0.712	20	a
4-CH <sub>3</sub> O	H	0.640	20	a
2-F	2-F	9.10	20	[27]
2-F	H	10.4	20	[27]
3-F	3-F	6.10	20	[27]
3-F	H	6.80	20	[27]
4-F	4-F	3.40	20	[27]
4-F	H	3.93	20	[27]
2-Cl	2-Cl	8.10	22	[22]
2-Cl	H	10.1	22	[22]
3-Cl	3-Cl	6.43	22	[22]
3-Cl	H	6.37	22	[22]
4-Cl	4-Cl	5.37	22	[22]
4-Cl	H	5.43	22	[22]
2-Br	2-Br	7.10	15	[23]
2-Br	H	7.37	15	[23]
3-Br	3-Br	6.10	15	[23]
3-Br	H	6.21	15	[23]
4-Br	4-Br	5.80	15	[23]
4-Br	H	5.61	15	[23]
2-I	2-I	17.5	20	a
2-I	H	10.9	20	a
4-I	H	6.83	20	a

(2-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CO)<sub>2</sub>O; 75.6 ( $2.00 \times 10^{-4}$  M) and >95% ( $8.00 \times 10^{-4}$  M) for (3-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CO)<sub>2</sub>O; 37.1 ( $2.00 \times 10^{-4}$  M) and 55.5 ( $8.00 \times 10^{-4}$  M) for (4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CO)<sub>2</sub>O. Due to the considerably higher rate of hydrolysis of 2-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>COCl, the yield of (2-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>CO)<sub>2</sub> is very low even at  $[\text{PNO}]_{\text{iaq}} = 1.60 \times 10^{-3}$  M. The temperature dependence of  $k_{\text{obs}}$  and the apparent activation energies ( $E_a$ ) for methyl-, methoxy-, and iodo-benzoyl chlorides are shown in Table 4.

Interesting phenomenon was observed in the system of  $\text{NO}_2\text{C}_6\text{H}_4\text{COCl}$ . In the absence of PNO, complete hydrolysis reaction was observed for 2-, 3-, and 4- $\text{NO}_2\text{C}_6\text{H}_4\text{COCl}$ , whereas it reaches an equilibrium in the presence of PNO (Fig. 2). In

contrast to the analogous reactions of benzoyl chlorides [17,22,23,27,28], PNO catalyzes considerably the hydrolysis of  $\text{NO}_2\text{C}_6\text{H}_4\text{COCl}$ . The scheme of the PNO-catalyzed hydrolysis of  $\text{NO}_2\text{C}_6\text{H}_4\text{COCl}$  in  $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$  is shown in reactions (R4)–(R9).



Reactions (R4) and (R7) are negligible due to the very low solubility of  $\text{NO}_2\text{C}_6\text{H}_4\text{COCl}$  in water. For the 4- $\text{NO}_2\text{C}_6\text{H}_4\text{COCl}$  system, the presence of 0.5 M  $\text{NaCl}(\text{aq})$  does not shift effectively the position of equilibrium (Fig. 2e), which implies that reaction (R8) is insignificant and that the distribution of  $\text{Cl}^-$  ion in the organic phase is unfavorable. However, the presence of both 0.5 M  $\text{NaCl}(\text{aq})$  and 0.01 M ( $n\text{-C}_4\text{H}_9$ )<sub>4</sub>N<sup>+</sup>(aq) shifts the equilibrium considerably to the left (Fig. 2d versus Fig. 2c), which implies that ( $n\text{-C}_4\text{H}_9$ )<sub>4</sub>N<sup>+</sup> ion promotes the distribution of  $\text{Cl}^-$  ion in the organic phase and that reaction (R6) plays an important role in this system. The values of  $k_{\text{obs}}$  for the PNO-catalyzed hydrolysis of  $\text{NO}_2\text{C}_6\text{H}_4\text{COCl}$  in  $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$  medium were estimated by using the method of initial rate. The plots of  $k_{\text{obs}}$  versus  $[\text{PNO}]_{\text{iaq}}$  are quite linear, which implies that  $k_{\text{obs}}$  can be expressed by  $k_{\text{obs}} = k_{\text{h}} + k_{\text{hc}}[\text{PNO}]_{\text{iaq}}$ , where  $k_{\text{hc}}$  is the PNO-catalyzed rate constant of hydrolysis. The values of  $k_{\text{hc}}$  at 20 $^\circ\text{C}$  are 3.3, 2.4, and  $3.4 \text{ M}^{-1} \text{ s}^{-1}$  for 2-, 3-, and 4- $\text{NO}_2\text{C}_6\text{H}_4\text{COCl}$ , respectively. The PNO-catalyzed reactions of 2-, 3-, and 4- $\text{NO}_2\text{C}_6\text{H}_4\text{COCl}$  and  $\text{C}_6\text{H}_5\text{COONa}$  to

Table 4

Effects of temperature on the observed rate constants ( $k_{\text{obs}}$ ) of the PNO-catalyzed reactions of  $\text{XC}_6\text{H}_4\text{COCl}$  and  $\text{XC}_6\text{H}_4\text{COONa}$  in 50 ml  $\text{H}_2\text{O}/50\text{ ml CH}_2\text{Cl}_2$  medium<sup>a</sup>

	$k_{\text{obs}}$ ( $10^{-4} \text{ s}^{-1}$ )						$E_a$ ( $\text{kJ mol}^{-1}$ )	
	10°C	13°C	15°C	17°C	20°C	25°C		30°C
(a) 3- $\text{CH}_3\text{C}_6\text{H}_4\text{COCl}$	7.08		9.17		11.7	14.1	18.7	$34.6 \pm 1.5$
(b) 4- $\text{CH}_3\text{C}_6\text{H}_4\text{COCl}$	4.52		5.72		7.60	9.83	14.9	$41.7 \pm 3.0$
(c) 3- $\text{CH}_3\text{OC}_6\text{H}_4\text{COCl}$	5.05		6.23		8.52	10.5	12.6	$33.4 \pm 1.6$
(d) 4- $\text{CH}_3\text{OC}_6\text{H}_4\text{COCl}$	7.27		8.35		14.1	16.8	24.0	$44.1 \pm 4.5$
(e) 2- $\text{IC}_6\text{H}_4\text{COCl}$	21.3	25.5		30.5	32.0			$28.3 \pm 4.1$
(f) 4- $\text{IC}_6\text{H}_4\text{COCl}$	11.9	13.1	15.3	17.0	21.0			$38.6 \pm 2.9$

<sup>a</sup>  $[\text{XC}_6\text{H}_4\text{COCl}]_{\text{org}} = 0.0100 \text{ M}$ ;  $\text{pH} = 7.5$ ;  $[\text{XC}_6\text{H}_4\text{COONa}]_{\text{iaq}} = 0.500 \text{ M}$  (a–e);  $[\text{C}_6\text{H}_5\text{COONa}]_{\text{iaq}} = 0.500 \text{ M}$  (f);  $[\text{PNO}]_{\text{iaq}} = 4.00 \times 10^{-4} \text{ M}$  (a, b, d);  $2.00 \times 10^{-4} \text{ M}$  (c, e);  $3.00 \times 10^{-4} \text{ M}$  (f).

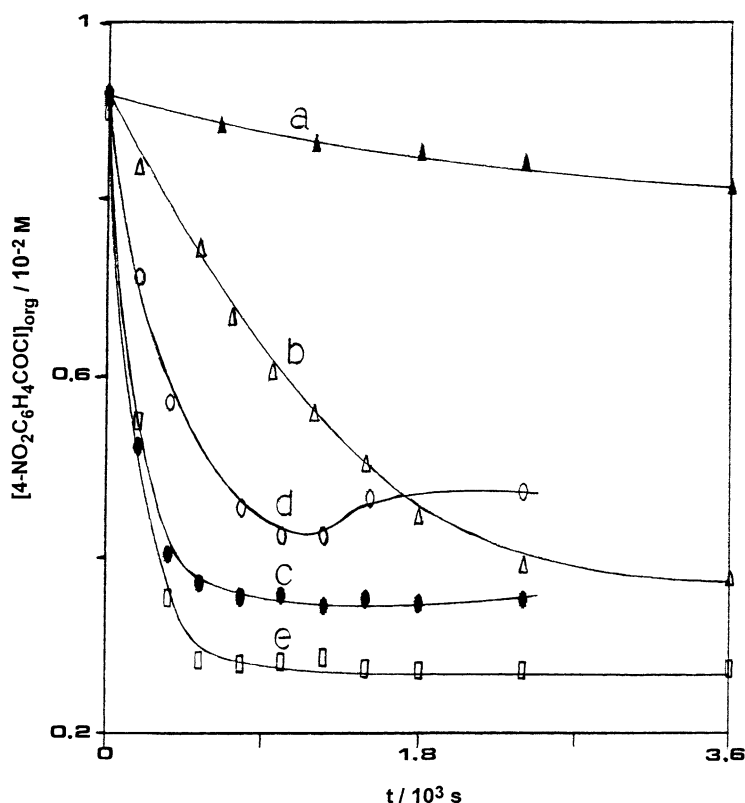


Fig. 2. Plots of  $[\text{4-NO}_2\text{C}_6\text{H}_4\text{COCl}]_{\text{org}}$  vs. time for the uncatalyzed and PNO-catalyzed hydrolysis reaction of  $\text{4-NO}_2\text{C}_6\text{H}_4\text{COCl}$  in 50 ml  $\text{H}_2\text{O}/50\text{ ml CH}_2\text{Cl}_2$  medium at  $20^\circ\text{C}$  and  $\text{pH} = 7.5$ .  $[\text{4-NO}_2\text{C}_6\text{H}_4\text{COCl}]_{\text{org}} = 0.0100 \text{ M}$ ;  $[\text{PNO}]_{\text{iaq}} = 0 \text{ M}$  (a);  $1.00 \times 10^{-4} \text{ M}$  (b);  $8.00 \times 10^{-4} \text{ M}$  (c, d);  $1.60 \times 10^{-3} \text{ M}$  (e);  $[\text{NaNO}_3]_{\text{iaq}} = 0.500 \text{ M}$  (a, b, c);  $0 \text{ M}$  (d, e);  $[\text{NaCl}]_{\text{iaq}} = 0 \text{ M}$  (a, b, c);  $0.500 \text{ M}$  (d, e);  $[(n\text{-C}_4\text{H}_9)_4\text{NOH}]_{\text{iaq}} = 0 \text{ M}$  (a, b, c, e);  $0.0100 \text{ M}$  (d).

synthesize  $\text{NO}_2\text{C}_6\text{H}_4\text{COOCOC}_6\text{H}_5$  were unsuccessful. For  $[\text{4-NO}_2\text{C}_6\text{H}_4\text{COCl}]_{\text{org}} = 0.0100 \text{ M}$ ,  $[\text{4-NO}_2\text{C}_6\text{H}_4\text{COONa}]_{\text{aq}} = 0.500 \text{ M}$ , and  $[\text{PNO}]_{\text{aq}} = 4.00 \times 10^{-4} \text{ M}$  in  $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$  medium, the reaction reaches an equilibrium rapidly with the yield of  $(\text{4-NO}_2\text{C}_6\text{H}_4\text{CO})_2\text{O}$  being about 40%.

### 3.3. Hammett correlations

In the PNO-catalyzed reaction of  $\text{XC}_6\text{H}_4\text{COCl}$  and  $\text{YC}_6\text{H}_4\text{COONa}$  in  $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$  medium, it is generally observed that the reaction of  $\text{XC}_6\text{H}_4\text{COCl}$  and PNO in the organic phase is the rate-determining step (reaction (R1)). It is reasonable to correlate the

catalyzed rate constant ( $k_c$ ) with the effect of the substituent (X) of  $\text{XC}_6\text{H}_4\text{COCl}$ . It is observed that this reaction is accelerated by the electron-withdrawing substituent and retarded by the electron-donating substituent (Table 3). As shown in Fig. 3, good Hammett correlations were obtained for the *meta*- and *para*-substituents [29–31] in the plot of  $\log(k_c/k_{\text{CH}})$  versus  $\sigma$ , where  $\sigma$  is the substituent constant and  $k_{\text{CH}}$  is the catalyzed rate constant of the parent compound ( $\text{C}_6\text{H}_5\text{COCl}$ ). The reaction constant ( $\rho$ ) of the Hammett equation [ $\log(k_c/k_{\text{CH}}) = \sigma\rho$ ] obtained for this reaction series is +1.3, which implies that this reaction is a nucleophilic substitution reaction and is expected to be accelerated by the

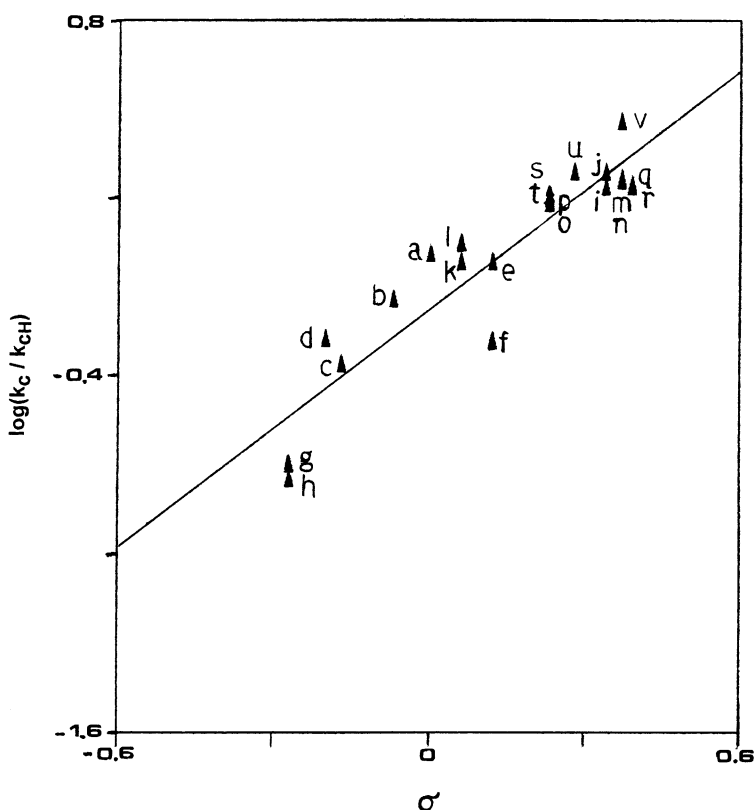


Fig. 3. Plots of  $\log(k_c/k_{\text{CH}})$  vs.  $\sigma$  (Hammett plot) for the PNO-catalyzed substitution reactions of benzoyl chlorides and benzoate ions in  $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$  medium to synthesize symmetric and mixed benzoic anhydrides: (a)  $\text{C}_6\text{H}_5\text{COCl}$  (sba); (b) 3- $\text{CH}_3\text{C}_6\text{H}_4\text{COCl}$  (sba); (c) 4- $\text{CH}_3\text{C}_6\text{H}_4\text{COCl}$  (sba); (d) 4-( $\text{CH}_3$ ) $_3\text{C}_6\text{H}_4\text{COCl}$  (mba); (e) 3- $\text{CH}_3\text{OC}_6\text{H}_4\text{COCl}$  (sba); (f) 3- $\text{CH}_3\text{OC}_6\text{H}_4\text{COCl}$  (mba); (g) 4- $\text{CH}_3\text{OC}_6\text{H}_4\text{COCl}$  (sba); (h) 4- $\text{CH}_3\text{OC}_6\text{H}_4\text{COCl}$  (mba); (i) 3- $\text{FC}_6\text{H}_4\text{COCl}$  (sba); (j) 3- $\text{FC}_6\text{H}_4\text{COCl}$  (mba); (k) 4- $\text{FC}_6\text{H}_4\text{COCl}$  (sba); (l) 4- $\text{FC}_6\text{H}_4\text{COCl}$  (mba); (m) 3- $\text{ClC}_6\text{H}_4\text{COCl}$  (sba); (n) 3- $\text{ClC}_6\text{H}_4\text{COCl}$  (mba); (o) 4- $\text{ClC}_6\text{H}_4\text{COCl}$  (sba); (p) 4- $\text{ClC}_6\text{H}_4\text{COCl}$  (mba); (q) 3- $\text{BrC}_6\text{H}_4\text{COCl}$  (sba); (r) 3- $\text{BrC}_6\text{H}_4\text{COCl}$  (mba); (s) 4- $\text{BrC}_6\text{H}_4\text{COCl}$  (sba); (t) 4- $\text{BrC}_6\text{H}_4\text{COCl}$  (mba); (u) 4- $\text{IC}_6\text{H}_4\text{COCl}$  (mba); (v) 3,5- $\text{Cl}_2\text{C}_6\text{H}_3\text{COCl}$  (mba). (sba): symmetric benzoic anhydride; (mba): mixed benzoic anhydride.



electron-withdrawing substituent, as observed in this study. It is well known that the application of the Hammett equation to the *ortho*-substituent is usually poor mainly due to the steric effect. As shown in Table 3, besides the inductive and resonance effects, the electron-withdrawing *ortho*-substituent (F, Cl, Br, or I) also facilitates the reaction considerably by stabilizing the transition state via complexing with the positively charged nitrogen-atom of the pyridinium moiety. In contrast, besides the inductive effect, the electron-donating *ortho*-substituent (CH<sub>3</sub> or CH<sub>3</sub>O) also retards the reaction via the steric effect.

#### 4. Conclusions

The reactions of XC<sub>6</sub>H<sub>4</sub>COCl [X = 2-, 3-, or 4-CH<sub>3</sub>; 2-, 3-, or 4-CH<sub>3</sub>O; 2-, or 4-I; or 2-, 3-, or 4-NO<sub>2</sub>] and YC<sub>6</sub>H<sub>4</sub>COONa [Y = 2-, 3-, or 4-CH<sub>3</sub>; 2-, 3-, or 4-CH<sub>3</sub>O; 2-I; 4-NO<sub>2</sub>; or H] in a two-phase H<sub>2</sub>O/H<sub>2</sub>Cl<sub>2</sub> medium with PNO as an inverse phase transfer catalyst were investigated. The main conclusions are as follows:

1. In general, the kinetics of the reaction follows a pseudo-first-order rate law with the observed rate constant being a linear function of the initial concentration of PNO in the water phase.
2. The reaction of XC<sub>6</sub>H<sub>4</sub>COCl with PNO in the organic phase to produce the intermediate, XC<sub>6</sub>H<sub>4</sub>COONP<sup>+</sup> ion, is the rate-determining step.
3. The order of reactivities of XC<sub>6</sub>H<sub>4</sub>COCl toward reaction with PNO in CH<sub>2</sub>Cl<sub>2</sub> is 2-IC<sub>6</sub>H<sub>4</sub>COCl > 4-IC<sub>6</sub>H<sub>4</sub>COCl > 3-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>COCl > 3-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>COCl > (2-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>COCl, 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>COCl, 4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>COCl) > 2-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>COCl.
4. In contrast to the other analogous reactions, the hydrolysis reaction of 2-, 3-, or 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>COCl in H<sub>2</sub>O/H<sub>2</sub>Cl<sub>2</sub> medium is catalyzed considerably by PNO and reaches an equilibrium.
5. Good Hammett correlations with positive reaction constant are obtained for *meta*- and *para*-substituents by combining the present results with those of other analogous reactions.

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