

# Inverse phase transfer catalysis: kinetics of the pyridine 1-oxide-catalyzed two-phase reactions of fluoro- and butyl-benzoyl chlorides and benzoate ions

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## Abstract

The substitution reactions of  $\text{XC}_6\text{H}_4\text{COCl}$  ( $\text{X} = 2\text{-F}, 3\text{-F}, 4\text{-F},$  or  $4\text{-(CH}_3)_3\text{C}$ ) and  $\text{YC}_6\text{H}_4\text{COONa}$  ( $\text{Y} = 2\text{-F}, 3\text{-F}, 4\text{-F},$  or  $\text{H}$ ) 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. Under suitable reaction conditions, the kinetics of the reaction follows a pseudo-first-order rate law, with a constant observed rate being a linear function of the concentration of PNO in the water phase. The order of reactivities of  $\text{XC}_6\text{H}_4\text{COCl}$  toward reaction with PNO is  $2\text{-FC}_6\text{H}_4\text{COCl} > 3\text{-FC}_6\text{H}_4\text{COCl} > 4\text{-FC}_6\text{H}_4\text{COCl} > \text{C}_6\text{H}_5\text{COCl} > 4\text{-(CH}_3)_3\text{CC}_6\text{H}_4\text{COCl}$ . The order of reactivities of  $\text{YC}_6\text{H}_4\text{COO}^-$  ions toward reaction with 1-(benzoyloxy)pyridinium ( $\text{C}_6\text{H}_5\text{COONP}^+$ ) ion is  $\text{C}_6\text{H}_5\text{COO}^- > 3\text{-FC}_6\text{H}_4\text{COO}^- > 4\text{-FC}_6\text{H}_4\text{COO}^- > 2\text{-FC}_6\text{H}_4\text{COO}^-$ . For the water phase with  $\text{pH} > 12$ , the reaction is complicated by the competitive reaction of  $\text{XC}_6\text{H}_4\text{COCl}$  and  $\text{OH}^-$  ion in the organic phase. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Phase transfer; Pyridine 1-oxide; Fluorobenzoyl chloride; Butylbenzoyl chloride; Benzoate ion

## 1. Introduction

Phase transfer catalysis (PTC) has been widely used to promote a variety of interfacial reactions, making the numerous organic synthetic reactions feasible and utilizing two-phase water-organic solvent media. Extensive PTC reactions have been studied focusing on the normal phase transfer catalysis (NPTC), which involves transport of anionic reactant with a cationic phase transfer catalyst from the water

phase into the organic phase for reaction with a second reactant [1–7]. A complementary methodology named by Mathias and Vaidya [8] as inverse phase transfer catalysis (IPTC) 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 [9,10] provides one of the most attractive methods for synthesizing acid anhydrides [9–16], which being less reactive than acylchlorides, are very important intermediates for the synthesis of esters, amides, and peptides. Jwo et al. [17–23] have studied the kinetics and mechanism of the two-phase substitution reactions of benzoyl

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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 2-, 3-, or 4-fluorobenzoyl chloride or 4-*tert*-butyl-benzoyl chloride with benzoate ions in a two-phase medium were studied. The effects of the substituent, the catalyst, the organic solvent, the pH value, the temperature, and the agitation rate were investigated. Both symmetric and mixed benzoic anhydrides were synthesized. The experimental results are rationalized.

## 2. Experimental

### 2.1. Materials

PNO (Aldrich); biphenyl (Ferak); 2-benzyl-oxybenzaldehyde, 2-,3-, and 4-fluoro-benzoyl chlorides, 2-, 3-, and 4-fluoro-benzoic acids, 4-*tert*-butyl-benzoyl chloride, and *tert*-butyl-benzoic acid (Lancaster); and tetra-*n*-butyl-ammonium hydroxide (Merck) were used. De-ionized water was obtained from reverse osmosis (Millipore Milli-RO 20). Due to the hygroscopic property of PNO, (PNO)H<sup>+</sup>Cl<sup>-</sup> crystals (mp 179–181°C) 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<sub>2</sub>Cl<sub>2</sub> solution of XC<sub>6</sub>H<sub>4</sub>COCl [X = F or C(CH<sub>3</sub>)<sub>3</sub>] (0.2 M) was mixed with a 50 ml aqueous solution containing the desired benzoate salt YC<sub>6</sub>H<sub>4</sub>COONa [Y = H, F, or C(CH<sub>3</sub>)<sub>3</sub>] (0.5M) and PNO (0.02 M) in a 250 ml three-necked Pyrex flask. After the reaction was complete, the CH<sub>2</sub>Cl<sub>2</sub> layer was separated and washed with NaOH solution (0.02 M) to remove benzoic acids. It was then washed twice with de-ionized water and dried with anhydrous MgSO<sub>4</sub>. The symmetric benzoic anhydrides were obtained after concentrating the CH<sub>2</sub>Cl<sub>2</sub> 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 [10]. The HPLC analysis of the anhydride product showed only one peak. Anal. Calcd. for C<sub>14</sub>H<sub>8</sub>F<sub>2</sub>O<sub>3</sub>: C, 64.12; H, 3.05. Found: C, 64.10; H, 3.07 [(2-FC<sub>6</sub>H<sub>4</sub>CO)<sub>2</sub>O]; C, 64.12; H, 3.13 [(3-FC<sub>6</sub>H<sub>4</sub>CO)<sub>2</sub>O]; C, 64.08; H, 3.07 [(4-FC<sub>6</sub>H<sub>4</sub>CO)<sub>2</sub>O]. Calcd. for C<sub>14</sub>H<sub>9</sub>FO<sub>3</sub>: C, 68.85; H, 3.69. Found: C, 68.77; H, 3.74 (3-FC<sub>6</sub>H<sub>4</sub>COOCOC<sub>6</sub>H<sub>5</sub>); C, 68.86; H, 3.72 (4-FC<sub>6</sub>H<sub>4</sub>COOCOC<sub>6</sub>H<sub>5</sub>). Calcd. for C<sub>22</sub>H<sub>26</sub>O<sub>3</sub>: C, 78.11; H, 7.69. Found: C, 78.34, H, 7.77 [(C<sub>4</sub>H<sub>9</sub>C<sub>6</sub>H<sub>4</sub>CO)<sub>2</sub>O].

#### 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 ±0.2°C) for at least 30 min. The kinetic run was started by adding 50 ml of aqueous solution [containing a known amount of YC<sub>6</sub>H<sub>4</sub>COONa and (PNO)H<sup>+</sup>Cl<sup>-</sup>] to 50 ml of organic solution (containing known amounts of XC<sub>6</sub>H<sub>4</sub>COCl and internal standard) under constant agitation. During the reaction, an aliquote (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<sub>2</sub>O 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. The following are HPLC analysis conditions and data.

(A) Column, Lichrospher 100 RP-18 (5 μm); wavelength, 254 nm: (i) eluent, CH<sub>3</sub>CN/H<sub>2</sub>O = 55:45 by volume; flow rate, 1.5 ml/min; elution time (min): 2-FC<sub>6</sub>H<sub>4</sub>COCl (6.13), C<sub>6</sub>H<sub>5</sub>COCl (7.04), 4-FC<sub>6</sub>H<sub>4</sub>COCl (7.21), 3-FC<sub>6</sub>H<sub>4</sub>COCl (7.61), (2-FC<sub>6</sub>H<sub>4</sub>CO)<sub>2</sub>O (8.00), 2-FC<sub>6</sub>H<sub>4</sub>COOCOC<sub>6</sub>H<sub>5</sub> (8.82), 4-FC<sub>6</sub>H<sub>4</sub>COOCOC<sub>6</sub>H<sub>5</sub> (9.82), 3-FC<sub>6</sub>H<sub>4</sub>COOCOC<sub>6</sub>H<sub>5</sub>

(10.23), (4-FC<sub>6</sub>H<sub>4</sub>CO)<sub>2</sub>O (10.63), (3-FC<sub>6</sub>H<sub>4</sub>-CO)<sub>2</sub>O (11.70), and C<sub>12</sub>H<sub>10</sub> (14.80); (ii) eluent, CH<sub>3</sub>CN/H<sub>2</sub>O = 52:48; flow rate, 1.5 ml/min; elution time (min): C<sub>6</sub>H<sub>5</sub>COCl (7.63), (C<sub>6</sub>H<sub>5</sub>CO)<sub>2</sub>O (10.01), 3-FC<sub>6</sub>H<sub>4</sub>COOCOC<sub>6</sub>H<sub>5</sub> (11.30), and C<sub>12</sub>H<sub>10</sub> (16.18); (iii) eluent, CH<sub>3</sub>CN/H<sub>2</sub>O = 50:50; flow rate, 1.5 ml/min; elution time (min): C<sub>6</sub>H<sub>5</sub>COCl (9.56), (C<sub>6</sub>H<sub>5</sub>CO)<sub>2</sub>O (13.46), 2-FC<sub>6</sub>H<sub>4</sub>COOCOC<sub>6</sub>H<sub>5</sub> (12.65), 4-FC<sub>6</sub>H<sub>4</sub>COOCOC<sub>6</sub>H<sub>5</sub> (14.76), and C<sub>12</sub>H<sub>10</sub> (21.88).

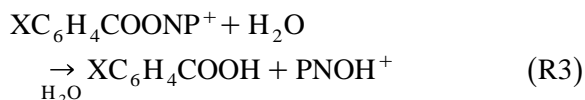
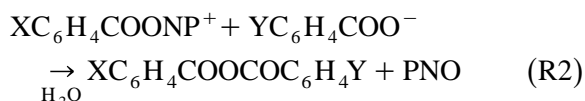
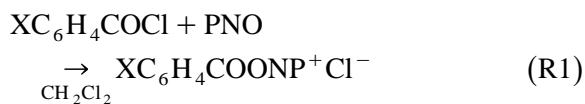
(B) Column, Lichrospher Si 60 (5 μm); wavelength, 254 nm; eluent, *n*-hexane; flow rate, 1.0 ml/min; elution time (min): 4-(CH<sub>3</sub>)<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>COCl (2.74), 4-(CH<sub>3</sub>)<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>-COOC<sub>6</sub>H<sub>5</sub> (5.10), and 2-(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>O)C<sub>6</sub>H<sub>4</sub>-CHO (6.50).

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) 2.821 (2-FC<sub>6</sub>H<sub>4</sub>COCl), 2.382 (3-FC<sub>6</sub>H<sub>4</sub>COCl), 1.725 (4-FC<sub>6</sub>H<sub>4</sub>COCl), 1.677 [(2-FC<sub>6</sub>H<sub>4</sub>CO)<sub>2</sub>O], 1.619 [(3-FC<sub>6</sub>H<sub>4</sub>CO)<sub>2</sub>O], 1.065 [(C<sub>6</sub>H<sub>5</sub>CO)<sub>2</sub>O], 1.456 (2-FC<sub>6</sub>H<sub>4</sub>COOCOC<sub>6</sub>H<sub>5</sub>), 1.260 (3-FC<sub>6</sub>H<sub>4</sub>COOCOC<sub>6</sub>H<sub>5</sub>), and 0.968 (4-FC<sub>6</sub>H<sub>4</sub>COOCOC<sub>6</sub>H<sub>5</sub>) (vs. *is* = C<sub>12</sub>H<sub>10</sub>); (ii) 0.429 [4-(CH<sub>3</sub>)<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>COCl] and 0.501 [4-(CH<sub>3</sub>)<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>COOCOC<sub>6</sub>H<sub>5</sub>] [vs. *is* = 2-(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>O)C<sub>6</sub>H<sub>4</sub>CHO]. The pseudo-first-order rate constant (*k*<sub>obs</sub>) was determined by the linear-least-square (LLS) fit of the plot of ln[XC<sub>6</sub>H<sub>4</sub>COCl] vs. time.

### 3. Results and discussion

Preliminary study of the PNO-catalyzed reaction of XC<sub>6</sub>H<sub>4</sub>COCl [X = F or C(CH<sub>3</sub>)<sub>3</sub>] and C<sub>6</sub>H<sub>5</sub>COONa in H<sub>2</sub>O/CH<sub>2</sub>Cl<sub>2</sub> medium showed that the rate of reaction depended on the amounts of reactants and catalyst, the organic solvent, the agitation rate, the pH value, and the temperature. The reaction scheme can be sim-

plified 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). All three reactions are essentially irreversible. In general, reaction R1 is considerably slower than both reactions R2 and R3 and is the rate-determining step. 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).

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

#### 3.1. Effect of agitation

The rate of reaction increases asymptotically with increased rate of agitation to a limited value. For [2-FC<sub>6</sub>H<sub>4</sub>COCl]<sub>iorg</sub> = 0.0100 M, [C<sub>6</sub>H<sub>5</sub>COONa]<sub>iaq</sub> = 0.500 M, [PNO]<sub>iaq</sub> = 4.00 × 10<sup>-4</sup> M in 50 ml H<sub>2</sub>O/50 ml CH<sub>2</sub>Cl<sub>2</sub>, the values of *k*<sub>obs</sub> at 20°C were (2.07, 2.50, 2.85, 3.42, 3.75, and 3.80) × 10<sup>-3</sup> s<sup>-1</sup> at the agitation rate of 700, 900, 1000, 1100, 1200 and 1300 rpm, respectively. For [4-(CH<sub>3</sub>)<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>-COCl]<sub>iorg</sub> = 0.0100 M, [C<sub>6</sub>H<sub>5</sub>COONa]<sub>iaq</sub> = 0.500 M, [PNO]<sub>iaq</sub> = 6.00 × 10<sup>-4</sup> M in 50 ml H<sub>2</sub>O/50 ml CH<sub>2</sub>Cl<sub>2</sub>, the values of *k*<sub>obs</sub> at 20°C were (0.207, 0.715, 1.00, 1.02, 1.07, 1.11, 1.10,

and  $1.09) \times 10^{-3} \text{ s}^{-1}$  at 300, 400, 500, 600, 700, 900, 1000 and 1200 rpm, respectively. When the agitation rate was 1200 rpm or higher, it appeared that the two phases exhibited uniform mixing. Therefore, most experiments were run at 1200 rpm.

### 3.2. Solvent effect

Dichloromethane, benzene, and *n*-hexane were chosen for studying the effect of organic solvent. For  $[2\text{-FC}_6\text{H}_4\text{COCl}]_{\text{iorg}} = 0.0100 \text{ M}$ ,  $[\text{C}_6\text{H}_5\text{COONa}]_{\text{iaq}} = 0.500 \text{ M}$ , and  $[\text{PNO}]_{\text{iaq}} = 3.00 \times 10^{-4} \text{ M}$  at  $20^\circ\text{C}$ , the values of  $k_{\text{obs}}$ , yield were  $2.83 \times 10^{-3} \text{ s}^{-1}$ , 96%;  $1.34 \times 10^{-3} \text{ s}^{-1}$ , 64%; and  $2.18 \times 10^{-3} \text{ s}^{-1}$ , 56% in  $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$ , *n*- $\text{C}_6\text{H}_{14}/\text{H}_2\text{O}$ , and  $\text{C}_6\text{H}_6/\text{H}_2\text{O}$  media, respectively. For  $[4\text{-(CH}_3)_3\text{CC}_6\text{H}_4\text{COCl}]_{\text{iorg}} = 0.0100 \text{ M}$ ,  $[\text{C}_6\text{H}_5\text{COONa}]_{\text{iaq}} = 0.500 \text{ M}$ , and  $[\text{PNO}]_{\text{iaq}} = 3.00 \times 10^{-4} \text{ M}$  at  $20^\circ\text{C}$ , the values of  $k_{\text{obs}}$ , yield were  $5.65 \times 10^{-4} \text{ s}^{-1}$ , 98% and  $5.77 \times 10^{-5} \text{ s}^{-1}$ , 19% in  $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$  and *n*- $\text{C}_6\text{H}_{14}/\text{H}_2\text{O}$  media, respectively. The low yield of acid anhydride in  $\text{C}_6\text{H}_6/\text{H}_2\text{O}$  or *n*- $\text{C}_6\text{H}_{14}/\text{H}_2\text{O}$  medium was due to the low distribution of PNO in *n*- $\text{C}_6\text{H}_{14}$  or  $\text{C}_6\text{H}_6$  phase, which led to produce higher yield of the hydrolysis product. For example, for

$[2\text{-FC}_6\text{H}_4\text{COCl}]_{\text{iorg}} = 0.0100 \text{ M}$ ,  $[\text{C}_6\text{H}_5\text{COONa}]_{\text{iaq}} = 0.500 \text{ M}$ , and  $[\text{PNO}]_{\text{iaq}} = 0 \text{ M}$  at  $20^\circ\text{C}$ , the values of  $k_{\text{obs}}$  or  $k_{\text{h}}$  of hydrolysis reaction were  $5.58 \times 10^{-5}$  and  $1.12 \times 10^{-3} \text{ s}^{-1}$  in  $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$  and *n*- $\text{C}_6\text{H}_{14}/\text{H}_2\text{O}$  media, respectively. Therefore, most experiments were run in  $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$  medium.

### 3.3. Uncatalyzed reaction

In the absence of PNO catalyst,  $\text{XC}_6\text{H}_4\text{COCl}$  reacted with  $\text{YC}_6\text{H}_4\text{COONa}$  in a two-phase medium to produce mainly the hydrolysis product,  $\text{XC}_6\text{H}_4\text{COOH}$  (reaction R3). The observed rate constant  $k_{\text{obs}}$  or  $k_{\text{h}}$  depended on the ionic strength ( $\mu$ ) and the salt in the water phase. For example, for  $[2\text{-FC}_6\text{H}_4\text{COCl}]_{\text{iorg}} = 0.0100 \text{ M}$  in  $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$ , the values of  $k_{\text{h}}$  at  $20^\circ\text{C}$  were  $(3.20, 3.28, \text{ and } 5.58) \times 10^{-5} \text{ s}^{-1}$  with  $\mu = 0 \text{ M}$ ,  $0.5 \text{ M}$  (adjusted with  $\text{NaNO}_3$ ), and  $0.5 \text{ M}$  (adjusted with  $\text{C}_6\text{H}_5\text{COONa}$ ), respectively. In most experiments, the ionic strength in the water phase was kept constant at  $0.5 \text{ M}$  (adjusted with  $\text{YC}_6\text{H}_4\text{COONa}$ ). Under similar conditions, the relative rate of hydrolysis was  $4\text{-FC}_6\text{H}_4\text{COCl} > (2\text{-FC}_6\text{H}_4\text{COCl}, 3\text{-FC}_6\text{H}_4\text{COCl}) \gg 4\text{-(CH}_3)_3\text{CC}_6\text{H}_4\text{COCl}$ . The temperature dependence of  $k_{\text{h}}$  and the apparent activation energies

Table 1

Effects of temperature on the observed rate constants of the uncatalyzed and PNO-catalyzed reactions of  $\text{XC}_6\text{H}_4\text{COCl}$  and  $\text{C}_6\text{H}_5\text{COONa}$  in 50 ml  $\text{H}_2\text{O}/50 \text{ ml } \text{CH}_2\text{Cl}_2$  medium

$[\text{XC}_6\text{H}_4\text{COCl}]_{\text{iorg}} = 0.0100 \text{ M}$ ;  $[\text{C}_6\text{H}_5\text{COONa}]_{\text{iaq}} = 0.500 \text{ M}$ ; pH = 7.62.

<i>T</i> ( $^\circ\text{C}$ )	$k_{\text{obs}}$ ( $10^{-4} \text{ s}^{-1}$ )					$E_{\text{a}}$ ( $\text{kJ mol}^{-1}$ )
	10	15	20	25	30	
<i>Uncatalyzed reaction</i> <sup>a</sup>						
2- $\text{FC}_6\text{H}_4\text{COCl}$	0.237	0.387	0.558	–	1.49	$65.5 \pm 2.1$
3- $\text{FC}_6\text{H}_4\text{COCl}$	0.210	0.355	0.403	–	0.887	$48.3 \pm 5.2$
4- $\text{FC}_6\text{H}_4\text{COCl}$	0.288	0.465	0.802	–	2.33	$75.6 \pm 1.8$
4-( $\text{CH}_3$ ) <sub>3</sub> $\text{CC}_6\text{H}_4\text{COCl}$	–	–	0.074	–	–	–
<i>PNO-catalyzed reaction</i> <sup>b</sup>						
2- $\text{FC}_6\text{H}_4\text{COCl}$	18.3	20.8	22.9	–	31.2	$18.9 \pm 1.3$
3- $\text{FC}_6\text{H}_4\text{COCl}$	11.7	14.4	15.8	–	18.3	$15.1 \pm 2.4$
4- $\text{FC}_6\text{H}_4\text{COCl}$	5.78	6.93	9.10	–	13.5	$30.6 \pm 1.2$
4-( $\text{CH}_3$ ) <sub>3</sub> $\text{CC}_6\text{H}_4\text{COCl}$	2.47	3.08	3.98	5.05	5.98	$32.4 \pm 1.0$

<sup>a</sup> $[\text{PNO}]_{\text{iaq}} = 0 \text{ M}$ ,

<sup>b</sup> $[\text{PNO}]_{\text{iaq}} = 2.00 \times 10^{-4} \text{ M}$ .

( $E_a$ ) obtained by the LLS fits of the Arrhenius plots of  $\ln k_h$  vs.  $1/T$  are shown in Table 1.

### 3.4. PNO-catalyzed reaction

In the presence of PNO,  $\text{XC}_6\text{H}_4\text{COCl}$  reacted quite rapidly 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 are shown in Fig. 1 and Tables 1 and 2. The temperature dependence of  $k_{\text{obs}}$  and the apparent activation energies are also shown in Table 1. The plots of  $k_{\text{obs}}$  vs.  $[\text{PNO}]_{\text{iaq}}$  is linear (Fig. 2), implying that the reaction is also first-order with respect to PNO. The value of  $k_{\text{obs}}$  at the intercept is 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

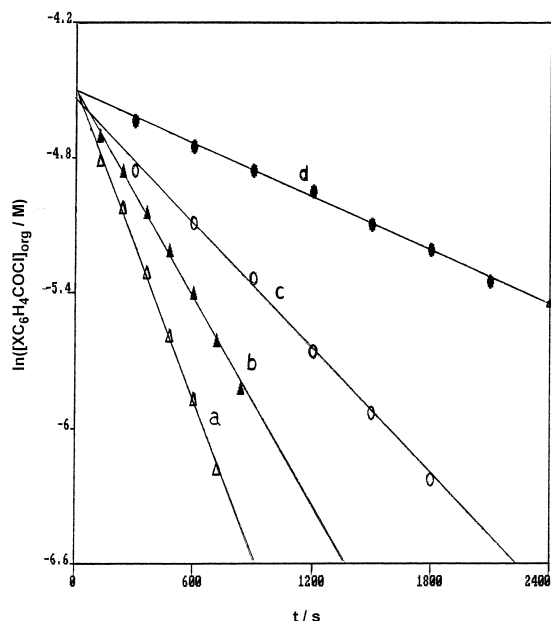


Fig. 1. Plots of  $\ln[\text{XC}_6\text{H}_4\text{COCl}]_{\text{org}}$  vs. time for the PNO-catalyzed reactions of  $\text{XC}_6\text{H}_4\text{COCl}$  and  $\text{C}_6\text{H}_5\text{COONa}$  in 50 ml  $\text{H}_2\text{O}/50$  ml  $\text{CH}_2\text{Cl}_2$  medium.  $[\text{XC}_6\text{H}_4\text{COCl}]_{\text{org}} = 0.0100$  M,  $[\text{C}_6\text{H}_5\text{COONa}]_{\text{iaq}} = 0.500$  M,  $[\text{PNO}]_{\text{iaq}} = 2.00 \times 10^{-4}$  M, pH = 7.62, 20°C. (a) 2- $\text{FC}_6\text{H}_4\text{COCl}$ ; (b) 3- $\text{FC}_6\text{H}_4\text{COCl}$ ; (c) 4- $\text{FC}_6\text{H}_4\text{COCl}$ ; (d) 4-( $\text{CH}_3$ ) $_3\text{CC}_6\text{H}_4\text{COCl}$ .

Table 2

Effects of the pH value on the observed rate constants of the PNO-catalyzed two-phase reactions of  $\text{XC}_6\text{H}_4\text{COCl}$  and  $\text{C}_6\text{H}_5\text{COONa}$

$[\text{XC}_6\text{H}_4\text{COCl}]_{\text{org}} = 0.0100$  M;  $[\text{C}_6\text{H}_5\text{COONa}]_{\text{iaq}} = 0.500$  M, 20°C, 50 ml  $\text{H}_2\text{O}/50$  ml  $\text{CH}_2\text{Cl}_2$ .

pH	$[\text{PNO}]_{\text{iaq}}$ ( $10^{-4}$ M)	$k_{\text{obs}}$ ( $10^{-4}$ s $^{-1}$ )			
		X = 2-F	X = 3-F	X = 4-F	X = 4-( $\text{CH}_3$ ) $_3\text{C}$
5.93	0.50	7.45	6.55	2.90	1.07
	1.00	14.6	10.8	5.28	1.68
	1.50	20.0	15.7	7.43	–
	2.00	25.5	20.0	9.62	3.68
	4.00	–	–	–	7.32
	6.00	–	–	–	11.2
7.62	0.50	6.77	5.73	2.83	–
	1.00	12.1	9.80	4.98	1.95
	2.00	22.9	15.8	9.10	3.80
	3.00	31.8	21.3	12.6	–
	4.00	–	–	–	7.77
	6.00	–	–	–	11.2
11.2	0.50	5.97	5.00	2.57	0.620
	1.00	10.3	7.48	4.37	1.18
	2.00	19.8	13.7	8.43	2.45
	3.00	29.7	19.7	11.9	–
	4.00	–	–	–	5.78
	6.00	–	–	–	8.92
12.5	0.50	10.9	12.0	5.98	–
	1.00	15.0	14.7	7.15	–
	1.50	18.2	18.2	8.53	–
	2.00	22.7	19.2	10.3	–

law of this PNO-catalyzed reaction can generally be expressed by Eq. 2.

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

where  $k_{\text{obs}} = k_h + k_c[\text{PNO}]_{\text{iaq}}$  and  $k_h$  and  $k_c$  are the uncatalyzed and catalyzed rate constants, respectively. The order of relative reactivity toward reaction with PNO is 2- $\text{FC}_6\text{H}_4\text{COCl} > 3\text{-FC}_6\text{H}_4\text{COCl} > 4\text{-FC}_6\text{H}_4\text{COCl} > \text{C}_6\text{H}_5\text{COCl} > 4\text{-(CH}_3\text{)}_3\text{CC}_6\text{H}_4\text{COCl}$ . The effects of the electron-withdrawing fluoro-substituent and the electron-donating *tert*-butyl-substituent on the reactivity of  $\text{XC}_6\text{H}_4\text{COCl}$  toward reaction with PNO imply that the inductive effect predomi-

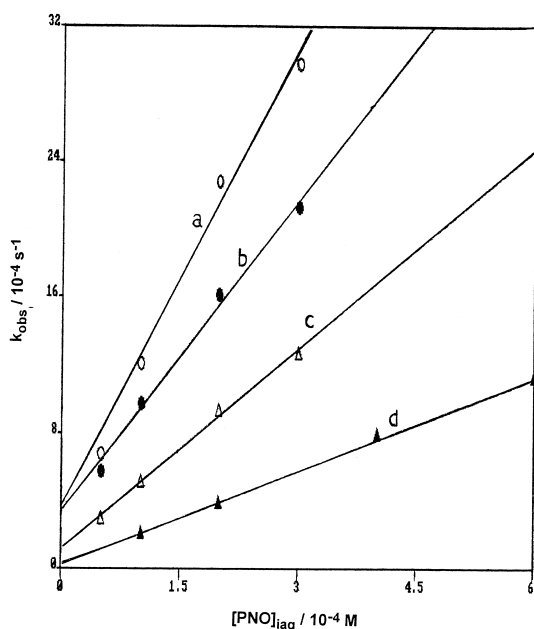


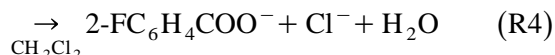
Fig. 2. Plots of  $k_{\text{obs}}$  vs.  $[\text{PNO}]_{\text{iaq}}$  for the PNO-catalyzed reactions of  $\text{XC}_6\text{H}_4\text{COCl}$  and  $\text{C}_6\text{H}_5\text{COONa}$  in 50 ml  $\text{H}_2\text{O}/50$  ml  $\text{CH}_2\text{Cl}_2$  medium.  $[\text{XC}_6\text{H}_4\text{COCl}]_{\text{org}} = 0.0100$  M,  $[\text{C}_6\text{H}_5\text{COONa}]_{\text{iaq}} = 0.500$  M,  $\text{pH} = 7.62$ ,  $20^\circ\text{C}$ . (a) 2- $\text{FC}_6\text{H}_4\text{COCl}$ ; (b) 3- $\text{FC}_6\text{H}_4\text{COCl}$ ; (c) 4- $\text{FC}_6\text{H}_4\text{COCl}$ ; (d) 4- $(\text{CH}_3)_3\text{CC}_6\text{H}_4\text{COCl}$ .

nates over the resonance effect during the formation of the activated complex.

### 3.5. pH effect

It was observed that the reaction rate depended on the pH value in the water phase. The effects of PNO on the values of  $k_{\text{obs}}$  at various pH values are shown in Table 2 and the corresponding values of  $k_c$  are given in Table 3. For  $\text{FC}_6\text{H}_4\text{COCl}$  systems, the values of  $k_c$  increase with acidity in water phase. Due to the solubility of  $\text{FC}_6\text{H}_4\text{COOH}$  in the water phase, it is not suitable to study this reaction for  $\text{pH} < 5$ . The values of  $k_c$  decreased gradually with increased pH value for  $7 < \text{pH} < 11$ . Noticeably, the value of  $k_{\text{obs}}$  increases substantially whereas the value of the corresponding  $k_c$  decreases for  $\text{pH} > 12$  (Tables 2 and 3). These results can be rationalized by invoking that the increase in basicity in

the water phase decreases the distribution of PNO in the organic phase and also accelerates the rate of hydrolysis. The effect of pH value on the rate of hydrolysis of 2- $\text{FC}_6\text{H}_4\text{COCl}$  is shown in Fig. 3. For  $\text{pH} < 11.2$ , the rate of hydrolysis is quite independent of the pH value. At  $\text{pH} = 12.2$ , 2- $\text{FC}_6\text{H}_4\text{COCl}$  undergoes a two-stage hydrolysis reaction (Fig. 3b). In the first-stage reaction, the rate of hydrolysis is considerably faster than that at  $\text{pH} = 11.2$ , whereas in the second-stage reaction, it is similar to that at  $\text{pH} = 11.2$ . For  $\text{pH} > 12.6$ , the rate of hydrolysis is about one order of magnitude faster than that at  $\text{pH} = 11.2$  (Fig. 3d). These results can be explained by considering the participation of reaction R4.



For  $\text{pH} < 12.5$ , the concentration of  $\text{OH}^-$  ion distributed in the organic phase is insufficient and not maintained at equilibrium value, whereas it appears to be maintained at a sufficient value for  $\text{pH} > 12.5$ . At  $\text{pH} = 12.2$ , the presence of tetra-*n*-butylammonium hydroxide ( $4.00 \times 10^{-3}$  M) in the water phase accelerates the rate of hydrolysis considerably (Fig. 3c vs. b). For

Table 3

Effects of the pH value on the PNO-catalyzed rate constants of the two-phase reactions of  $\text{XC}_6\text{H}_4\text{COCl}$  and  $\text{YC}_6\text{H}_4\text{COONa}$   $[\text{XC}_6\text{H}_4\text{COCl}]_{\text{org}} = 0.0100$  M;  $[\text{C}_6\text{H}_5\text{COONa}]_{\text{iaq}} = 0.500$  M.

pH	$k_c$ ( $\text{M}^{-1} \text{s}^{-1}$ )			
	X = 2-F	X = 3-F	X = 4-F	X = 4- $(\text{CH}_3)_3\text{C}$
5.93	12.4	9.10	4.47	1.87 <sup>a</sup>
7.62	10.4	6.80	3.93	1.87
	9.10 <sup>b</sup>	6.10 <sup>b</sup>	3.40 <sup>b</sup>	— <sup>c</sup>
11.2	9.77	5.93	3.77	~1.5 <sup>d</sup>
12.5	7.88	5.02	2.88	—

<sup>a</sup>pH = 5.29.

<sup>b</sup> $[\text{FC}_6\text{H}_4\text{COONa}]_{\text{iaq}} = 0.500$  M;  $[\text{C}_6\text{H}_5\text{COONa}]_{\text{iaq}} = 0$  M.

<sup>c</sup>The kinetics of the reaction could not be followed by the HPLC method because the separation of 4- $(\text{CH}_3)_3\text{CC}_6\text{H}_4\text{COCl}$  and 4- $(\text{CH}_3)_3\text{CC}_6\text{H}_4\text{CO}_2\text{O}$  was not feasible.

<sup>d</sup>Deviation from linearity was observed in the plot of  $k_{\text{obs}}$  vs.  $[\text{PNO}]_{\text{iaq}}$  for  $[\text{PNO}]_{\text{iaq}} \leq 1.00$  M.

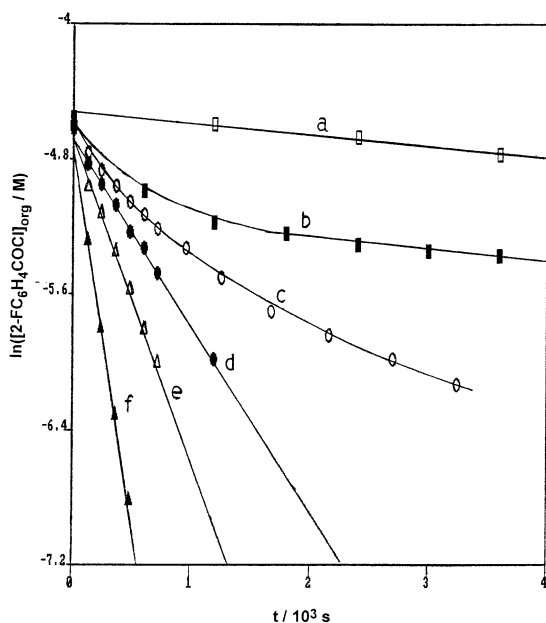


Fig. 3. Plots of  $\ln[2\text{-FC}_6\text{H}_4\text{COCl}]_{\text{org}}$  vs. time for the uncatalyzed reaction of  $2\text{-FC}_6\text{H}_4\text{COCl}$  and  $\text{C}_6\text{H}_5\text{COONa}$  in  $50\text{ ml H}_2\text{O}/50\text{ ml CH}_2\text{Cl}_2$  medium at various pH values.  $[2\text{-FC}_6\text{H}_4\text{COCl}]_{\text{org}} = 0.0100\text{ M}$ ,  $[\text{PNO}]_{\text{iaq}} = 0\text{ M}$ ,  $20^\circ\text{C}$ . pH = (a) 7.6 or 11.2, (b) 12.2, (c) 12.0, (d) 12.6, (e) 13.0, (f) 13.5;  $[\text{C}_6\text{H}_5\text{CO ONa}]_{\text{iaq}} = (\text{a-c,f}) 0.500\text{ M}$ , (d,e)  $0\text{ M}$ ;  $[\text{NaNO}_3]_{\text{iaq}} = (\text{a-c,f}) 0\text{ M}$ , (d,e)  $0.500\text{ M}$ ;  $[(n\text{-C}_4\text{H}_9)_4\text{NOH}]_{\text{iaq}} = (\text{a-b,d-f}) 0\text{ M}$ , (c)  $4.00 \times 10^{-3}\text{ M}$ .

pH = 12.2,  $[\text{NaNO}_3]_{\text{iaq}} = 0.500\text{ M}$  in  $50\text{ ml H}_2\text{O}/50\text{ ml CH}_2\text{Cl}_2$  at  $20^\circ\text{C}$ , the measured concentration of  $\text{OH}^-$  ion in the  $\text{CH}_2\text{Cl}_2$  phase was  $8.1 \times 10^{-7}$  and  $6.8 \times 10^{-5}\text{ M}$  for  $[(n\text{-C}_4\text{H}_9)_4\text{NOH}]_{\text{iaq}} = 0$  and  $4.00 \times 10^{-3}\text{ M}$ , respectively. Thus,  $(n\text{-C}_4\text{H}_9)_4\text{N}^+$  ion acts as a normal phase transfer catalyst to carry  $\text{OH}^-$  ion into the organic phase to react with  $2\text{-FC}_6\text{H}_4\text{COCl}$  (reaction R4). Furthermore, for  $[2\text{-FC}_6\text{H}_4\text{COCl}]_{\text{iaq}} = 0.0100\text{ M}$ ,  $[\text{C}_6\text{H}_5\text{COONa}]_{\text{iaq}} = 0.500\text{ M}$ , and  $[\text{PNO}]_{\text{iaq}} = 2.00 \times 10^{-4}\text{ M}$ , the yields of  $2\text{-FC}_6\text{H}_4\text{COOCOC}_6\text{H}_5$  were 98%, 98%, 97%, and 71% at pH = 5.93, 7.62, 11.2, and 12.5, respectively. In contrast, for  $4\text{-(CH}_3)_3\text{CC}_6\text{H}_4\text{COCl}$  system, the value of  $k_c$  is independent of the pH value for pH < 7.6, however deviation from linearity was observed in the plot of  $k_{\text{obs}}$  vs.  $[\text{PNO}]_{\text{iaq}}$  for pH > 11.2.

### 3.6. Reactivities of fluoro-benzoate ions

Since the rate of the ionic reaction of the intermediate  $\text{XC}_6\text{H}_4\text{COONP}^+$  ion with  $\text{YC}_6\text{H}_4\text{COO}^-$  ion (reaction R2) is much faster than that of the rate-determining reaction R1, the direct measurement of its rate is not feasible. However, the relative reactivities of  $\text{YC}_6\text{H}_4\text{COO}^-$  ions can be deduced from studying the competitive reactions of mixed  $\text{YC}_6\text{H}_4\text{COO}^-$  ions with the  $\text{XC}_6\text{H}_4\text{COONP}^+$  (e.g., X = H) ion to yield their corresponding acid anhydrides. Typical results are shown in Fig. 4, in which  $\text{C}_6\text{H}_5\text{COO}^-$  ion competes with 2-, 3-, or 4- $\text{FC}_6\text{H}_4\text{COO}^-$  ion for reaction with  $\text{C}_6\text{H}_5\text{COONP}^+$  ion to produce  $(\text{C}_6\text{H}_5\text{CO})_2\text{O}$  and 2-, 3-, or 4- $\text{FC}_6\text{H}_4\text{COOCOC}_6\text{H}_5$ , respectively. Assuming other things being equal and  $[\text{mixed benzoate}]_{\text{iaq}} > [\text{C}_6\text{H}_5\text{COCl}]_{\text{org}}$ , the relative reactivities of  $\text{XC}_6\text{H}_4\text{COO}^-$  and  $\text{YC}_6\text{H}_4$

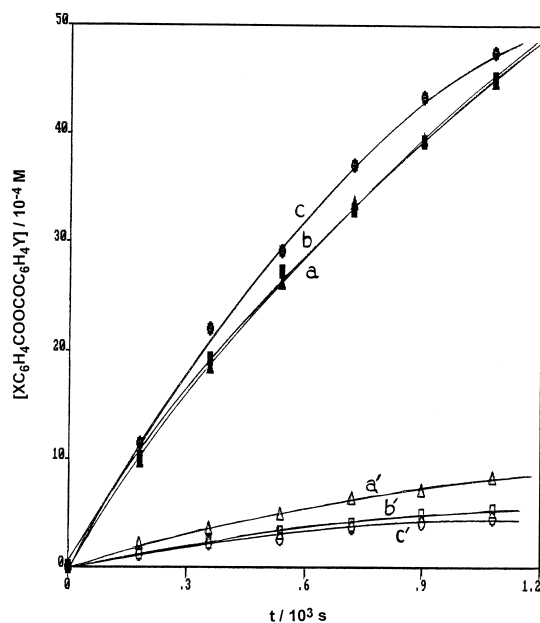


Fig. 4.  $[\text{XC}_6\text{H}_4\text{COOCOC}_6\text{H}_4\text{Y}]$  vs. time for the PNO-catalyzed reactions of  $\text{C}_6\text{H}_5\text{COCl}$  and mixed  $\text{YC}_6\text{H}_4\text{COO}^-$  (Y = F or H) ions in  $50\text{ ml H}_2\text{O}/50\text{ ml CH}_2\text{Cl}_2$  medium.  $[\text{C}_6\text{H}_5\text{COCl}]_{\text{org}} = 0.0100\text{ M}$ ;  $[\text{PNO}]_{\text{iaq}} = 2.00 \times 10^{-4}\text{ M}$ ;  $[\text{C}_6\text{H}_5\text{COONa}]_{\text{iaq}} = 0.0625\text{ M}$ ;  $[\text{FC}_6\text{H}_4\text{COONa}]_{\text{iaq}} = 0.438\text{ M}$ ,  $20^\circ\text{C}$ ; pH = 7.62.  $\text{XC}_6\text{H}_4\text{COOCOC}_6\text{H}_4\text{Y}$  = (a)  $2\text{-FC}_6\text{H}_4\text{COOCOC}_6\text{H}_5$ ; (b)  $3\text{-FC}_6\text{H}_4\text{COOCOC}_6\text{H}_5$ ; (c)  $4\text{-FC}_6\text{H}_4\text{COOCOC}_6\text{H}_5$ ; (a', b', c')  $(\text{C}_6\text{H}_5\text{CO})_2\text{O}$ .

COO<sup>-</sup> ions toward reaction with C<sub>6</sub>H<sub>5</sub>CO ONP<sup>+</sup> ion can be deduced from the expression of  $(\Delta[\text{XC}_6\text{H}_4\text{COOCOC}_6\text{H}_5]/\Delta[\text{YC}_6\text{H}_4\text{COOCOC}_6\text{H}_5]) = (k_X[\text{XC}_6\text{H}_4\text{COONa}]_{\text{iaq}}/k_Y[\text{YC}_6\text{H}_4\text{COONa}]_{\text{iaq}})$ . For  $[\text{C}_6\text{H}_5\text{COCl}]_{\text{org}} = 0.0100$  M,  $[\text{PNO}]_{\text{iaq}} = 2.00 \times 10^{-4}$  M,  $[\text{mixed benzoate}]_{\text{iaq}} = 0.500$  M, and at 20°C, the results are summarized as follows.

(i)  $\Delta[2\text{-FC}_6\text{H}_4\text{COOCOC}_6\text{H}_5]/\Delta[(\text{C}_6\text{-H}_5\text{CO})_2\text{O}] = (5.4 \pm 0.2)/1.0$  and  $1.0/(9.1 \pm 0.3)$  for  $[2\text{-FC}_6\text{H}_4\text{COONa}]/[\text{C}_6\text{H}_5\text{COONa}] = 7.0/1.0$  and  $1.0/7.0$ , respectively.

(ii)  $\Delta[3\text{-FC}_6\text{H}_4\text{COOCOC}_6\text{H}_5]/\Delta[(\text{C}_6\text{-H}_5\text{CO})_2\text{O}] = (5.5 \pm 0.2)/1.0$  and  $1.0/(8.4 \pm 0.2)$  for  $[3\text{-FC}_6\text{H}_4\text{COONa}]/[\text{C}_6\text{H}_5\text{COONa}] = 7.0/1.0$  and  $1.0/7.0$ , respectively.

(iii)  $\Delta[4\text{-FC}_6\text{H}_4\text{COOCOC}_6\text{H}_5]/\Delta[(\text{C}_6\text{-H}_5\text{CO})_2\text{O}] = (4.5 \pm 0.1)/1.0$  and  $1.0/(10.4 \pm 0.2)$  for  $[4\text{-FC}_6\text{H}_4\text{COONa}]/[\text{C}_6\text{H}_5\text{COONa}] = 7.0/1.0$  and  $1.0/7.0$ , respectively.

(iv)  $\Delta[2\text{-FC}_6\text{H}_4\text{COOCOC}_6\text{H}_5]/\Delta[4\text{-FC}_6\text{H}_4\text{COOCOC}_6\text{H}_5] = (4.6 \pm 0.2)/1.0$  and  $1.0/(10.6 \pm 0.2)$  for  $[2\text{-FC}_6\text{H}_4\text{COONa}]/[4\text{-FC}_6\text{H}_4\text{COONa}] = 7.0/1.0$  and  $1.0/7.0$ , respectively.

(v)  $\Delta[2\text{-FC}_6\text{H}_4\text{COOCOC}_6\text{H}_5]/\Delta[3\text{-FC}_6\text{H}_4\text{COOCOC}_6\text{H}_5] = (4.0 \pm 0.1)/1.0$  and  $1.0/(11.8 \pm 0.3)$  for  $[2\text{-FC}_6\text{H}_4\text{COONa}]/[3\text{-FC}_6\text{H}_4\text{COONa}] = 7.0/1.0$  and  $1.0/7.0$ , respectively.

(vi)  $\Delta[3\text{-FC}_6\text{H}_4\text{COOCOC}_6\text{H}_5]/\Delta[4\text{-FC}_6\text{H}_4\text{COOCOC}_6\text{H}_5] = (10.1 \pm 0.2)/1.0$  for  $[3\text{-FC}_6\text{H}_4\text{COONa}]/[4\text{-FC}_6\text{H}_4\text{COONa}] = 7.0/1.0$ .

(vii) The rates of the reactions in (i)–(vi) are quite insensitive to the change in the mixed benzoate ions. The average value of  $k_{\text{obs}}$  is  $(9.49 \pm 0.27) \times 10^{-4} \text{ s}^{-1}$  consistent with the value of  $1.03 \times 10^{-3} \text{ s}^{-1}$  at 22°C for  $[\text{C}_6\text{H}_5\text{COCl}]_{\text{org}} = 0.0100$  M,  $[\text{PNO}]_{\text{iaq}} = 2.00 \times 10^{-4}$  M,  $[\text{C}_6\text{H}_5\text{COONa}]_{\text{iaq}} = 0.500$  M [17].

These results indicate that the difference in reactivities among these benzoate ions is small

with the order of relative reactivities being  $\text{C}_6\text{H}_5\text{COO}^- > 3\text{-FC}_6\text{H}_4\text{COO}^- > 4\text{-FC}_6\text{H}_4\text{COO}^- > 2\text{-FC}_6\text{H}_4\text{COO}^-$ .

#### 4. Conclusion

The reactions of  $\text{XC}_6\text{H}_4\text{COCl}$  [ $X = 2\text{-F}, 3\text{-F}, 4\text{-F},$  or  $4\text{-(CH}_3)_3\text{C}$ ] and  $\text{YC}_6\text{H}_4\text{COONa}$  ( $Y = 2\text{-F}, 3\text{-F}, 4\text{-F},$  or  $\text{H}$ ) in a two-phase  $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$  medium with PNO as an inverse phase transfer catalyst were investigated. The main conclusions are:

(i) under suitable reaction conditions, 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 water phase;

(ii) the reaction of  $\text{XC}_6\text{H}_4\text{COCl}$  with PNO in the organic phase to produce the intermediate,  $\text{XC}_6\text{H}_4\text{COONP}^+$  ion, is the rate-determining step;

(iii) the order of reactivities of  $\text{XC}_6\text{H}_4\text{COCl}$  toward reaction with PNO is  $2\text{-FC}_6\text{H}_4\text{COCl} > 3\text{-FC}_6\text{H}_4\text{COCl} > 4\text{-FC}_6\text{H}_4\text{COCl} > \text{C}_6\text{H}_5\text{COCl} > 4\text{-(CH}_3)_3\text{CC}_6\text{H}_4\text{COCl}$ ;

(iv) the order of reactivities of  $\text{YC}_6\text{H}_4\text{COO}^-$  ions toward reaction with 1-(benzoyloxy)-pyridinium ion ( $\text{C}_6\text{H}_5\text{COONP}^+$ ) is  $\text{C}_6\text{H}_5\text{COO}^- > 3\text{-FC}_6\text{H}_4\text{COO}^- > 4\text{-FC}_6\text{H}_4\text{COO}^- > 2\text{-FC}_6\text{H}_4\text{COO}^-$ ;

(v) for the water phase with  $\text{pH} > 12$ , the reaction is complicated by the competitive reaction of  $\text{XC}_6\text{H}_4\text{COCl}$  and  $\text{OH}^-$  ion in the organic phase.

#### Acknowledgements

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