

Study of the exchange reaction of benzoic and 2-chlorobenzoic anhydrides in chloroform. Effects of pyridine 1-oxide and benzoate salts

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Abstract

Benzoic anhydride ((PhCO)₂O) and 2-chlorobenzoic anhydride ((2-ClC₆H₄CO)₂O) undergo slow exchange reaction in CHCl₃ to produce mixed benzoic 2-chlorobenzoic anhydride (2-ClC₆H₄COOCOPh). The rate of conversion changes abnormally with the concentration ratio of [(PhCO)₂O]/[(2-ClC₆H₄CO)₂O]. The reaction is catalyzed by pyridine 1-oxide (PNO). When (2-ClC₆H₄CO)₂O is the limiting reactant, the presence of benzoate salt promotes the reaction substantially with the order of effectiveness being PhCOOLi, PhCOONBu₄ > PhCOONa > PhCOOH. This exchange reaction does not follow simple second-order or pseudo-first-order kinetics. However, under pseudo-order reaction condition and in the presence of PNO or benzoate salt, the reaction follows pseudo-first-order kinetics. The mechanism of the reaction is more complicated than expected. Mechanistic rationalization of experimental results is presented. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Benzoic anhydride; 2-Chlorobenzoic anhydride; Pyridine 1-oxide; Catalyzed exchange reaction; Kinetics

1. Introduction

Carboxylic acid anhydrides, being less reactive than acyl chlorides and more reactive than esters or amides, are very important intermediates for the synthesis of esters, amides and peptides [1]. Transacylation with symmetric anhydrides precludes formation of side products due to the reaction with the second acyl carbonyl of mixed anhydrides, which is particularly important in reactions of anhydrides of relatively weak acids. The phase transfer catalysis (PTC) technique provides one of the most

attractive methods [2–4] for the synthesis of carboxylic acid anhydrides [2–9]. Fife and Xin [2] applied the inverse PTC (IPTC) technique [10] to synthesize acid anhydrides via the reaction of acid chloride with carboxylate ion catalyzed by pyridine 1-oxide (PNO). Jwo et al. studied the kinetics and mechanism of the PNO-catalyzed IPTC reactions of benzoyl chlorides with carboxylate or dicarboxylate ions, which produced symmetric or mixed benzoic anhydrides [11–17]. Like others, mixed benzoic anhydrides are prone to disproportionation and/or decomposition [18] in the presence of carboxylic acids, salts and PNO. Bunton et al. investigated the kinetics of acid-catalyzed hy-

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drolisis of carboxylic anhydrides [19–23]. However, very scant work was carried out for the kinetic study of the exchange and disproportionation reactions of carboxylic anhydrides [24]. In this work, we studied the kinetics of the exchange reaction of benzoic and 2-chlorobenzoic anhydrides to produce the mixed anhydrides in chloroform. The effects of PNO and benzoate salts were investigated. The rate law and the mechanism of this exchange reaction are more complicate than expected. This work provides significant insight into the mechanism of this exchange reaction.

2. Experimental section

2.1. Materials

Pyridine 1-oxide (PNO, C_5H_5NO , 98%), 2-chlorobenzoyl chloride (2- ClC_6H_4COCl (95%, Aldrich), benzoyl chloride (extra pure), sodium benzoate (99%), 2-chlorobenzoic acid (99%, Ferak), naphthalene ($C_{10}H_8$, 99%, Merck), dichloromethane (99%) and chloroform (99%) (Lab Scan) were used. Other chemicals used were of the highest reagent grade commercially available. Deionized water was obtained from the Millipore Milli-RO 20 reverse osmosis.

2.2. Procedures

2.2.1. Synthesis of benzoic anhydrides

Symmetric benzoic anhydrides ($(XC_6H_4CO)_2O$), $X = Cl$ or H) were prepared by the IPTC reactions of benzoyl chloride (XC_6H_4COCl) and benzoate ions ($XC_6H_4COO^-$) in two-phase H_2O/CH_2Cl_2 medium catalyzed by PNO as described elsewhere [16]. A similar method was used to prepare mixed benzoic 2-chlorobenzoic anhydrides (2- $ClC_6H_4COOCOPh$). However, pure 2- $ClC_6H_4COOCOPh$ was obtained by concentrating the CH_2Cl_2 solution in an ice water bath instead of a hot bath with a rotary evaporator to avoid the disproportionation of mixed anhydride. The HPLC analysis of the product showed

only one peak. Anal. Calcd. for $ClC_6H_4COOCOC_6H_5$: C, 64.50; H, 3.46; O, 18.43; Cl, 13.61. Found: C, 64.66; H, 3.54; O, 18.34; Cl, 13.46. Analysis by mass spectroscopy gave m/e (relative intensity %): 260 (2.8, M^+), 259 (16.2, $(M-1)^+$), 225 (74.1, $(M-Cl)^+$), 139 (96.3, $ClC_6H_4CO^+$), 111 (38.0, $ClC_6H_4^+$), 105 (100, $C_6H_5CO^+$), 77 (86.1, $C_6H_5^+$), 76 (15.3, $C_6H_4^+$), 75 (38.4, $C_6H_3^+$).

2.2.2. Synthesis of benzoate salts

Lithium or sodium salt of benzoic or 2-chlorobenzoic acid was prepared by neutralizing 0.1 mol of $PhCOOH$ or 2- ClC_6H_4COOH with an equivalent amount of $LiOH$ or $NaOH$ in 100 ml water. The solution was heated to evaporate water until precipitation was observed. It was cooled to room temperature and then 5–10 ml of acetone was added. After the precipitation was complete, the solution was filtered and the white crude product was recrystallized in aqueous acetone solution.

Benzoate salt containing PNO was prepared by dissolving 0.05 mol of PNO and 0.05 mol of $PhCOOLi$ or 2- ClC_6H_4COOLi in 20 ml water. The solution was heated until a brownish precipitate appeared on the surface. It was cooled to room temperature and then was put in the ice water bath to complete the precipitation. In contrast to the hygroscopic property of PNO, the product (presumably $PNOLi^+PhCOO^-$ or $PNOLi^+2-ClC_6H_4COO^-$) was not hygroscopic. Under similar conditions, no reaction was observed between PNO and $PhCOONa$ or 2- ClC_6H_4COONa .

Benzoate salts $PhCOONC_5H_5^+PhCOO^-$ and 2- $ClC_6H_4COONC_5H_5^+2-ClC_6H_4COO^-$ were prepared by adding 30 ml of $CHCl_3$ solution containing 0.03 mol of PNO to 10 ml of $CHCl_3$ solution containing 0.01 mol of $(PhCO)_2O$ or $(2-ClC_6H_4CO)_2O$. After the reaction was complete (about 30 min), 10 ml water was added to extract the excess PNO in $CHCl_3$. Then, the crystals of benzoate salt were obtained by concentrating the $CHCl_3$ phase with a rotary evaporator. The hygroscopic powder of

$\text{PhCOONC}_5\text{H}_5^+\text{PhCOO}^-$ was identified by mass spectrometry, which gave m/e (relative intensity %): 322 (8.61, M^+), 200 (100, $\text{C}_5\text{H}_5\text{NOCOC}_6\text{H}_5^+$), 105 (100, $\text{C}_6\text{H}_5\text{CO}^+$), 95 (100, $\text{C}_5\text{H}_5\text{NO}^+$), and 97 (35.2, C_6H_5^+). The powder of $2\text{-ClC}_6\text{H}_4\text{COONC}_5\text{H}_5^+ 2\text{-ClC}_6\text{H}_4\text{COO}^-$ was stable; Anal. Calcd.: C, 58.48; H, 3.33; N, 3.59. Found: C, 58.16; H, 3.83; N, 3.57.

2.2.3. Kinetic experiment

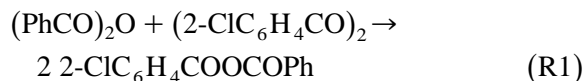
The kinetic experiments were run in a 125 ml ground Erlenmeyer fitted with a stopper. The kinetic run for the exchange reaction of symmetric benzoic and 2-chlorobenzoic anhydrides was started by adding two 25 ml CHCl_3 solutions of reactants to a 50 ml CHCl_3 solution which contained the internal standard (naphthalene) and might also contain the catalyst (PNO) and saturated benzoate salt. The initial amount of each species was known. Before mixing, all solutions were thermostated at the desired temperature in a thermostated water bath, in which the temperature was controlled within $\pm 0.2^\circ\text{C}$. After starting the reaction, 0.1–0.2 ml of reaction solution was withdrawn at a chosen time interval and put into the cooled dilution sample bottle containing 1 ml CH_3CN or 1 ml aqueous CH_3CN (50% by volume) if extraction was necessary. The sample was then analyzed by HPLC (Hitachi L6200 series) using the internal standard method; HPLC analysis conditions: column, Lichrospher 100 RP18 (5 μm); wavelength, 254 nm (UV detector); eluent, $\text{CH}_3\text{CN}/\text{H}_2\text{O} = 58/42$; flow rate, 1.0 ml/min; elution time (min): $(\text{PhCO})_2\text{O}$ (10.6); C_{10}H_8 (11.8); $2\text{-ClC}_6\text{H}_4\text{COOCOPh}$ (12.9) and $(2\text{-ClC}_6\text{H}_4\text{CO})_2\text{O}$ (15.5).

3. Results and discussion

3.1. Kinetics of the exchange reaction of benzoic and 2-chlorobenzoic anhydrides

The kinetics of the reaction of benzoic anhydride $(\text{PhCO})_2\text{O}$ and 2-chlorobenzoic anhy-

dride $(2\text{-ClC}_6\text{H}_4\text{CO})_2\text{O}$ (Eq. (R1)) was studied in CHCl_3 . Chloroform (b.p. 61°C) was chosen as the solvent for the kinetic study since it has higher boiling point than dichloromethane (b.p. 40°C) and the uncatalyzed reaction of $(\text{PhCO})_2\text{O}$ and $(2\text{-ClC}_6\text{H}_4\text{CO})_2\text{O}$ is slow. Some preliminary results indicated that the kinetics and mechanism were more complicated than expected. Therefore, the effects of benzoic anhydrides, pyridine 1-oxide and benzoate salts were investigated.



3.1.1. Effect of benzoic anhydride

The rate of reaction is not linearly proportional to the concentration of benzoic anhydride. Even under pseudo-order reaction conditions with $(\text{PhCO})_2\text{O}$ in excess amount (up to 40-fold), the plots of $\ln[(\text{RCO})_2\text{O}]$ versus time were not linear (Fig. 1(a and b), $\text{R} = 2\text{-ClC}_6\text{H}_4$; Fig. 1(c), $\text{R} = \text{Ph}$). Notably, the reaction rate for $[(\text{PhCO})_2\text{O}] = 0.045\text{ M}$ and $[(2\text{-ClC}_6\text{H}_4\text{CO})_2\text{O}]$

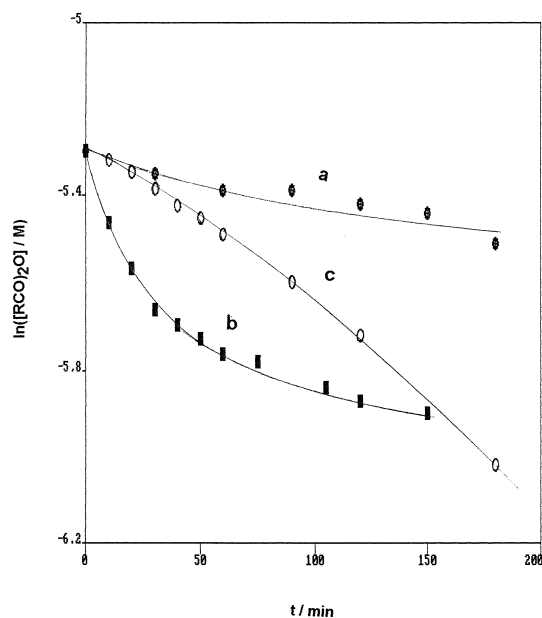


Fig. 1. Plots of $\ln[(\text{RCO})_2\text{O}]$ versus time for the uncatalyzed reaction of $(\text{PhCO})_2\text{O}$ and $(2\text{-ClC}_6\text{H}_4\text{CO})_2\text{O}$ in CHCl_3 at 50°C . $\text{R} =$ (a and b) $2\text{-ClC}_6\text{H}_4$; (c) Ph ; $[(\text{PhCO})_2\text{O}]_0 / 10^{-3}\text{ M} =$ (a) 45.0; (b) 75.0 and (c) 5.00; $[(2\text{-ClC}_6\text{H}_4\text{CO})_2\text{O}]_0 / 10^{-3}\text{ M} =$ (a and b) 5.00; (c) 45.0.

$= 5.00 \times 10^{-3}$ M was considerably slower than that for $[(\text{PhCO})_2\text{O}] = 5.00 \times 10^{-3}$ M and $[(2\text{-ClC}_6\text{H}_4\text{CO})_2\text{O}] = 0.045$ M (Fig. 1a and c), which was contrary to what was expected if the reaction in Eq. (R1) was an elementary reaction. The above results imply that the reaction of $(2\text{-ClC}_6\text{H}_4\text{CO})_2\text{O}$ and $(\text{PhCO})_2\text{O}$ does not follow simple second-order kinetics, especially in the high concentration region.

3.1.2. Effect of pyridine 1-oxide

As shown in Fig. 2, the conversion x ($= 1 - [2\text{-ClC}_6\text{H}_4\text{CO})_2\text{O}] / [(2\text{-ClC}_6\text{H}_4\text{CO})_2\text{O}]_0$) at a chosen time depends greatly on the initial concentration ratio p ($[(\text{PhCO})_2\text{O}]_0 / [(2\text{-ClC}_6\text{H}_4\text{CO})_2\text{O}]_0$). There is a substantial change in conversion when p is about 10 (Fig. 2a and b). The presence of PNO alone increases the reaction rate considerably (Fig. 2a and c) and the concentration of $(2\text{-ClC}_6\text{H}_4\text{CO})_2\text{O}$ changes more gradually with p . Under pseudo-order reaction conditions ($p > 5$ or $p < 1/5$), the plot

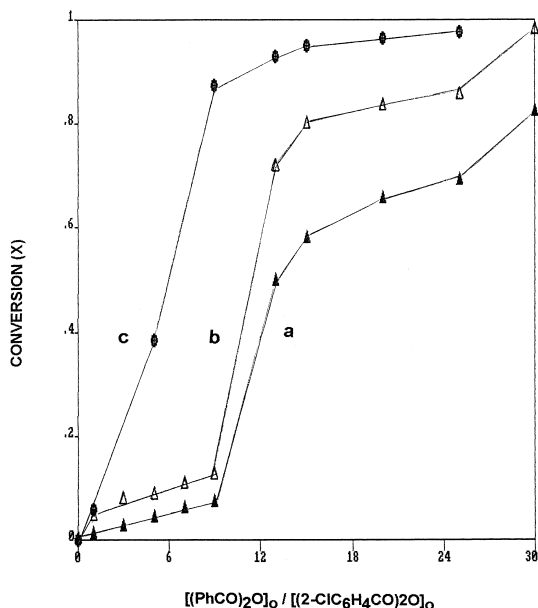


Fig. 2. The dependence of the conversion at a chosen time of the $(\text{PhCO})_2\text{O}$ - $(2\text{-ClC}_6\text{H}_4\text{CO})_2\text{O}$ reaction on the concentrations of PNO, $(\text{PhCO})_2\text{O}$ and $(2\text{-ClC}_6\text{H}_4\text{CO})_2\text{O}$ with $(2\text{-ClC}_6\text{H}_4\text{CO})_2\text{O}$ being the limiting reactant. $[(2\text{-ClC}_6\text{H}_4\text{CO})_2\text{O}]_0 = 5.00 \times 10^{-3}$ M, CHCl_3 , 50°C . $[\text{PNO}]_0 / 10^{-3}$ M = (a and b) 1.00; (c) 3.00; t = (a and c) 2 h; (b) 4 h.

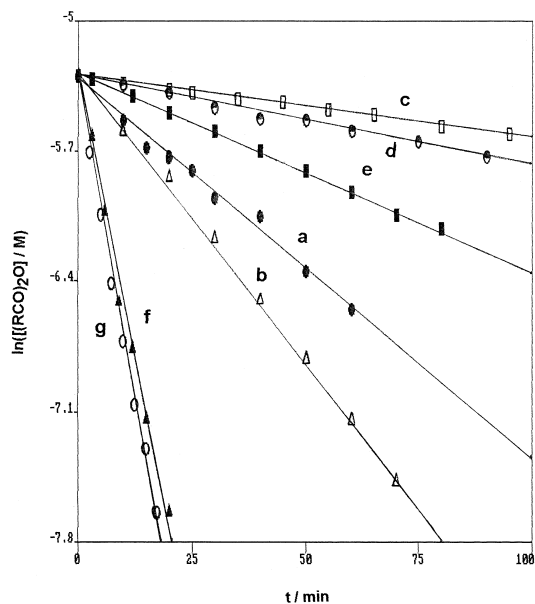


Fig. 3. Plots of $\ln([(RCO)_2O])$ versus time for the $(2\text{-ClC}_6\text{H}_4\text{CO})_2\text{O}$ - $(\text{PhCO})_2\text{O}$ reaction in CHCl_3 at 50°C . R = (a–c and e–g) $2\text{-ClC}_6\text{H}_4$; (d) Ph; $[(2\text{-ClC}_6\text{H}_4\text{CO})_2\text{O}]_0 / 10^{-3}$ M = (a–b and e–g) 5.00; (c and d) 45.0; $[(\text{PhCO})_2\text{O}]_0 / 10^{-3}$ M = (a–b and e–g) 45.0; (c and d) 5.00; $[\text{PNO}]_0 / 10^{-3}$ M = (a) 1.00; (c and e–g) 2.00; (b) 3.00; (d) 4.00; (e) saturated with PhCOOH ; (f) saturated with PhCOONa and (g) saturated with PhCOOLi .

of $\ln([(RCO)_2O])$ versus time is linear (Fig. 3a and b: R = $2\text{-ClC}_6\text{H}_4$; Fig. 3c and d: R = Ph). The rate law of this reaction can be expressed by Eq. (1):

$$-d[(RCO)_2O]/dt = k_{\text{obs}}[(RCO)_2O] \quad (1)$$

The pseudo-first-order rate constant (k_{obs}) was calculated from the linear-least-squares (LLS) fit of the plot of $\ln([(RCO)_2O])$ versus time. The dependence of k_{obs} on $[\text{PNO}]$ is shown in Table 1. The plots of k_{obs} versus $[\text{PNO}]$ are linear. However, the slope (k_c) of the line changes nonlinearly with $[(\text{PhCO})_2\text{O}]$. For $[(2\text{-ClC}_6\text{H}_4\text{CO})_2\text{O}]_0 = 5.00 \times 10^{-3}$ M, the values of k_c are $(6.31 \pm 0.87) \times 10^{-2}$, (0.115 ± 0.014) , (0.628 ± 0.047) and (0.865 ± 0.028) $\text{M}^{-1} \text{s}^{-1}$ for $[(\text{PhCO})_2\text{O}]_0 = 0.0250$, 0.0450 , 0.0750 and 0.100 M, respectively. Furthermore, for $[(\text{PhCO})_2\text{O}]_0 = 0.0450$ M and $[(2\text{-ClC}_6\text{H}_4\text{CO})_2\text{O}]_0 = 5.00 \times 10^{-3}$ M, the values of k_{obs} at 50°C are 1.68×10^{-5} , 3.34×10^{-4}

Table 1

Effect of pyridine 1-oxide on k_{obs} of the exchange reaction of benzoic and 2-chlorobenzoic anhydrides in CHCl_3

[BA] (10^{-3} M)	[PNO] (10^{-3} M)	k_{obs} (10^{-3} s $^{-1}$)	[BA] (10^{-3} M)	[PNO] (10^{-3} M)	k_{obs} (10^{-3} s $^{-1}$)
25.0	1.00	0.020	25.0	3.00	0.112
25.0	4.00	0.233	25.0	5.00	0.327
25.0	7.50	0.405			
45.0	0	0.019	45.0	1.00	0.325
45.0	3.00	0.547	45.0	4.00	0.650
45.0	5.00	0.725	45.0	7.50	0.938
75.0	0	0.029	75.0	1.00	0.607
75.0	2.00	1.43	75.0	3.00	2.30
75.0	4.00	2.52	75.0	5.00	3.10
100	0	0.083	100	1.00	0.783
100	2.00	1.78	100	3.00	2.70
100	4.00	3.45			

[CBA] = 5.00×10^{-3} M, 50°C.

and 5.21×10^{-4} s $^{-1}$ for $[\text{PNO}]_0 = 0$, 1.00×10^{-3} and 3.00×10^{-3} M, respectively. In contrast, for $[(\text{PhCO})_2\text{O}]_0 = 5.00 \times 10^{-3}$ M and

$[(2\text{-ClC}_6\text{H}_4\text{CO})_2\text{O}]_0 = 0.0450$ M, the values of k_{obs} at 50°C are 6.65×10^{-5} , 5.24×10^{-5} and 7.40×10^{-5} s $^{-1}$ for $[\text{PNO}]_0 = 0$, 2.00×10^{-3}

Table 2

Effects of benzoic anhydride, 2-chlorobenzoic anhydride, pyridine 1-oxide and benzoate salts on the values of k_{obs}

Entry	[BA] (10^{-3} M)	[CBA] (10^{-3} M)	[PNO] (10^{-3} M)	k_{obs} (10^{-3} s $^{-1}$)	Entry	[BA] (10^{-3} M)	[CBA] (10^{-3} M)	[PNO] (10^{-3} M)	k_{obs} (10^{-3} s $^{-1}$)
1	0	5.00	0	1.12 ^a	2	0	5.00	2.00	1.21 ^a
3	0	5.00	2.00	0.0474 ^b	4	0	5.00	15.0	1.25 ^a
5	0	5.00	15.0	~ 0 ^c	6	15.0	5.00	2.00	1.47 ^a
7	15.0	5.00	15.0	1.66 ^a	8	15.0	5.00	15.0	0.427 ^c
9	25.0	5.00	2.00	1.68 ^a	10	25.0	5.00	2.00	0.217 ^d
11	25.0	5.00	2.00	0.475 ^e	12	30.0	5.00	15.0	2.12 ^a
13	30.0	5.00	15.0	0.978 ^c	14	45.0	5.00	0	2.20 ^a
15	45.0	5.00	0	0.430 ^d	16	45.0	5.00	1.00	2.28 ^a
17	45.0	5.00	1.00	0.712 ^d	18	45.0	5.00	2.00	2.22 ^a
19	45.0	5.00	2.00	2.00 ^d	20	45.0	5.00	2.00	0.180 ^b
21	45.0	5.00	3.00	2.18 ^a	22	45.0	5.00	3.00	2.48 ^d
23	45.0	5.00	5.00	2.22 ^a	24	45.0	5.00	7.50	2.32 ^a
25	45.0	5.00	10.0	2.32 ^a	26	45.0	5.00	15.0	2.73 ^a
27	45.0	5.00	15.0	1.87 ^c	28	45.0	5.00	20.0	3.07 ^a
29	55.0	5.00	2.00	2.58 ^a	30	60.0	5.00	15.0	4.03 ^a
31	60.0	5.00	15.0	6.92 ^c	32	65.0	5.00	2.00	2.82 ^a
33	75.0	5.00	0	2.97 ^a	34	75.0	5.00	2.00	3.12 ^a
35	100	5.00	0	3.58 ^a	36	100	5.00	2.00	3.68 ^a
37	5.00	0	0	0.410 ^f	38	5.00	15.0	2.00	0.670 ^f
39	5.00	25.0	2.00	0.718 ^f	40	5.00	45.0	2.00	0.672 ^f
41	5.00	45.0	5.00	0.735 ^f	42	5.00	45.0	0	0.067 ^c

BA: benzoic anhydride; CBA: 2-chlorobenzoic anhydride; 50°C; CHCl_3 .^aSaturated with PhCOOLi .^bSaturated with PhCOOH .^cNo benzoate salt being added.^dSaturated with PhCOONa .^e PhCOONBu_4 (3.00×10^{-3} M).^fSaturated with $2\text{-ClC}_6\text{H}_4\text{COOLi}$.

and 4.00×10^{-3} M, respectively. Notably, this result indicates that the effect of PNO on the values of k_{obs} for $p = 9$ (Fig. 3a and b) is considerably greater than that for $p = 1/9$ (Fig. 3c and d). These results also support the above argument that the reaction in Eq. (R1) is not an elementary reaction.

3.1.3. Effect of benzoate salt

The addition of benzoate salt or benzoic acid accelerates the reaction considerably. In the presence of a saturated amount of benzoate salt or benzoic acid, the plot of $\ln[(\text{XC}_6\text{H}_4\text{CO})_2\text{O}]$ versus time is linear (Fig. 3e–g). The effect of benzoate salt was investigated mostly for reactions with $(2\text{-ClC}_6\text{H}_4\text{CO})_2$ as the limiting reactant. Some results are shown in Table 2. Comparing the results in Table 2 (entries 2, 3, 9, 10, 11, 14, 15, 18, 19 and 20), it can be concluded that the order of reactivity toward reaction with $(2\text{-ClC}_6\text{H}_4\text{CO})_2$ is $\text{PhCOOLi} > \text{PhCOONBu}_4 > \text{PhCOONa} > \text{PhCOOH}$, which is consistent with the order of the tendency to liberate benzoate ion.

3.1.4. Combined effects of benzoic anhydride, pyridine 1-oxide, and benzoate salt

The combined effects of $(\text{PhCO})_2\text{O}$, PNO and benzoate salt on k_{obs} are shown in Table 2 and Fig. 4. The results indicate that the presence of PhCOOLi changes considerably the effect of PNO. The presence of PhCOOLi may retard the catalysis of PNO. When $[\text{PNO}]$ is low (2.00×10^{-3} M), PNO exhibits only small catalytic effect (comparing entries 1 with 2, 14 with 18, 33 with 34 and 35 with 36). When $[\text{PNO}]$ is high (0.0150 M), PNO catalyzes the reaction significantly for $p \geq 5$ ($[(\text{PhCO})_2\text{O}]_0 = 0.0250$ M) (Fig. 4a and b). In contrast, in the absence of PhCOOLi or PhCOONa , PNO always catalyzes the reaction (Fig. 4c) and its catalytic effect is considerably larger than that in the presence of PhCOOLi (Fig. 4b). Similar behavior was observed for $[(2\text{-ClC}_6\text{H}_4\text{CO})_2\text{O}]_0 = 5.00 \times 10^{-3}$ M, $[(\text{PhCO})_2\text{O}]_0 = 0.0450$ M, Ph -

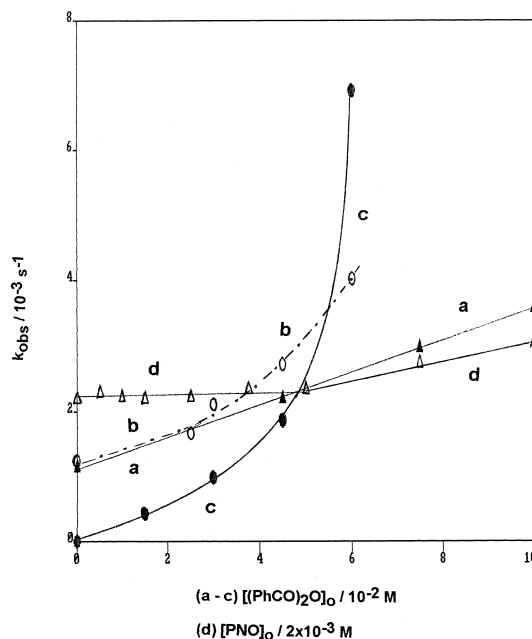


Fig. 4. Dependence of k_{obs} of the $(2\text{-ClC}_6\text{H}_4\text{CO})_2\text{O}-(\text{PhCO})_2\text{O}$ reaction on the concentrations of $(\text{PhCO})_2\text{O}$ and PNO with the presence of benzoate salt. $[(2\text{-ClC}_6\text{H}_4\text{CO})_2\text{O}]_0 = 5.00 \times 10^{-3}$ M, CHCl_3 , 50°C ; (a–c) dependence of k_{obs} on $[(\text{PhCO})_2\text{O}]_0$; (d) dependence of k_{obs} on $[\text{PNO}]_0$; (a) $[\text{PNO}]_0 = 0$ M, saturated with PhCOOLi ; (b) $[\text{PNO}]_0 = 0.0150$ M, saturated with PhCOOLi ; (c) $[\text{PNO}]_0 = 0.0150$ M, no benzoate salt being added; (d) $[(\text{PhCO})_2\text{O}]_0 = 0.0450$ M, saturated with PhCOOLi .

COOLi (saturated) and $[\text{PNO}]_0 = (0\text{--}0.0200$ M) (Fig. 4d), the catalytic effect of PNO appeared around $[\text{PNO}]_0 = 0.0100$ M. This result can be explained by invoking the formation of $\text{C}_5\text{H}_5\text{NOLi}^+\text{PhCOO}^-$ produced from the reaction of PNO and PhCOOLi as mentioned in Section 2. Therefore, the presence of PhCOOLi may diminish the catalytic effect of PNO. In contrast, PhCOONa does not retard the catalytic effect of PNO (Table 2, entries 15, 17, 19 and 22), which is also consistent with the fact that PNO does not react with PhCOONa to produce $\text{C}_5\text{H}_5\text{NONa}^+\text{PhCOO}^-$ as mentioned in Section 2.

3.1.5. Effect of 2-chlorobenzoic anhydride

Some kinetic runs were carried out for the reaction of $(\text{PhCO})_2\text{O}$ and $(2\text{-ClC}_6\text{H}_4\text{CO})_2\text{O}$ with $(\text{PhCO})_2\text{O}$ being the limiting reactant. The

results are shown in Table 2 (entries 37–42). Similar to the effect of PhCOOLi, the presence of 2-ClC₆H₄COOLi also accelerates the reaction. However, the effect of 2-ClC₆H₄COOLi is somewhat smaller than that of PhCOOLi (comparing entries 38 with 6, 39 with 9 and 40 with 18). This result can be attributed mainly to the difference in solubilities of PhCOOLi (~0.7 g) and 2-ClC₆H₄COOLi (~0.4 g) in 50 ml CHCl₃ at 50°C and partly to the difference in reactivities of (PhCO)₂O and (2-ClC₆H₄CO)₂O. Similar to the effect of PhCOOLi mentioned above, the presence of 2-ClC₆H₄COOLi also diminishes the catalytic effect of PNO (entries 38–40). The above argument is supported by the following observations. When the concentrations of (PhCO)₂O and (2-ClC₆H₄CO)₂O are equal, the effects of PhCOOLi and/or 2-ClC₆H₄COOLi on the rates of disappearance of (PhCO)₂O and (2-ClC₆H₄CO)₂O are illustrated in Fig. 5. The effect of PhCOOLi alone on $-d[(2\text{-ClC}_6\text{H}_4\text{CO})_2\text{O}]/dt$ is more than that of 2-

ClC₆H₄COOLi alone on $-d[(\text{PhCO})_2\text{O}]/dt$ (Fig. 5b and c). As expected, the effect of PhCOOLi on $-d[(\text{PhCO})_2\text{O}]/dt$ or the effect of 2-ClC₆H₄COOLi on $-d[(2\text{-ClC}_6\text{H}_4\text{CO})_2\text{O}]/dt$ is small (Fig. 5a and d). When both PhCOOLi and 2-ClC₆H₄COOLi are present, $-d[(\text{PhCO})_2\text{O}]/dt$ and $-d[(2\text{-ClC}_6\text{H}_4\text{CO})_2\text{O}]/dt$ are depressed somewhat (Fig. 5e and f), which can be explained by considering the competitive opposite reactions to form the symmetric anhydrides (PhCO)₂O and (2-ClC₆H₄CO)₂O.

3.2. Mechanism

Based on the above kinetic results, Scheme 1 is proposed for the exchange reaction of (PhCO)₂O and (2-ClC₆H₄CO)₂O in CHCl₃ and with the presence of PNO or benzoate salt. Reactions M1–M4' describe the uncatalyzed reaction of (2-ClC₆H₄CO)₂O (A₂) and (PhCO)₂O (B₂), in which A₂ and B₂ first undergo the association or complex formation reaction to produce A₂B₂ (reaction M1). The A₂B₂ complex can further form complexes with B₂ and A₂ to produce A₂B₄ and A₄B₂, respectively (reactions M2 and M2'). Complexes A₂B₂, A₂B₄ and A₄B₂ then undergo the exchange reactions to produce the mixed anhydride AB (reactions M3, M4 and M4'). The PNO-catalyzed reactions consist of reactions M5–M7', PNO can react with A₂, B₂ and A₂B₂ to produce PNOA⁺, PNOB⁺, A⁻ and B⁻ ions, respectively (reactions M5, M5', M6 and M6'). PNOA⁺ and PNOB⁺ ions then react rapidly with the counter B⁻ and A⁻ ions, respectively, to produce AB (reactions M7 and M7'). Reactions M8–M11' are for reactions involving lithium benzoates (2-ClC₆H₄COOLi (LiA) and PhCOOLi (LiB)). B⁻ and A⁻ ions promote the reaction by reacting with A₂, B₂ and A₂B₂, respectively, to produce AB (reactions M8, M8', M9 and M9'). Due to the low solubilities of LiB(s) and LiA(s) in CHCl₃, reactions M10 and M10' remain at equilibrium when saturated amounts of LiB(s) and LiA(s) are present. In the

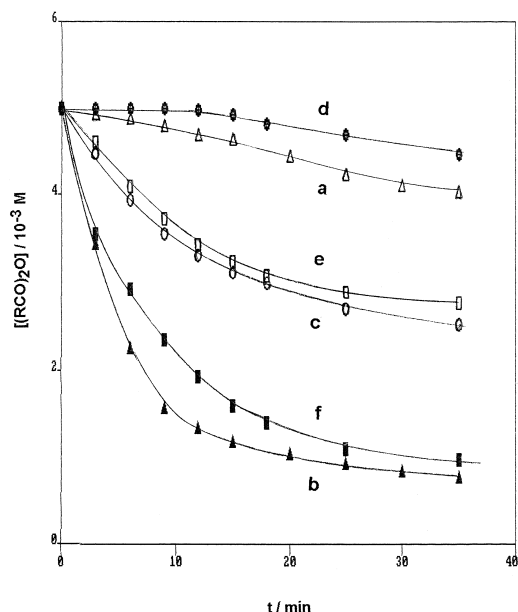
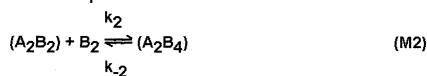
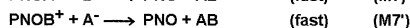
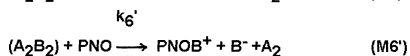
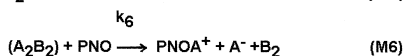
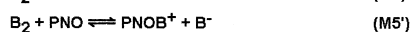
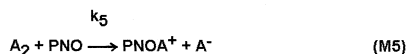


Fig. 5. Plots of [(RCO)₂O] versus time for the (2-ClC₆H₄CO)₂O-(PhCO)₂O reaction. [(PhCO)₂O]₀ = [(2-ClC₆H₄CO)₂O]₀ = 5.00 × 10⁻³ M, CHCl₃, 50°C; R = (a, c and e) Ph; (b, d and f) 2-ClC₆H₄; (a and b) saturated with 2 g PhCOOLi; (c and d) saturated with 2 g 2-ClC₆H₄COOLi; (e and f) saturated with 1.5 g PhCOOLi and 1.5 g 2-ClC₆H₄COOLi.

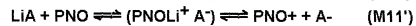
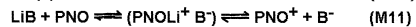
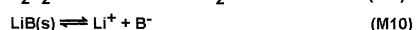
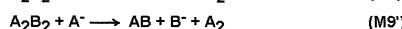
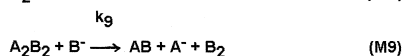
Uncatalyzed reactions



PNO-catalyzed reactions



Reactions involving benzoate ions



Scheme 1.

presence of both PNO and lithium benzoates, PNO can react with Li^+B^- and Li^+A^- to produce $PNOLi^+B^-$ and $PNOLi^+A^-$, respectively (reactions M11 and M11'). A sketch of A_2B_2 , A_2B_4 , $PNOA^+$ ion and $PNOLi^+$ ion is depicted in Scheme 2.

3.2.1. PNO-catalyzed reaction of A_2 and B_2

In the absence of lithium benzoate, the mechanism for the PNO-catalyzed reaction of A_2 and B_2 consists of reactions M1–M7'. If initially $[B_2]_0 \gg [A_2]_0$, reactions M2', M4' and M5' can

be neglected. Then, the following rate equations can be written

$$d[A_2]/dt = -(k_1[B_2] + k_5[PNO])[A_2] + (k_{-1} + k'_6[PNO])[A_2B_2] \quad (4)$$

$$d[A_2B_2]/dt = k_1[B_2][A_2] - (k_{-1} + k_2[B_2] + k_3 + (k_6 + k'_6)[PNO])[A_2B_2] + k_{-2}[A_2B_4] \quad (5)$$

$$d[A_2B_4]/dt = k_2[B_2][A_2B_2] - (k_{-2} + k_4) \times [A_2B_4] \quad (6)$$

Applying steady-state approximation to A_2B_2 and A_2B_4 , i.e. $d[A_2B_2]/dt = d[A_2B_4]/dt = 0$ gives Eq. (7):

$$[A_2B_2]_{ss} = \frac{k_1(k_{-2} + k_4)[B_2][A_2]}{k_{p1} + k_{p2}[B_2] + k_{p3}[PNO]} \quad (7)$$

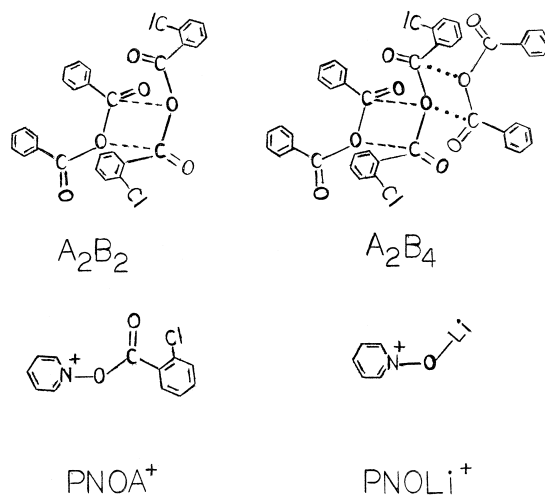
where $k_{p1} = (k_{-1} + k_3)(k_{-2} + k_4)$, $k_{p2} = k_2k_4$, $k_{p3} = (k_6 + k'_6)(k_{-2} + k_4)$.

Substituting Eq. (7) into Eq. (4) gives Eq. (8):

$$-d[A_2]/dt = (k_B[B_2] + k_5[PNO])[A_2] \quad (8)$$

where $k_B = (k_{m1} + k_{m2}[PNO] + k_{m3}[B_2]) / (k_{p1} + k_{p2}[B_2] + k_{p3}[PNO])$, $k_{m1} = k_1k_3(k_{-2} + k_4)$, $k_{m2} = k_1k_6(k_{-2} + k_4)$, $k_{m3} = k_1k_2k_4$.

If $[B_2]$ and $[PNO]$ are sufficiently low and the terms in the denominator of k_B containing



Scheme 2.

$[B_2]$ and $[PNO]$ and the $k_5[PNO]$ term are negligible, then Eq. (8) reduces to Eq. (9), which rationalize the main features of the results in Table 2 and Fig. 4a and b, i.e. when $[B_2]_0 \gg [A_2]_0$, k_{obs} depends linearly on $[PNO]$ and when $[PNO]_0$ is kept constant, k_{obs} varies nonlinearly with $[B_2]_0$.

$$\begin{aligned} -d[A_2]/dt &= \left\{ (k_{m1} + k_{m2}[PNO])[B_2] \right. \\ &\quad \left. + k_{m3}[B_2]^2 \right\} / k_{p1} \{ [A_2] \\ &= k_{obs}[A_2] \end{aligned} \quad (9)$$

3.2.2. Benzoate-promoted reaction of A_2 and B_2

In the absence of PNO catalyst, the presence of benzoate salts, $LiB(s)$ and $LiA(s)$, can promote the exchange reaction of A_2 and B_2 . The main reaction steps consist of reactions M1–M4', M8, M8', M9 and M9'. If initially $[B_2]_0 \gg [A_2]_0$, reactions M8' and M9' can be neglected. Then, the rate equations can be written as Eqs. (6), (10) and (11).

$$-d[A_2]/dt = (k_1[B_2] + k_8[B^-])[A_2] - k_{-1}[A_2B_2] \quad (10)$$

$$\begin{aligned} d[A_2B_2]/dt &= k_1[B_2][A_2] - (k_{-1} + k_2[B_2] \\ &\quad + k_3 + k_9[B^-])[A_2B_2] \\ &\quad + k_{-2}[A_2B_4] \end{aligned} \quad (11)$$

Applying steady-state approximation to A_2B_2 and A_2B_4 (reactions M11 and M6) gives Eq. (12):

$$[A_2B_2]_{ss} = \frac{k_1(k_{-2} + k_4)[B_2][A_2]}{(k_{p1} + k_{p2}[B_2] + k'_{p3}[B^-])} \quad (12)$$

where $k_{p1} = (k_{-1} + k_3)(k_{-2} + k_4)$, $k_{p2} = k_2k_4$ and $k'_{p3} = k_9(k_{-2} + k_4)$.

Substituting Eq. (12) into Eq. (10) gives Eq. (13):

$$-d[A_2]/dt = (k'_B[B_2] + k_8[B^-])[A_2] \quad (13)$$

where $k'_B = (k_{m1} + k'_{m2}[B^-] + k_{m3}[B_2]) / (k_{p1} + k_{p2}[B_2] + k'_{p3}[B^-])$, $k_{m1} = k_1k_3(k_{-2} + k_4)$, and $k_{m3} = k_1k_2k_4$. If $[B_2]$ and $[B^-]$ are sufficiently low, the terms in the denominator of k'_B con-

taining $[B_2]$ and $[B^-]$ are negligible. Then, Eq. (13) reduces to Eq. (14), which explains the results in Table 2 (entries 1, 14, 33 and 35), i.e. the value of k'_{obs} is not zero at $[B_2]_0 = 0$ M and k'_{obs} varies nonlinearly with $[B_2]_0$.

$$\begin{aligned} -d[A_2]/dt &= \left\{ (k_{m1} + k'_{m2}[B^-])[B_2] \right. \\ &\quad \left. + k_{m3}[B_2]^2 \right\} / k_{p1} + k_8[B^-] \{ [A_2] \\ &= k'_{obs}[A_2] \end{aligned} \quad (14)$$

In the presence of both PNO and lithium benzoates, the catalytic effect of PNO is diminished by Li^+B^- and Li^+A^- due to reactions M11 and M11'. However, when saturated amounts of $PNOLi^+B^-$ (s) and $PNOLi^+A^-$ (s) are produced, reactions M11 and M11' reach equilibrium and PNO will regain its catalytic effect as shown in Fig. 4d.

4. Conclusion

The pyridine 1-oxide-catalyzed exchange reaction of benzoic and 2-chlorobenzoic anhydrides in chloroform in the absence or presence of benzoate salt was investigated. The main conclusions are:

(a) The rate of reaction changes abnormally with the ratio of $[(PhCO)_2O] / [(2-ClC_6H_4CO)_2O]$.

(b) The uncatalyzed reaction does not follow the simple second-order or pseudo-first-order kinetics.

(c) Under pseudo-order reaction condition, the pyridine 1-oxide-catalyzed exchange reaction follows the pseudo-first-order kinetics.

(d) The presence of benzoate salt promotes the reaction substantially with the order of effectiveness being $PhCOOLi$, $PhCOONBu_4 > PhCOONa > PhCOOH$.

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