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Kinetics of the reaction of benzoyl chloride and sodium carboxylate under inverse phase-transfer catalysis

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Abstract

The reaction of benzoyl chloride and sodium carboxylate using pyridine 1-oxide (PNO) as an inverse phase-transfer catalyst in a system of the two phases H_2O and CH_2Cl_2 was investigated. Carboxylate ions including formate, acetate, propionate, 2-methylpropanoate, pentanoate, hexanoate, heptanoate and octanoate were selected to compare their reactivities. The rate of reaction depended on the concentration of pyridine 1-oxide (PNO) in the organic phase. The concentration of carboxylate ion affected the distribution of pyridine 1-oxide (PNO) between the organic and aqueous phases. The rate of reaction thus depended on the concentration of the carboxylate ion even though the rate-determining step occurred in the organic phase.

Keywords: Benzoyl chloride; Carboxylate ion effect; Inverse phase-transfer catalysis (IPTC); Kinetics; Unsymmetric acid anhydride

1. Introduction

In organic synthesis one encounters the utility of a two-phase system of water and organic solvent. Phase-transfer catalysis (PTC) is an effective tool for synthesis of organic chemicals from two immiscible reactants [1–3]. This process involves transport of a reactant from the aqueous phase into the organic phase. The greatest advantage of organic synthesis by PTC is that a high rate of reaction is achieved, even at a moderate operating temperature. Both a high conversion of the product and a high selectivity are achieved. Inexpensive quaternary salts were commonly used as the phase-transfer catalyst [4,5].

Several synthetic procedures are reported [6–11], in which an organic reactant is activated by conversion to an ionic intermediate and then transported to the aqueous phase for reaction. Mathias and Vaidya [12] recently described an example of this virtually unexplored method called the inverse phase-transfer catalysis (IPTC). The reaction of benzoyl chloride (halide) and carboxylate ions was carried out with pyridine 1-oxide (PNO) or 4-dimethylaminopyridine (DMAP) as inverse phase-transfer catalyst [12]. The inverse phase-transfer catalysis (IPTC) is employed to produce an acid anhydride from a substitution reaction [13,14] and a ketone from the oxidation of an alcohol [15]. Little work has been done on the kinetics of this reaction system. Several peculiar phenomena were found from the reaction which was carried out under inverse phase-transfer catalysis (IPTC).

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We undertook the reaction of benzoyl chloride with carboxylic acid in a system of organic solvent and NaOH solution with inverse phase-transfer catalysis. Several carboxylic acids, such as formic, acetic, propanoic, 2-methylpropanoic, pentanoic, hexanoic, heptanoic and octanoic acids were examined. Pyridine 1-oxide (PNO) served as catalyst. The rate of reaction in the aqueous phase is generally higher than that in the organic phase. Therefore, the rate coefficient is expected to be the same under similar conditions of reaction of varied carboxylate ions. In our work, the observed rate coefficients were not the same for distinct carboxylate ions. Our main objective was to investigate the factors that affect the rate of reaction between benzoyl chloride and carboxylic acid in a $H_2O(NaOH)/CH_2Cl_2$ medium using pyridine 1-oxide (PNO) as inverse phase-transfer catalyst (IPTC).

2. Experimental section

Materials: Benzoyl chloride, pyridine 1-oxide (PNO), monocarboxylic acids, such as formic, acetic, propanoic, 2-methylpropanoic, pentanoic, hexanoic, heptanoic, octanoic acids, and other reagent were all of G.R. grade. Due to the hydroscopic property of PNO, $PNO(H^+Cl^-)$ crystals were used instead. These crystals were prepared by adding dropwise 4 ml of concentrated HCl to 20 ml of aqueous solution containing 10 g of PNO.

2.1. Procedures

2.1.1. Synthesis and characterization of unsymmetric anhydrides

A 50 ml CH_2Cl_2 solution containing PhCOCl (0.1 M) and 50 ml aqueous solution containing RCOONa (0.5 M) and PNO (0.005 M) were poured into a 250 ml three-necked Pyrex flask. The reaction was carried out under agitation at 1200 rpm. After the reaction was complete, the CH_2Cl_2 solution was separated immediately and washed with diluted alkaline solution to remove benzoic acid. Then, it was further twice washed with deionized water and dried with anhydrous magnesium sulfate. The symmetric anhydrides were produced during the purification of unsymmetric anhydride due to its instability. Therefore, the product of unsymmetric anhydride was analyzed directly by using the HPLC and NMR methods.

The HPLC analysis shows that the major product is unsymmetric anhydride PhCOOCOR and only a trace amount of benzoic anhydride is produced. The ^1H NMR analysis gives the following data: $PhCOOCOCH_3$ δ 2.35 (S, 3H, $-CH_3$), $PhCOOCOC_2H_5$ δ 1.28–1.32 (t, 3H, $-CH_3$), 2.69–2.74 (q, 2H, $-CH_2$), $PhCOOCOCH(CH_3)_2$ δ 1.36–1.40 (m, 6H, 2–CH_3), 2.88–2.90 (q, 1H, CH), $PhCOOCOCH_2CH_2CH_2CH_3$ δ 1.01–1.05 (t, 3H, $-CH_3$), 1.48–1.54 (m, 2H, $-CH_2CH_2CH_2CH_3$), 1.76–1.83 (m, 2H, $-CH_2CH_2CH_2CH_3$), 2.67–2.71 (t, 2H, $-CH_2CH_2CH_2CH_3$), $PhCOOCOCH_2CH_2(CH_2)_2CH_3$ δ 0.974–1.01 (m, 3H, CH_3), 1.44–1.48 (m, 4H, $-CH_2CH_2(CH_2)_2CH_3$), 1.79–1.82 (m, 2H, $-CH_2CH_2(CH_2)_2CH_3$), 2.66–2.70 (t, 2H, $-CH_2CH_2(CH_2)_2CH_3$).

2.1.2. Kinetic run

The reactor was a three-necked Pyrex flask (250 ml), serving the purposes of agitating the solution, accepting the thermometer, withdrawing samples, and accepting feed. The reactor was submerged in a water bath the temperature of which was maintained constant within 0.1°C. To start a kinetic run, known quantities of carboxylic acid, sodium hydroxide and PNO as IPTC were prepared and dissolved in deionized water. The solution was then introduced into the water, which was thermostated at the required temperature. Measured quantities of benzoyl chloride and naphthalene ($C_{10}H_8$, internal standard) were dissolved in dichloromethane, which was also at the desired temperature, and were then added to the reactor. During the reaction, an aliquot (0.2 ml) was withdrawn from the reaction solution at a chosen time and was immediately extracted with n-hexane (0.2 ml) and water (0.5 ml). The solution was

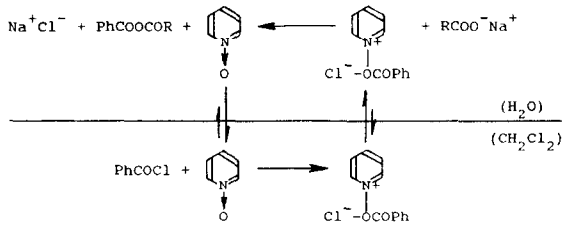
then shaken vigorously for 30 s. After the two phases separated, the organic phase (0.1 ml) was further diluted with dichloromethane. The sample was then analyzed by HPLC.

For analysis on a high pressure liquid chromatograph (Shimadzu LC-9A, Japan), the conditions were: column, CLC-ODS (M); eluent, $CH_3CN/H_2O = 65/35$ by volume; flow rate, 1.2 ml/min; wavelength, 254 nm (UV detector); elution time/min, PhCOCl (7.00), $C_{10}H_8$ (8.70); elution time of product of the PNO-catalyzed PhCOCl–RCOONa reaction/min, HCOONa (4.30), CH_3COONa (4.40), C_2H_5COONa (5.40), $(CH_3)_2CHCOONa$ (6.50), C_4H_9COONa (9.20), $C_5H_{11}COONa$ (12.3), $C_6H_{13}COONa$ (17.5), and $C_7H_{15}COONa$ (26.0). The response factor f was calibrated using $C_r/C_{is} = f(S_r/S_{is})$ (C, concentration; S, peak area; is, internal standard; r, unknown compound). The value of f measured was 0.310 ± 0.003 for PhCOCl (0.002–0.02 M) with $[C_{10}H_8] = 0.0200$ M. The apparent rate coefficient was determined in a fit by linear least squares of the plot of $-\ln(1-X)$ vs. time.

Pyridine 1-oxide (PNO) in CH_2Cl_2 exhibits an absorption maximum at 275 nm. The absorbances at 275 nm are 0.134, 0.361, 0.678, 0.861 and 1.34 for $[PNO]_{org} = 9.36 \times 10^{-6}$, 2.34×10^{-5}, 4.68×10^{-5}, 5.85×10^{-5} and 9.36×10^{-5} M, respectively. The calculated molar absorptivity of PNO in CH_2Cl_2 at 275 nm is $(1.43 \pm 0.17) \times 10^4$ M^{-1} min^{-1}. The effect of sodium carboxylate on the distribution of PNO between aqueous and CH_2Cl_2 phase was tested by measuring the PNO concentration in CH_2Cl_2 phase spectrophotometrically at 275 nm.

3. Kinetics of the two phase reaction

The reaction of benzoyl chloride and sodium carboxylate takes place in both aqueous and organic phases with or without PNO as catalyst. However, the rate of the reaction of benzoyl chloride and carboxylate ions catalyzed by PNO is faster than that of the reaction in the absence of PNO. Thus, the reaction of benzoyl chloride and



Scheme 1.

sodium carboxylate using pyridine 1-oxide as an inverse phase-transfer catalyst dominates the reaction in a system of the two phases H_2O and CH_2Cl_2 solution. The schematic diagram of the reactions, mass transfer and phase equilibrium is depicted in Scheme 1.

The intermediate product, 1-(benzoyloxy)pyridinium chloride ($PhCOONP^+Cl^-$), which was synthesized from the reaction of benzoyl chloride with pyridine 1-oxide (PNO) in the organic phase, transferred to the aqueous phase for reaction with sodium carboxylate. The rate was determined by the reaction in the organic phase. Applying the pseudo-steady-state approximation, the apparent rate coefficient of the rate of consumption of benzoyl chloride was used to express the reaction rate. Hence, the rate of reaction is expressed as

$$\frac{-d[PhCOCl]_o}{dt} = k_{obs}[PhCOCl]_o \quad (1)$$

in which k_{obs} is a linear function of the initial concentration of pyridine 1-oxide (PNO) in the aqueous phase, i.e.,

$$k_{obs} = k_h + k_c[PNO]_{i,aq} \quad (2)$$

The expressions for k_h and k_c are complicated; these parameters are called the uncatalyzed rate coefficient and catalyzed rate coefficient, respectively. Both k_h and k_c depend on the concentration of carboxylate ion, ionic strength and temperature.

Integrating Eq. 1, one obtains the conversion of PhCOCl as

$$-\ln(1-X) = k_{obs}t \quad (3)$$

in which

$$X = 1 - [PhCOCl_o/[PhCOCl]_o^0 \quad (4)$$

Table 1
Effect of the carboxylate ion on the apparent reaction rate constant (k_{obs}) and the catalyzed reaction rate constant (k_c)

RCOONa	$k_{obs}/10^{-3}$ min^{-1}					k_c/min^{-1} M^{-1}
	$[PNO]_{i,aq}/10^{-4}$ M					
	0.00	2.00	4.00	6.00	8.00	
HCOONa	8.49	50.6	92.1	140	176	210±4
CH_3COONa	5.73	48.5	92.9	133	177	213±3
C_2H_5COONa	6.00	51.2	90.4	134	177	211±3
$(CH_3)_2CHCOONa$	6.23	51.8	103	146	188	226±8
C_4H_9COONa	6.84	51.7	100	146	190	230±3
$C_5H_{11}COONa$	6.93	55.4	103	149	199	225±5
$C_6H_{13}COONa$	7.52	55.1	102	148	193	230±3
$C_7H_{15}COONa$	13.2	57.9	104	142	179	201±8

$[PhCOCl]_{i,org}$ = 0.0100 M, $[RCOONa]_{i,aq}$ = 0.500 M, 18°C, 50 ml of H_2O, 50 ml of CH_2Cl_2.

and $[PhCOCl]_o^0$ is the initial concentration of benzoyl chloride in the organic phase.

4. Results and discussion

4.1. PNO-catalyzed reaction between benzoyl chloride and carboxylate ion

4.1.1. Effect of carboxylate ion

In this study, we found that the reaction rate was independent of the agitation speed when the latter exceeded 1100 rpm in the two-phase reaction of benzoyl chloride and carboxylate ions. For a rate of agitation greater than 1100 rpm, the two-phase system was uniformly mixed and distributed. Thus, we obtained the kinetic data at 1200 rpm to eliminate mass-transfer resistance of the transferring components. We used eight sodium carboxylates to investigate their reactivities. Except for sodium 2-methylpropanoate, these were all salts with a linear carbon chain of organic acid. As shown in Table 1, the reaction rate varied with the carboxylate ion used. A typical result for the C_2H_5COONa reaction system appears in Fig. 1. Except for sodium formate, the value of k_{obs} seems to correlate with the number of carbon atoms in the carboxylate ion. The apparent rate coefficient increased with increasing number of carbon atoms in the carboxylate anion. However, when the carbon number exceeded four, the apparent rate coefficient was insensitive to the number

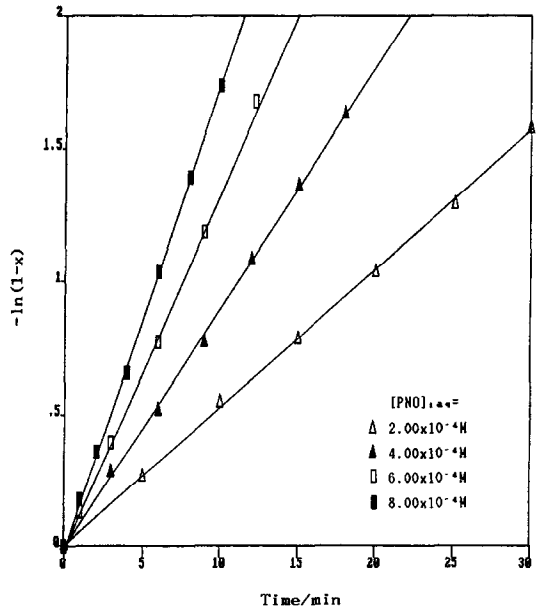


Fig. 1. Effect of pyridine 1-oxide (PNO) on the conversion of benzoyl chloride for C_2H_5COONa reaction system; $[C_2H_5COONa]_{i,aq}$ = 0.500 M, $[PhCOCl]_{i,org}$ = 0.0100 M, 18°C, 50 ml of H_2O, 50 ml of CH_2Cl_2.

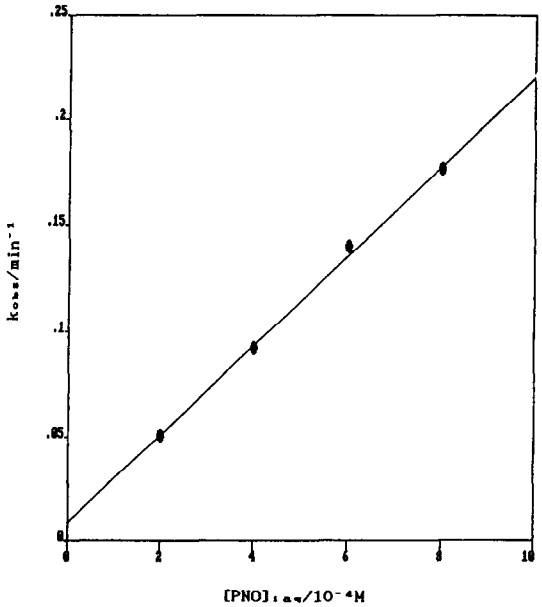


Fig. 2. Effect of pyridine 1-oxide (PNO) on the apparent reaction rate constant (k_{obs}) for HCOONa reaction system; $[HCOONa]_{i,aq}$ = 0.500 M, $[PhCOCl]_{i,org}$ = 0.0100 M, 18°C, 50 ml of H_2O, 50 ml of CH_2Cl_2.

Table 2
Effect of the temperature on the apparent reaction rate constant (k_{obs})

RCOONa	$k_{obs}/10^{-3}$ min^{-1}				E_a/kJ mol^{-1}
	5°C	10°C	18°C	25°C	
HCOONa	28.2	34.5	50.6	64.1	28.9±1.2
CH_3COONa	24.7	32.3	48.5	65.8	33.9±0.6
C_2H_5COONa	24.5	33.7	51.2	60.0	31.3±3.8
$(CH_3)_2CHCOONa$	25.7	34.7	51.8	71.7	35.2±0.8
C_4H_9COONa	26.7	31.0	51.7	76.2	37.4±3.2
$C_5H_{11}COONa$	26.1	34.7	55.4	84.7	40.6±0.9
$C_6H_{13}COONa$	26.3	35.5	55.1	79.2	37.9±0.3
$C_7H_{15}COONa$	27.3	36.0	57.9	89.9	41.1±1.3

$[RCOONa]_{i,aq}=0.500$ M, $[PhCOCl]_{i,org}=0.010$ M, $[PNO]_{i,aq}=2.00\times10^{-4}$ M, 50 ml of H_2O, 50 ml of CH_2Cl_2.

of carbon atoms. Substituting k_{obs} and $[PNO]_{i,aq}$ into Eq. 2, we obtained a straight line with slope k_c (Fig. 2). This result implies that the intermediate product, $PhCOONP^+Cl^-$, transfers rapidly to the aqueous phase to react. As shown in Table 1, the value of k_c is also a function of the carboxylate ion used, similar to the value of k_{obs}.

The ionic reaction of carboxylate ion and intermediate is rapid. Therefore, the reaction in organic phase determines the rate, i.e., the reaction of benzoyl chloride and pyridine 1-oxide (PNO) to form $PhCOONP^+Cl^-$ in the organic phase. Therefore, a similar result is expected for various carboxylate ions when the reaction is carried out under the same conditions. However, the experimental results indicate that the apparent rate coefficient depends strongly on the sodium carboxylate used. Hence sodium carboxylate possesses a reactivity that affects the distribution of PNO between the two phases.

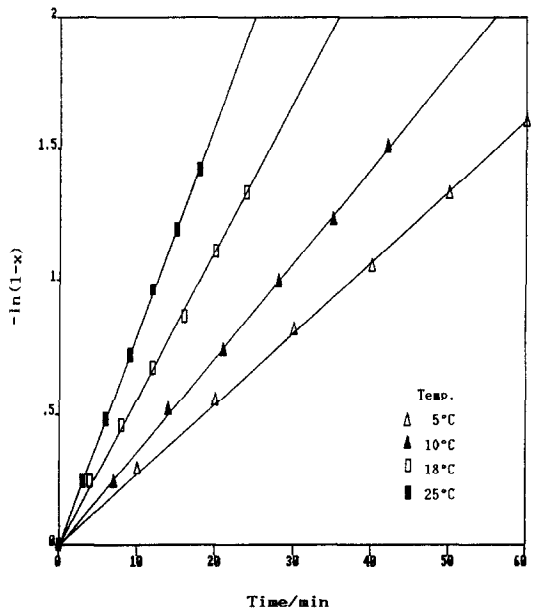


Fig. 3. Effect of the temperature on the conversion of benzoyl chloride for $C_6H_{13}COONa$ reaction system; $[C_6H_{13}COONa]_{i,q}=0.500$ M, $[PNO]_{i,aq}=2.00\times10^{-4}$, $[PhCOCl]_{i,org}=0.0100$ M, 50 ml of H_2O, 50 ml of CH_2Cl_2.

The solubility of a carboxylic acid in the aqueous phase is poor when the number of carbons exceeds four. Experiments indicated that an emulsion appears during IPTC using a carboxylic acid with more than four carbon atoms. The main product is the unsymmetric acid anhydride. Only a trace proportion of benzoic anhydride (<0.5%) was obtained. For example, acetic benzoic anhydride (85%) was produced from the two-phase reaction with $[CH_3COO^-]_{i,aq}=0.500$ M, $[PhCOCl]_{i,org}=0.0100$ M, $[PNO]_{i,aq}=6.00\times10^{-4}$ M, 18°C. Only about 0.3% of benzoic anhydride was obtained.

Another experiment was the two-phase reaction with decreased concentration of carboxylate ion in the aqueous phase and the ionic strength kept constant. Both the rate of reaction and the value of k_c increased with increasing concentration of carboxylate ion in the aqueous phase at constant ionic strength. When $[PhCOCl]_{i,org}=0.0100$ M, $[NaNO_3]_{i,aq}=0.400$ M, $T=18$°C, the obtained values of k_{obs} were 0.0337, 0.0609, 0.0886 and 0.114 min^{-1} for $[CH_3COO^-]_{i,aq}=0.100$ M at $[PNO]_{i,aq}=2.00\times10^{-4}$, 4.00×10^{-4}, 6.00×10^{-4} and 8.00×10^{-4} M, respectively, and the corresponding values of k_{obs} are 0.0484, 0.0873, 0.121 and 0.165 min^{-1} for $[C_5H_{11}COO^-]_{i,aq}=0.100$ M, respectively. A satisfactory linear relation between k_{obs} and $[PNO]_{i,aq}$ was obtained. The corresponding value of k_c obtained were 134 ± 2 min^{-1} M^{-1} and 192 ± 7 min^{-1} M^{-1} for $[CH_3COO^-]_{i,aq}$ and $[C_5H_{11}COO^-]_{i,aq}$ at 0.100 M with $[NaNO_3]=0.400$ M.

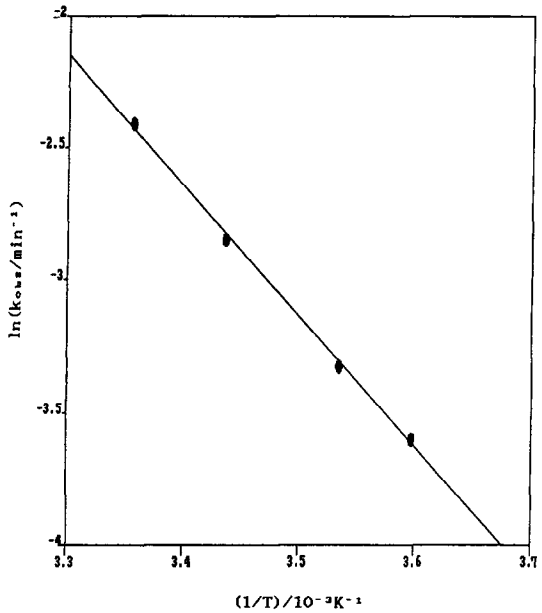


Fig. 4. Arrhenius plot of $\ln(k_{obs})$ vs. $1/T$ for $C_7H_{15}COONa$ reaction system; $[C_7H_{15}COONa]_{i,aq}=0.500$ M, $[PNO]_{i,aq}=2.00\times10^{-4}$ M, $[PhCOCl]_{i,org}=0.0100$ M, 50 ml of H_2O, 50 ml of CH_2Cl_2.

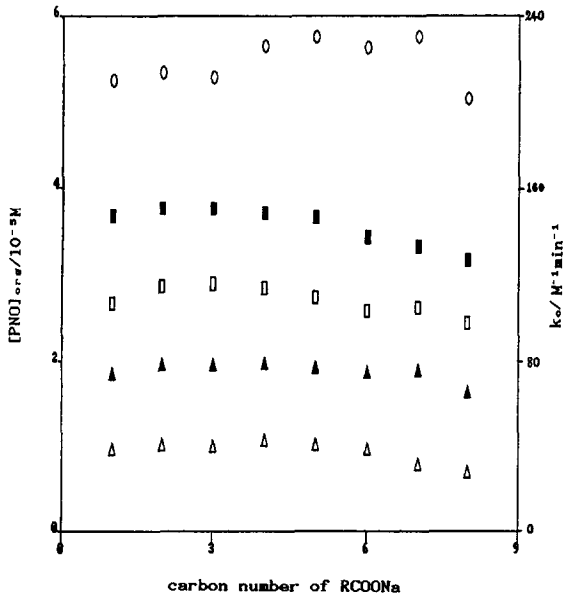


Fig. 5. Correlation of $[PNO]_{i,org}$ and k_c on the PNO-catalyzed RCOONa-PhCOCl reaction in a two-phase H_2O/CH_2Cl_2 medium; $[RCOONa]_{i,aq}=0.500$ M, $[PhCOCl]_{i,org}=0.0100$ M, 18°C, ○: k_c, $[PNO]_{i,aq}=$ △: 2.00×10^{-4} M, ▲: 4.00×10^{-4} M, □: 6.00×10^{-4} M, ■: 8.00×10^{-4} M.

4.1.2. Effect of temperature

The effect of temperature on the value of k_{obs} is presented in Table 2 and Fig. 3. The apparent activation energy which was obtained from the Arrhenius plot is 30–40 kJ/mol. A typical plot of $\ln(k_{obs})$ vs. $1/T$ appears in Fig. 4.

4.1.3. Relationship between relative reactivity of carboxylate ions and the distribution of pyridine 1-oxide

In order to rationalize the effect of carboxylate ion ($RCOO^-$) on the rate of reaction, the concentration of PNO in the organic phase was measured for $[PNO]_{i,aq}=2.00\times10^{-4}$ to 8.00×10^{-4}, 18°C, H_2O (25 ml) and CH_2Cl_2 (25 ml). The concentration of PNO in the organic phase first increased and then decreased on increased number of the carbon atoms in $RCOO^-$. This tendency is similar to that of k_c (Fig. 5). When the ionic strength was kept constant in the aqueous phase, the concentration of PNO in the organic phase increased with increasing concentration of CH_3COO^- in the aqueous phase. This result (Fig. 6) is similar to the variation of k_{obs} with the concentration of CH_3COO^- in the aqueous phase. A similar result was obtained with $C_5H_{11}COO^-$. For $I=0.500$ M (I: ionic strength) (adjusted by $NaNO_3$), the measured concentration of PNO in the organic phase was 4.62×10^{-5}, 4.48×10^{-5},

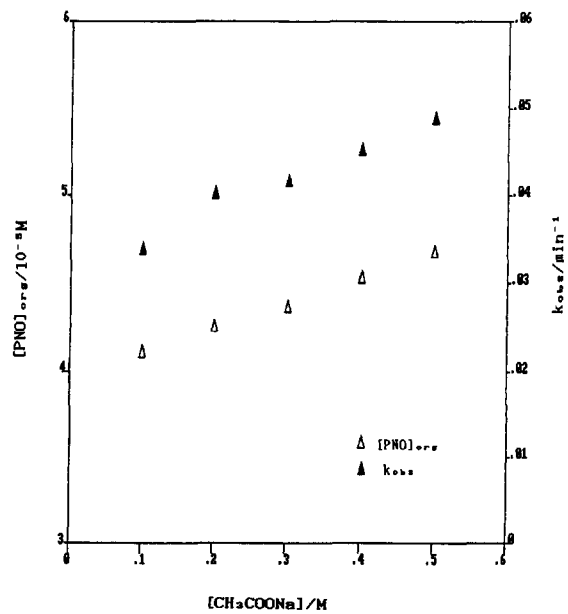


Fig. 6. Correlation of $[PNO]_{i,aq}$ and k_{obs} for CH_3COONa reaction system; 18°C, $[PhCOCl]_{i,org}=0.0100$ M, 50 ml of H_2O, 50 ml of CH_2Cl_2; $[PNO]_{i,aq}=2.00\times10^{-4}$ M for k_{obs}, and $[PNO]_{i,aq}=1.00\times10^{-3}$ M for $[PNO]_{org}$

4.32×10^{-5}, 4.13×10^{-5} and 3.97×10^{-5} M for $[C_5H_{11}COO^-]_{i,aq}=0.500$, 0.400, 0.300, 0.200, 0.100 M, and $[PNO]_{i,aq}=1.00\times10^{-3}$ M. The corresponding values of k_{obs} were 0.0556, 0.0506, 0.0478, 0.0481 and 0.0484 min^{-1}, respectively, at $[PNO]_{i,aq}=2.00\times10^{-4}$ M and $[PhCOCl]_{i,org}=0.0100$ M. This result indicates that the carboxylate ion influences the concentration of PNO in the organic phase. Hence, the reaction rate is affected by the concentration of the carboxylate ion in the aqueous phase.

For $[CH_3COO^-]_{i,aq}=0.500$ M, $[PhCOCl]_{i,org}=0.0100$ M, $[PNO]_{i,aq}=2.00\times10^{-4}$ M, 18°C, the value of k_{obs} was 0.0485 min^{-1}. However, k_{obs} increased to 0.0536 min^{-1} when extra CH_3COOH (0.100 M) was added. In these two experiments, the observed concentrations of PNO in the organic phase were 1.09×10^{-5} M and 9.60×10^{-6} M with and without added CH_3COOH respectively. This result shows that the rate of reaction was affected by the concentration of PNO in the organic phase: the rate increased with increased concentration of PNO in the organic phase. The extra addition of CH_3COOH to the reaction solution increased the polarity of the organic phase. Hence the rate of reaction increased when the concentration of PNO in the organic phase increased. The correlation between $[PNO]_{i,aq}$ vs. $[PNO]_{org}$ is presented in Table 3.

Table 3
Correlation of $[PNO]_{i,aq}$ and $[PNO]_{org}$

$[PNO]_{i,aq}/10^{-4}$ M:	2.00	4.00	6.00	8.00
RCOONa	$[PNO]_{org}/10^{-5}$ M			
HCOONa	0.930	1.82	2.66	3.67
CH_3COONa	0.986	1.92	2.86	3.76
C_2H_5COONa	0.972	1.92	2.90	3.76
$(CH_3)_2CHCOONa$	1.04	1.94	2.85	3.71
C_4H_9COONa	0.993	1.89	2.73	3.66
$C_5H_{11}COONa$	0.930	1.83	2.57	3.43
$C_6H_{13}COONa$	0.762	1.85	2.61	3.32
$C_7H_{15}COONa$	0.671	1.61	2.44	3.15

$[RCOONa]_{i,aq}=0.500$ M, 18°C, 25 ml of H_2O, 25 ml of CH_2Cl_2.

4.2. Uncatalyzed reaction between benzoyl chloride and carboxylate ion

Without inverse phase-transfer catalyst (IPTC), benzoic acid was produced from the reaction of benzoyl chloride and carboxylate ion in the system of the two phases H_2O and CH_2Cl_2. Only a trace proportion of PhCOOCOR is obtained. The rate coefficient of the uncatalyzed reaction was obtained from a plot of $-\ln(1-X)$ vs. time. The results are presented in Table 1 for $[PNO]_{i,aq}=0$ M. Except for formate ion, the apparent rate coefficient increased with increased number of carbon atoms in the carboxylate ion. An emulsion phenomenon was observed when the number of carbon atoms in the carboxylate ion exceeded four. Therefore, the reaction rate was relatively rapid when $C_7H_{15}COO^-$ was used. The hydrolysis of benzoyl chloride is also affected by the concentration of reactant in the aqueous phase. For example, the rate coefficient of the uncatalyzed reaction, k_h, is 0.00573 min^{-1} and 0.00673 min^{-1}, respectively for $[CH_3COO^-]=0.500$ M and 0.100 M at $I=0.500$ M, $[PhCOCl]_{i,org}=0.0100$ M. A similar result was obtained for other sodium carboxylates. For example, the rate coefficient for the uncatalyzed reaction was 0.00693 min^{-1} and 0.00677 min^{-1} for $[C_5H_{11}COO^-]_{i,aq}=0.500$ M and 0.100 M, $[PhCOCl]_{i,org}=0.0100$ M.

5. Conclusion

The reaction of benzoyl chloride and carboxylate ion in a system of the two phases H_2O and CH_2Cl_2 with pyridine 1-oxide (PNO) as inverse phase-transfer catalyst (IPTC) was carried out. Benzoyl chloride was transferred to the aqueous phase in the form of 1-(benzoyloxy)pyridinium chloride. The reaction of 1-(benzoyloxy)pyridinium chloride and $RCOO^-$ produced the unsymmetric acid anhydride or PhCOOH by hydrolysis. The reaction rate was strongly affected by the concentration of pyridine 1-oxide (PNO) in the organic phase which in turn was influenced by the concentration of carboxylate ion in the

aqueous phase. The reaction rate increased with increased concentration of PNO in the organic phase.

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