Kinetic Study of Carbonylation of α-Bromo-*p*-xylene with Iron Pentacarbonyl by Phase-Transfer Catalysis

Ho-Shing Wu[1] and Wen-Han Tan

Department of Chemical Engineering, Yuan-Ze University, 135, Far-East Road, ChungLi, Taoyuan, 32026, Taiwan, Republic of China

The reaction kinetics of the carbonylation of α-bromo-*p*-xylene $(BrCH_2C_6H_4CH_3$, BX) with iron pentacarbonyl $(Fe(CO)_5)$ by phase-transfer catalysis was studied in an organic solvent/alkaline solution. The concentration of tetra-*n*-butylammonium bromide $((n\text{-}C_4H_9)_4NBr$, TBAB), NaOH, NaBr, aqueous volume and temperature were evaluated to achieve the optimum reaction condition. The reaction behavior was discussed by the apparent reaction-rate constants for BX and bis(*p*-methylbenzyl) ketone $((p\text{-}CH_3C_6H_4CH_2)_2CO$, BMBK), respectively, and the relationship of consumption of BX and $Fe(CO)_5$. The product distributions of BX with $Fe(CO)_5$ on various reactions conditions were measured. The activation energies was obtained at TBAB $= 1.24$ and 0 mmol as well.   © 1998 Academic Press

INTRODUCTION

Many chemists (1–3) have studied the phase-transfer catalyzed reaction system. Advantages arising from the syntheses of organic chemicals with phase-transfer catalysis (PTC) are rapid rate of reaction, high selectivity of product, moderate operating temperature, and suitability for industrial-scale production. Moreover, phase-transfer catalysis is a valuable synthetic technique in transition metal organometallic chemistry. Transition metals are active catalysts for a variety of organic reactions. They are useful in conjunction with phase-transfer catalysts, particularly when hydroxide anions and other inorganic species are required to complete the reaction sequence. Use of phase-transfer catalysts as cocatalysts with transition metal compounds offers some additional options and advantages compared to the conventional reaction (4, 5).

The stoichiometric carbonylation of α-bromo-*p*-xylene $(BrCH_2C_6H_4CH_3$, BX) with $Fe(CO)_5$ under phase-transfer condition has been studied (6–10). The mechanistic features and the selectivity of this reaction have been reported (11–13). The results of their reports demonstrated that the syntheses of metal carbonyls under phase-transfer condi-

tions could be applied to organometallic chemistry. The reaction mechanism was corrected and clarified in our previous work (13). However, the nature of phase-transfer organometallic reaction is complicated, the reaction kinetics is rarely investigated so far. Here, we report the kinetic study of the stoichiometric carbonylation of α-bromo-*p*-xylene with iron pentacarbonyl by phase-transfer catalysis under nitrogen atmosphere.

EXPERIMENTAL

Materials

Tetra-*n*-butylammonium bromide $((n\text{-}C_4H_9)_4NBr$, TBAB), α-bromo-*p*-xylene $(BrCH_2C_6H_4CH_3)$ (Janssen), iron pentacarbonyl $(Fe(CO)_5)$ (Strem), and other reagents were all reagent grade chemicals.

Procedure

An aqueous solution (50 cm^3) of sodium hydroxide and tetra-*n*-butylammonium bromide (phase-transfer catalyst) was prepared and introduced into the reactor (250 cm^3, three-necked flask) which was thermostated at the desired temperature $(25 \pm 0.02°C)$. Measured quantities of α-bromo-*p*-xylene, diphenyl methane $((C_6H_5)_2CH_2)$ (internal standard for HPLC) and organic solvents (50 cm^3), which were also maintained at the desired temperature, were then added to the reactor. The solution was agitated at 700 rpm for 15 min and the reactor was purged with inert nitrogen gas (40 cm^3/min). After reaction, the flow rate of nitrogen and the agitated rate were set at 40 cm^3/min, 1000 rpm, respectively. A known quantity of iron pentacarbonyl was then added to the reactor. An aliquot sample was withdrawn from the reaction solution at a selected time interval. The sample (0.5 cm^3) was immediately added to 2 cm^3 dichloromethane (CH_2Cl_2)/2 cm^3 of water to quench the reaction. The organic phase contents (bis(*p*-methylbenzyl) ketone $((p\text{-}CH_3C_6H_4CH_2)_2CO)$ and *p*-xylene $(p\text{-}CH_3C_6H_4CH_3$, PX)) were then analyzed quantitatively by HPLC using the method of internal standard. The *p*-methylphenylacetic acid $(p\text{-}CH_3C_6H_4COOH$,

[1] To whom all correspondence should be addressed. E-mail: cehswu@ce.yzu.edu.tw.

MPAA) was extracted from the aqueous layer after acidification. The accuracy of these analytical techniques was within 2–3% and most of the data could be correctly reproduced within 5% of the values reported in this work. The yield of BMBK was calculated from the quotient of [BMBK] and n. [limiting reactant]. The n values for BX and Fe(CO)$_5$ were 0.5 and 1, respectively.

Liquid chromatography was carried out on a Shimadzu LC-10AD instrument, using a column packed with Chem-coPak 5-ODS-H. The eluent was CH$_3$OH/H$_2$O = 3/1 (flow rate 1.0 cm^3/min) and was monitored at 266 nm (UV detector). The bis(p-methylbenzyl) ketone, p-xylene, and p-methylphenylacetic acid were analyzed by means of elemental analysis on a Perkin-Elmer 2400-CHN, mass spectrometry on a JEOL SX-102A mass spectrometer, and NMR spectra in deuteriated chloroform on a JEOL 300 MHz FT-NMR spectrometer.

RESULTS AND DISCUSSION

Many reactions happened simultaneously in the stoichiometric carbonylation of α-bromo-p-xylene (BX) with iron pentacarbonyl under phase-transfer condition. The reaction mechanism is quite complex. The main products included bis(p-methylbenzyl) ketone (BMBK), p-xylene (PX), and p-methylphenylacetic acid (MPAA). In this study, the product distributions of carbonylation of BX with Fe(CO)$_5$ on various reaction conditions by phase-transfer catalysis were listed in Table 1. The major product is BMBK. The amount of PX is slight. The total yield of stoichiometric carbonylation of BX with Fe(CO)$_5$ for BMBK, MPAA, and PX ranged between 70 to 80%. When the amount of BX was excess to that of Fe(CO)$_5$, the yield approach 100%. Our previous work (13) has reported that BX and Fe(CO)$_5$ were self-decomposed in the alkaline solution during the course of the reaction.

On the basis of various literature sources (14–22) and the result in our previous study (13), the carbonylation
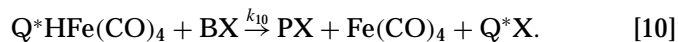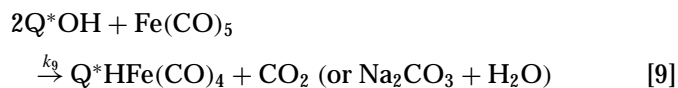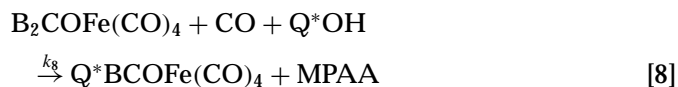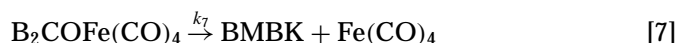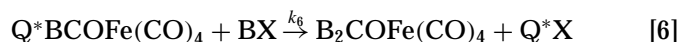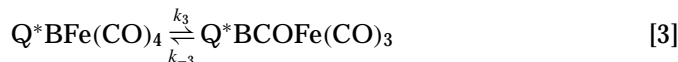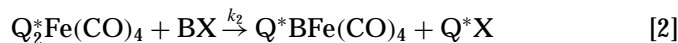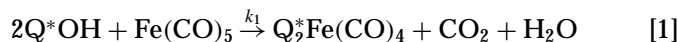
TABLE 1

Product Distributions of Carbonylation of BX with Fe(CO)$_5$ on Various Reaction Conditions

BX (mmol)	TBAB (mmol)	BMBK (%)	MPAA (%)	PX (%)
10.6	1.24	62.4	0.51	∼1
10.6	1.55	70.9	3.75	∼1
10.6	1.86	68.1	3.80	∼1
10.6	2.32	67.1	12.9	0
10.6	3.1	65.5	19.6	0
26.5	1.24	80	18.9	2
37.1	1.24	89	11.9	0
53.0	1.24	98.5	0.5	1

Note. Reaction conditions: Fe(CO)$_5$ = 5.3 mmol, NaOH = 0.125 mol, reaction time = 240 min, C$_6$H$_6$ = 50 cm^3, aqueous phase = 50 cm^3, N$_2$ = 40 cm^3/min, 25°C.

of α-bromo-p-xylene with iron pentacarbonyl is written as shown in Scheme 1. The seven reaction paths (i)–(vii) exist in this carbonylation reaction. Hence, the reaction expressions are listed as

$$2Q^*OH + Fe(CO)_5 \xrightarrow{k_1} Q_2^*Fe(CO)_4 + CO_2 + H_2O \qquad [1]$$

$$Q_2^*Fe(CO)_4 + BX \xrightarrow{k_2} Q^*BFe(CO)_4 + Q^*X \qquad [2]$$

$$Q^*BFe(CO)_4 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Q^*BCOFe(CO)_3 \qquad [3]$$

$$Q^*BCOFe(CO)_3 + BX \xrightarrow{k_4} BMBK + Q^*X + Fe(CO)_3 \qquad [4]$$

$$Q^*BFe(CO)_4 + CO \xrightarrow{k_5} Q^*BCOFe(CO)_4 \qquad [5]$$

$$Q^*BCOFe(CO)_4 + BX \xrightarrow{k_6} B_2COFe(CO)_4 + Q^*X \qquad [6]$$

$$B_2COFe(CO)_4 \xrightarrow{k_7} BMBK + Fe(CO)_4 \qquad [7]$$

$$B_2COFe(CO)_4 + CO + Q^*OH$$
$$\xrightarrow{k_8} Q^*BCOFe(CO)_4 + MPAA \qquad [8]$$

$$2Q^*OH + Fe(CO)_5$$
$$\xrightarrow{k_9} Q^*HFe(CO)_4 + CO_2 \; (\text{or } Na_2CO_3 + H_2O) \qquad [9]$$

$$Q^*HFe(CO)_4 + BX \xrightarrow{k_{10}} PX + Fe(CO)_4 + Q^*X. \qquad [10]$$

The rate expressions of BX, BMBK and Fe(CO)$_5$ are obtained and written as

$$\frac{d[BX]}{dt} = -(k_2[Q_2^*Fe(CO)_4] + k_4[Q^*BCOFe(CO)_3]$$
$$+ k_6[Q^*BCOFe(CO)_4] + k_{10}[Q^*HFe(CO)_4])[BX]$$
$$[11]$$

$$\frac{d[BMBK]}{dt} = (k_4[Q^*BCOFe(CO)_3]$$
$$+ k_6[Q^*BCOFe(CO)_4])[BX] \qquad [12]$$

$$\frac{d[Fe(CO)_5]}{dt} = -(k_1 + k_9)[Q^*OH]^2[Fe(CO)_5]. \qquad [13]$$

A generalized approach describing the phase-transfer catalyzed reaction system is to use a pseudo-first-order reaction (1, 2). Hence, Eqs. [11]–[13] can be rewritten as

$$\frac{d[BX]}{dt} = -k_{app,1}[BX]$$
$$k_{app,1} = k_2[Q_2^*Fe(CO)_4] + k_4[Q^*BCOFe(CO)_3]$$
$$+ k_6[Q^*BCOFe(CO)_4] + k_{10}[Q^*HFe(CO)_4] \quad [14]$$

$$\frac{d[BMBK]}{dt} = k_{app,2}[BX]$$
$$k_{app,2} = k_4[Q^*BCOFe(CO)_3] + k_6[Q^*BCOFe(CO)_4]$$
$$[15]$$

NaX + QOH ← ← NaOH + QX　　　　　　　　　　　　　aqueous phase
───
NaX + QOH ← ← NaOH + QX ←- - - - - - - - - - - - - 　organic phase

Q*OH + Fe(CO)$_5$ →(iii)→ Q*$^+$HFe(CO)$_4^-$ + CO$_2$(or Na$_2$CO$_3$ + H$_2$O)

BX ↓

PX + Fe(CO)$_4$ + Q*X

CO$_2$ + Fe$_2$O$_3$·H$_2$O ←(i)/H$_2$O

(iv)→ Q*$_2^+$Fe(CO)$_4^{2-}$ + CO$_2$ + H$_2$O

BX ↓

(ii) h$_v$

Fe(CO)$_4$

Q*$^+$BFe(CO)$_4^-$ + Q*X

+

CO → (v) ⇌ Q*BCOFe(CO)$_3$ —BX→ BMBK + Fe(CO)$_3$ + Q*X

→ Q*BCOFe(CO)$_4$

BX ↓

MPAA + Q*BCOFe(CO)$_4$ ←(vii)/Q*OH— BCOFe(CO)$_4$ —(vi)→ BMBK + Fe(CO)$_4$

|
B
+
Q*X
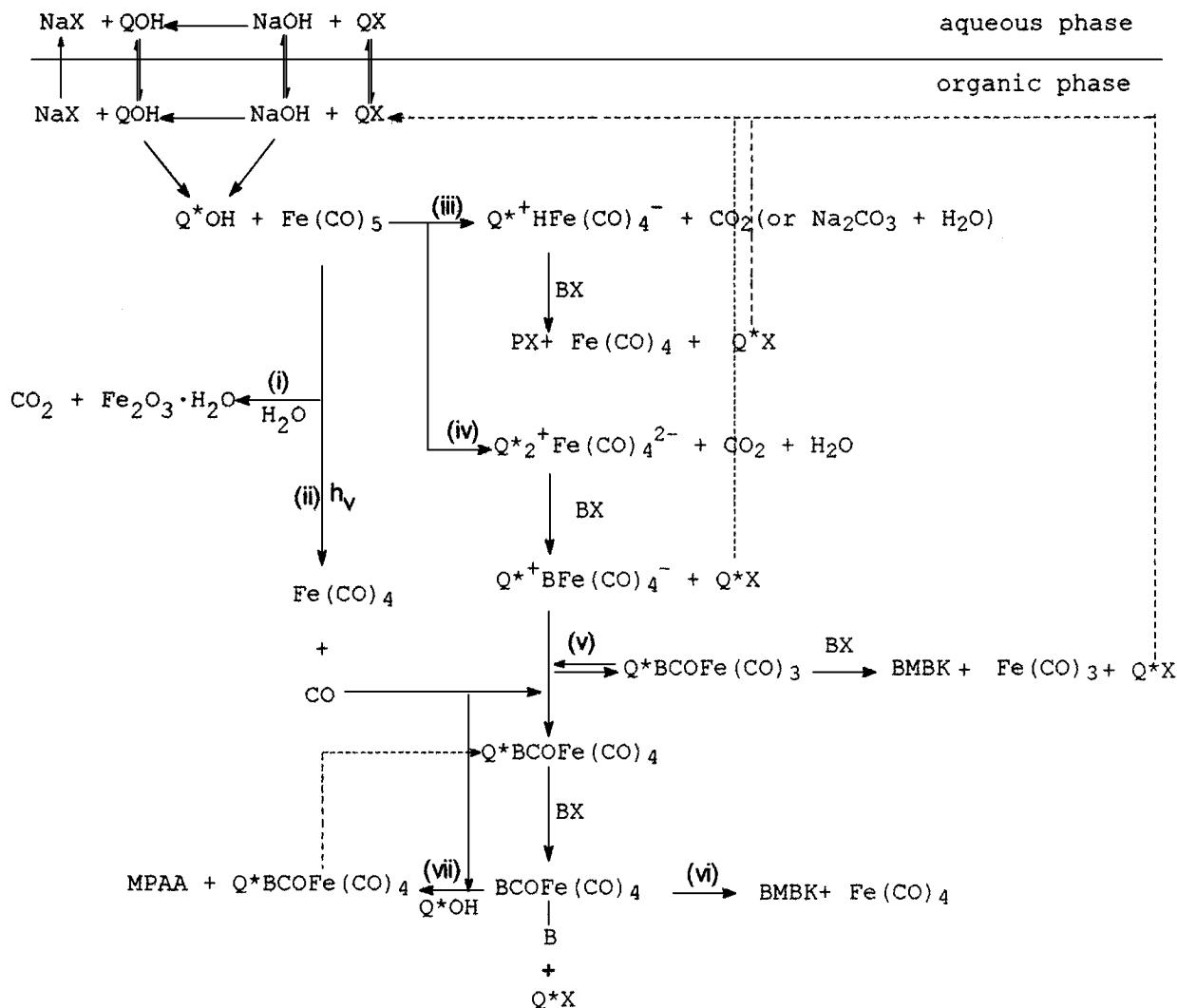
Q* : Na$^+$ or Q$^+$ (phase-transfer catalyst)

SCHEME 1

$$\frac{d[\text{Fe(CO)}_5]}{dt} = -k_{\text{app},3}[\text{Fe(CO)}_5]$$
$$k_{\text{app},3} = (k_1 + k_9)[\text{Q*OH}]^2. \tag{16}$$

The fixed value of k_{app} is called the apparent first-order reaction-rate constant which is obtained so that the consumption of BX is restricted below 15%.

As mentioned above, the BX and Fe(CO)$_5$ can be self-decomposed. A definition is employed to describe the relationship of consumption (abbreviated RC) of BX and Fe(CO)$_5$ (Eq. [17]):

$$\text{RC} = \frac{[\text{BX}]|_{240\,\text{min}} - [\text{BX}]|_{0\,\text{min}}}{[\text{Fe(CO)}_5]|_{240\,\text{min}} - [\text{Fe(CO)}_5]|_{0\,\text{min}}}. \tag{17}$$

The stoichiometric consumed moles of BX and Fe(CO)$_5$ are 2 and 1, respectively when 1 mole of BMBK produces and RC-value equal to 2. We discuss the reaction behavior of the carbonylation by Eqs. [14]–[17] in the following.

The effects of the amount of tetra-n-butylammonium bromide (phase-transfer catalyst, TBAB) on the consumption mole ratio of BX to Fe(CO)$_5$ and apparent reaction-rate constant are displayed in Fig. 1. The apparent reaction-rate constants are proportional linearly to the amount of TBAB when the amount of TBAB exceeded 0.3 mmol. The turnover number based on the concentration of TBAB was 132 min^{-1}. Because the turnover number kept constant for various [TBAB] and no improvement in the reaction rate was observed when the agitation rate exceeded
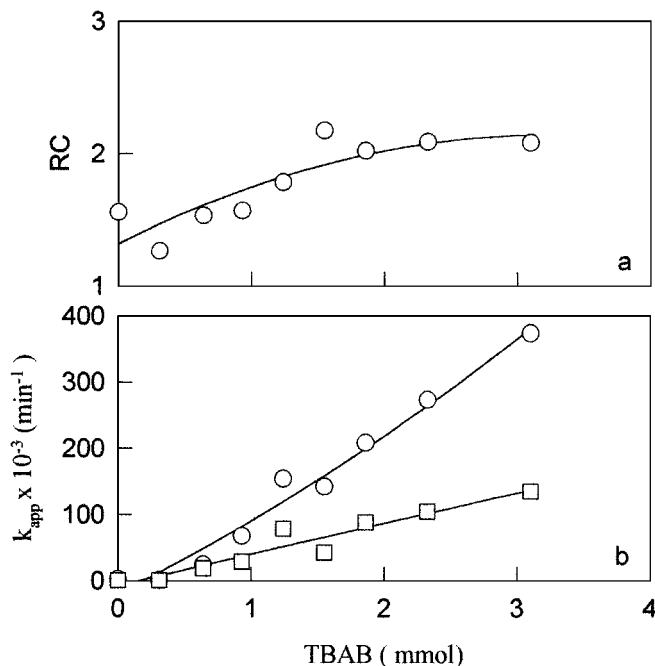
FIG. 1. Effects of the amount of tetra-n-butylammonium bromide (TBAB) on (a) RC and (b) k_{app}: ($\bigcirc$) $k_{app,1}$; ($\square$) $k_{app,2}$. $C_6H_6 = 50$ cm^3, BX $= 10.6$ mmol, Fe(CO)$_5 = 5.3$ mmol, aqueous phase $= 50$ cm^3, NaOH $= 0.125$ mol, N$_2 = 40$ cm^3/min, 25°C.

1000 rpm, the mass-transfer effect can be neglected in the present study. The RC-value increases and is less than 2 when the amount of TBAB increases up to 0.5 mmol. The increment of phase-transfer catalyst in the reaction system cannot obtain the larger amount of product BMBK, whereas the product of MPAA increased when the amount of TBAB increased (Table 1). The sum of yields of BMBK, MPAA, and PX was increased with an increasing amount of TBAB. When the mole ratio of TBAB to Fe(CO)$_5$ increases, the concentration of free QOH increases. Adding more catalyst enhanced the yield of MPAA. The phenomenon is similar to the result of Abbayes and Alper (22) and Collman *et al.* (17). Hence, if the product of BMBK is favored, the concentration of QOH must be low and the production of carbon monoxide must be eliminated (reaction path (ii)).

The mechanism of phase-transfer catalytic carbonylation was described by an interfacial mechanism (10–12). The evidence was that, since the onium hydroxide was not extractable into the organic phase and the reaction rate depended on the agitation rate, the reaction involving the hydroxide ion should occur at the interface. From the results of the previous work (24, 25), a small amount of onium hydroxide (QOH) was observed in the organic phase when alkaline solutions were used. The distribution ratios of QOH between two phases ($= [QOH]_{org}/[QOH]_{aq}$) were increased when the concentration of base was increased and also it increased when the concentration of onium hydroxide was increased. Tetra-n-butylammonium hydroxide
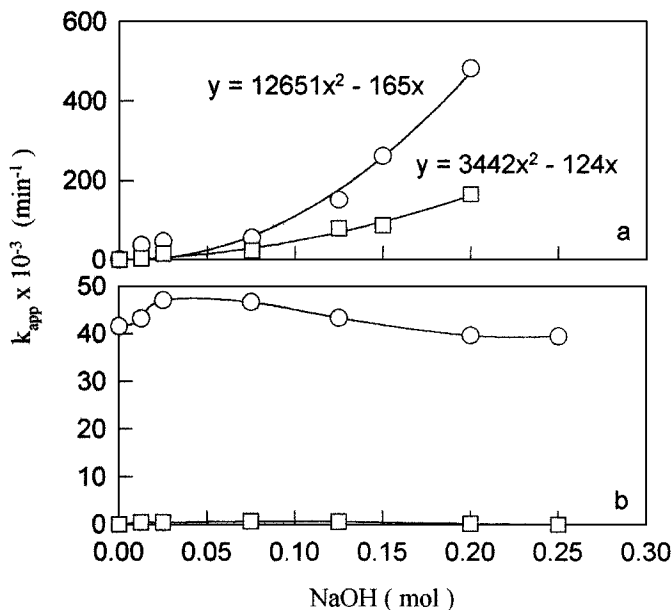

FIG. 2. Effects of NaOH on k_{app}: ($\bigcirc$) $k_{app,1}$; ($\square$) $k_{app,2}$ (a) TBAB $= 1.24$ mmol, (b) TBAB $= 0$ mmol. $C_6H_6 = 50$ cm^3, BX $= 10.6$ mmol, Fe(CO)$_5 = 5.3$ mmol, aqueous phase $= 50$ cm^3, N$_2 = 40$ cm^3/min, 25°C.

distributed itself in the aqueous phase rather than in the organic phase. Therefore, the onium hydroxide can exist in the organic phase, even in nonpolar media. The reaction mechanism of phase-transfer catalyst between two phases was clarified to be the extraction mechanism in the previous work (13). Figures 2 and 3 display the effects of the NaOH
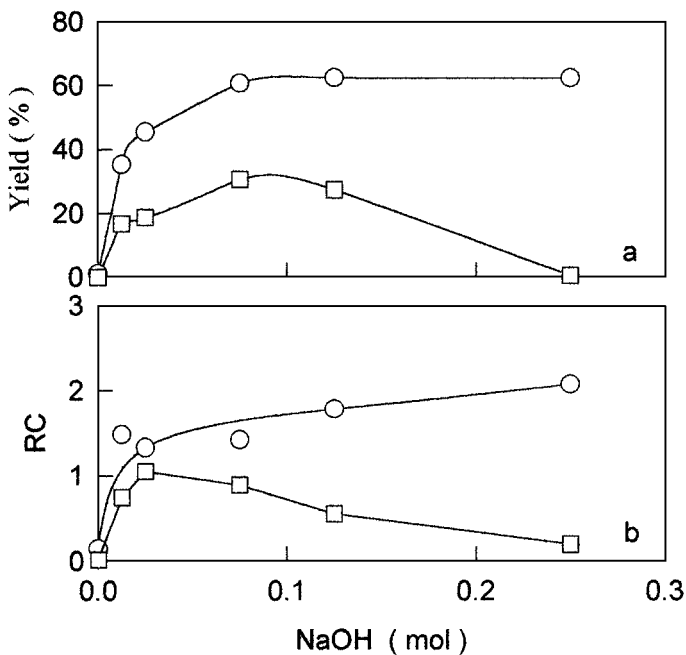

FIG. 3. Effects of NaOH on (a) yield of BMBK, (b) RC, ($\bigcirc$) TBAB $= 1.24$ mmol, ($\square$) TBAB $= 0$ mmol. The reaction conditions are the same as Fig. 2.

concentrations on the apparent rate constant, RC, and the yield of BMBK. Apparent rate constants were low and remain nearly constant in the absence of TBAB because the concentration of NaOH in the organic phase was saturated. The $k_{app,1}$ value was larger than the $k_{app,2}$ value. The reaction path (v) is not the favorite reaction. However, the apparent reaction rate constant was increased with an increasing amount of NaOH when the amount of TBAB = 1.24 mmol. The relationship between the apparent reaction rate constant and the amount of NaOH follows the second-order polynomial approximation. This finding corresponding to Eq. [16]. The consumption rate of BX and the yield of BMBK increased when the concentration of NaOH increased (Fig. 3). The yield and RC remain almost constant (62% and 2) as the NaOH concentration was larger than 0.125 mol. The increment of the concentration of NaOH cannot increase the maximum yield of BMBK.

While the amount of BX or $Fe(CO)_5$ was excess, the BMBK had a high yield (Table 1). When the molar ratio of BX to $Fe(CO)_5$ was more than 10, the yield of RCOR raised to 100%. This situation can inhibit the decay of $Fe(CO)_5$ and produce the single product of BMBK. Figure 4 shows a plot of RC and k_{app} against the concentration ratio of BX to $Fe(CO)_5$. When the amount of $Fe(CO)_5$ remained at 5.3 mmol, the amount of BX varied and the molar ratio of RX to $Fe(CO)_5$ varied from 0.5 to 10. The RC value was increased still to 3 with an increasing concentration ratio
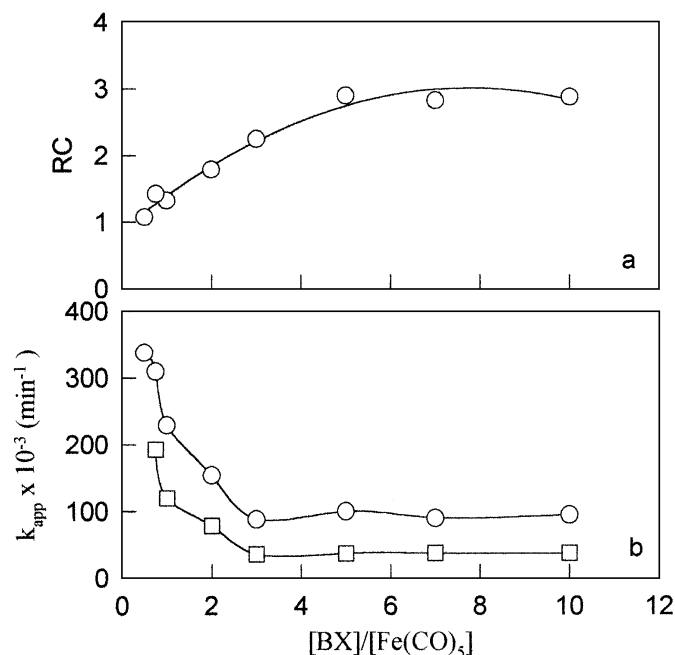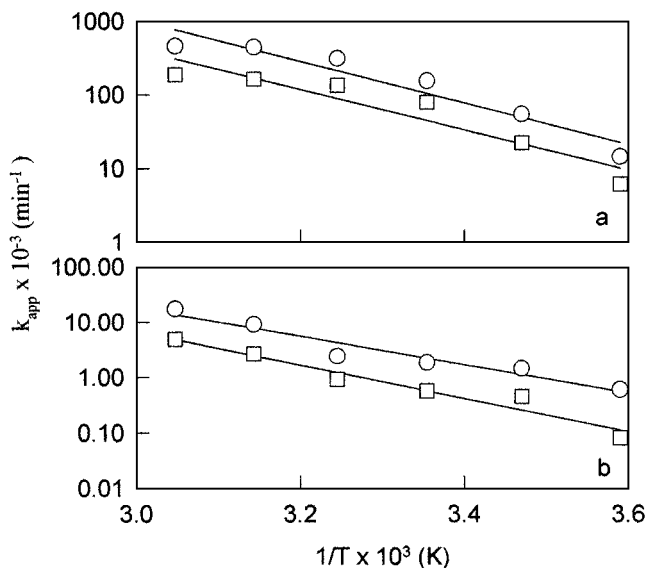

FIG. 5. Effects of temperature on k_{app}: ($\bigcirc$) $k_{app,1}$; ($\square$) $k_{app,2}$ (a) TBAB = 1.24 mmol, (b) TBAB = 0 mmol. $C_6H_6 = 50$ cm³, BX = 10.6 mmol, $Fe(CO)_5 = 5.3$ mmol, aqueous phase = 50 cm³, NaOH = 0.0125 mol, $N_2 = 40$ cm³/min.

of RX to $Fe(CO)_5$. For conventional kinetics, the changing amount of RX cannot vary the apparent reaction rate constant. However, this behavior may happen in the liquid–liquid phase-transfer catalyzed reaction (26–28). When the rate of organic reaction competes with the rate of mass transfer between the catalyst, the concentration of immediate catalyst QOH in the organic phase can not maintain constant. The rate of the side reaction and the decaying rate of $Fe(CO)_5$ increased when the concentration of QOH in the organic phase decreased.

Figure 5 depicts the temperature effect on the apparent reactant rate constant. The apparent rate constant increases when the temperature is increased. The reaction rate constant is sensible for high temperature in the blank reaction. The corresponding blank experiments without using the catalyst were also carried out in order to test the effect of the catalyst. The ratio of apparent reaction-rate constant of the catalyzed reaction to the uncatalyzed reaction exceeds by 100 times in Fig. 5. The activation energy was calculated by Arrhenius law. The activation energies of the blank reaction for $k_{app,1}$ and $k_{app,2}$ were 56.1 kJ/mol and 57.3 kJ/mol, respectively. Upon addition of TBAB, a much faster reaction rate was observed, and the activation energy $k_{app,1}$ and $k_{app,2}$ decreased to 53.7 kJ/mol and 52.2 kJ/mol, respectively, corresponding to 1.24 mmol of TBAB. This finding indicates that the contribution of TBAB for extracting the hydroxide ion is larger than that for increasing reactivity of hydroxide ion. In general, the catalyzing capability of phase-transfer catalyst results from the increasing the distance between anion and cation. NaOH and QOH are hydrophilic compound, and distributes itself in the aqueous
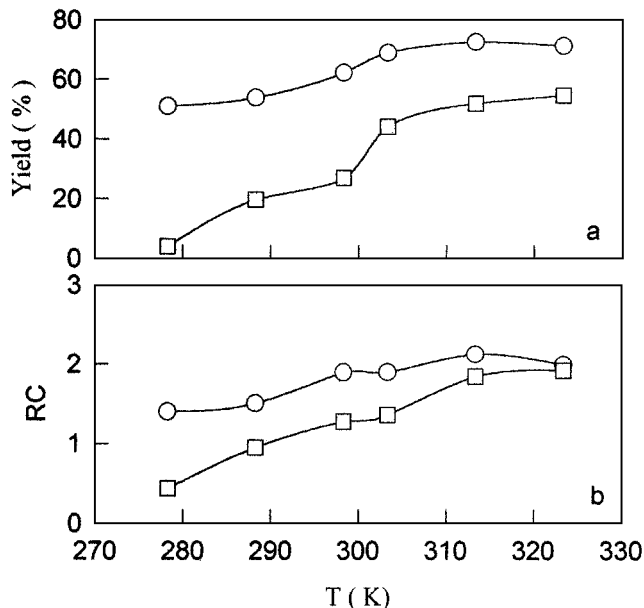

FIG. 4. Effects of [BX]/[Fe(CO)₅] on (a) RC and (b) k_{app}: ($\bigcirc$) $k_{app,1}$; ($\square$) $k_{app,2}$. $C_6H_6 = 50$ cm³, $Fe(CO)_5 = 53$ mmol, TBAB = 1.24 mmol, aqueous phase = 50 cm³, NaOH = 0.125 mol, $N_2 = 40$ cm³/min, 25°C.

FIG. 6.   Effects of temperature on (a) yield of BMBK, (b) RC, ($\bigcirc$) TBAB = 1.24 mmol, ($\square$) TBAB = 0 mmol. The reaction conditions are the same as Fig. 5.

FIG. 7.   Effects of NaBr on k_{app}: ($\bigcirc$) $k_{app,1}$; ($\square$) $k_{app,2}$ (a) TBAB = 1.24 mmol, (b) TBAB = 0 mmol. $C_6H_6 = 50$ cm^3, BX = 10.6 mmol, Fe(CO)$_5$ = 5.3 mmol, aqueous phase = 50 cm^3, NaOH = 0.0125 mol, N$_2$ = 40 cm^3/min, 25°C.

phase rather than in the organic phase. The reaction type of NaOH is similar to that of QOH. The tetra-n-butyl ammonium cation allows ion-pair to have a long distance. Hence, the activation energy is slightly decreased. In addition, the tetra-n-butyl ammonium cation is a lipophilic group so that the concentration of QOH in the organic phase is larger than that of NaOH. According to Fig. 5, the factor plays a crucial role in promoting the reaction rate. Figure 6 displays the effect of temperature on RC and yield of BMBK. When the temperature is high, the reactivity in the blank reaction approaches to that in PTC (1.24 mmol) reaction. The concentration of NaOH in the organic phase was increased with a temperature raise. Hence, the blank reaction can also obtain the higher yield of BMBK by using the higher temperature.

In general, bromide ions are generated during the reaction. The increase of sodium bromide salt will retard the reaction rate. In order to find the salt effect on the reaction, extra sodium bromide was added to the reactor. Figures 7 and 8 display the effect of NaBr in the reaction. When a larger amount of NaBr is added, the reaction rate is significantly reduced. Hence, the amount of by-product NaBr in the aqueous solution would directly influence the reaction rate. The reducing effect in the absence of TBAB makes more sense than that in the presence of TBAB.

For a constant quantity of organic solvent (50 mL), changing the aqueous volume in the reaction system not only affects the concentration of reactants in the aqueous phase but it also varies the equilibrium coefficients and mass transfer coefficient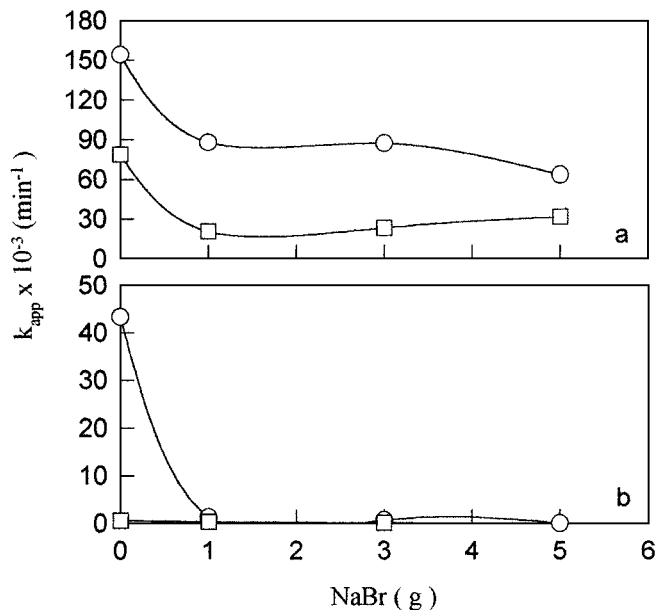s of the catalyst and interfacial areas between both phases. The effect of the aqueous volume ratio on the apparent reaction rate constant is shown in Fig. 9. The apparent reaction-rate constants have an optimum value when the aqueous volume is around 30 mL.
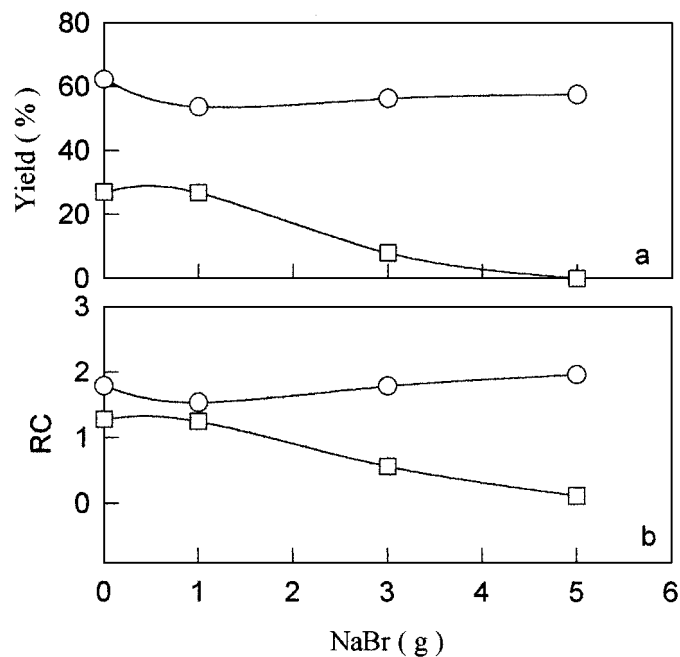

FIG. 8.   Effects of NaBr on (a) yield of BMBK, (b) RC, ($\bigcirc$) TBAB = 1.24 mmol, ($\square$) TBAB = 0 mmol. The reaction conditions are the same as Fig. 7.
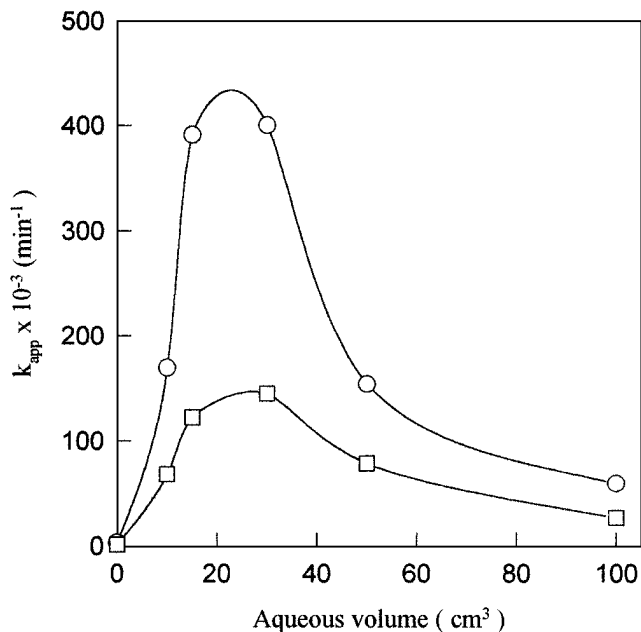
FIG. 9. Effects of aqueous volume on k_{app}: ($\bigcirc$) $k_{app,1}$; ($\square$) $k_{app,2}$. $C_6H_6 = 50$ cm^3, BX = 10.6 mmol, Fe(CO)$_5$ = 5.3 mmol, PTC = 1.24 mmol, NaOH = 0.125 mol, N$_2$ = 40 cm^3/min, 25°C.

CONCLUSION

The kinetics of carbonylation of α-bromo-p-xylene with iron pentacarbonyl in an organic/alkaline solution by phase-transfer catalysis was investigated. Apparent-rate constants were low and remain nearly constant in the absence of TBAB because the concentration of NaOH in the organic phase was saturated. The relationship between the apparent reaction rate constant and the amount of NaOH follows the second-order polynomial approximation when the amount of TBAB = 1.24 mmol. The contribution of TBAB for extracting the hydroxide ion is larger than that for increasing the reactivity of the hydroxide ion.

ACKNOWLEDGMENT

REFERENCES

1. Dehmlow, E. V., and Dehmlow, S. S., *Phase Transfer Catalysis.* Verlag Chemie, Weinheim, 1993.
2. Starks, C. M., Liotta, C., and Halpern, M., *Phase Transfer Catalysis, Fundamental, Application and Industrial Perspectives.* Chapman & Hall, London, 1994.
3. Weber, W. P., and Gokel, G. W., *Phase Transfer Catalysis in Organic Syntheses.* Springer-Verlag, New York, 1977.
4. Alper, H., *Advances in Organometallic Chemistry* **19**, 183 (1981).
5. Vancheesan, S., *J. Sci. Ind. Res.* **44**, 75 (1985).
6. Kimura, Y., Tomita, Y., Nakanishi, S., and Otsuji, Y., *Chem. Lett.*, 321 (1979).
7. Tanguy, G., Weinberger, B., and Abbayes, H. D., *Tetrahedron Lett.* **24**(37), 4005 (1983).
8. Tanguy, G., Weinberger, B., and Abbayes, H. D., *Tetrahedron Lett.* **25**(48), 5529 (1984).
9. Tustin, G., and Hembre, R. T., *J. Org. Chem.* **49**, 1761 (1984).
10. Ou, C. B., and Liu, L. K., *J. Chin. Chem. Soc.* **32**, 23 (1985).
11. Abbayes, H., Clement, J. C., Laurent, P., Tanguy, G., and Thilmont, N., *Organometallics* **7**, 2293 (1988).
12. Laurent, P., Tanguy, G., and Abbayes, H., *J. Chem. Soc. Chem. Commun.*, 1754 (1986).
13. Wu, H. S., and Tan, W. H., *J. Chem. Tech. Biotechnol.* **67**, 381 (1996).
14. Krusic, P. J., and Cote, W. J., *J. Am. Chem. Soc.* **106**, 4042 (1984).
15. Collman, J. P., Winter, S. R., and Clark, D. R., *J. Am. Chem. Soc.* **94**(5), 1788 (1972).
16. Siegl, W. O., and Collman, J. P., *J. Am. Chem. Soc.* **94**(7), 2516 (1972).
17. Collman, J. P., Finke, R. G., Cawse, J. N., and Brauman, J. I., *J. Am. Chem. Soc.* **99**(8), 2515 (1977).
18. Peake, B. M., Symons, M. C. R., and Wyatt, J. L., *J. Chem. Soc. Dalton Trans.*, 1171 (1983).
19. Norwood, K., Ali, A., Flesch, G. D., and Ng, C. Y., *J. Am. Chem. Soc.* **112**(21), 7502 (1990).
20. Cooke, M. P., Jr., *J. Am. Chem. Soc.* **92**(20), 6080 (1970).
21. Abbayes, H. D., and Buloup, A., *Tetrahedron Lett.* **21**, 4343 (1980).
22. Abbayes, H. D., and Alper, H., *J. Am. Chem. Soc.* **99**(1), 98 (1977).
23. Wu, H. S., and Lin, Y. K., *J. Chem. Eng. Japan* **27**(6), 818 (1994).
24. Wang, M. L., and Wu, H. S., *J. Org. Chem.* **55**(8), 2344 (1990).
25. Wu, H. S., Fang, T. R., Meng, S. S., and Hu, K. H., *J. Mol. Catal.* **136**(2), 135 (1998).
26. Wu, H. S., and Lai, J. J., *Ind. Eng. Chem. Res.* **34**(5), 1536 (1995).
27. Wang, M. L., and Wu, H. S., *Chem. Eng. Sci.* **46**(2), 509 (1991).
28. Wu, H. S., and S. S. Meng, *AIChE, J.* **43**(5), 1309 (1997).