

Phenolyses of 1-bromoethylbenzene by phase-transfer catalysis in a heterogeneous two-phase system

Ho-Shing Wu *, Monz-Chao Lu

Department of Chemical Engineering, Yuan-Ze Institute of Technology, No. 135, Far-East Road, NeiLi, Taoyuan, Taiwan, ROC

Received 22 November 1994; accepted 8 June 1995

Abstract

The reaction of phenol with 1-bromoethylbenzene by liquid–liquid phase-transfer catalysis in an organic solvent/alkaline solution was studied. The effects of solvents, catalysts, temperature, and basic concentration on reaction rate, and the yield of O-arylation product were studied in order to find the optimum operating conditions for this reaction. The addition of phase-transfer catalyst significantly enhanced the reaction rate and the yield of O-arylation product, and decreased the decomposition of O-arylation product. The proper basic concentration could decrease the capability of solvation between catalyst and water, and increase the O-arylated reactivity. In examining eight kinds of phase-transfer catalysts, benzyltributylammonium cation was found to be the best for increasing the reaction rate and the yield of O-arylation product.

Keywords: Bromoethylbenzene; Kinetics; Phase-transfer catalysis; Phenolysis; Selectivity; Synthesis

1. Introduction

The phase-transfer catalyzed reaction system has been studied by many chemists [1–3]. It has been extensively applied to the syntheses of special organic chemicals by displacement, alkylation, arylation, elimination, condensation, oxidation, reduction and free-radical polymerization. Advantages arising from the syntheses of organic chemicals with phase-transfer catalysis are, rapid rate of reaction, high selectivity of product, moderate operating temperature, and suitability for industrial-scale production.

Synthesized 1-methylbenzyl phenyl ether has found application in the fields of heat transfer fluids, pesticides, dyestuffs, odor substances, anti-

oxidants, and plastic additives [4,5]. Although many methods are known for the preparation of aryl alkyl ethers [6–10], the synthesis from methylbenzyl alcohol, using acid or base catalysts, was not very successful. Traditional methods of synthesis involving acid or base catalysis failed due to the facile dehydration of the methylbenzyl alcohol used as a starting material. The result was little or no aryl alkyl ether and a high styrene yield. The O-arylation product yield was low.

Phenoxide ion is well known to be an ambident anion capable of forming a covalent bond with the oxygen or carbon atom on alkylation. Ordinarily, the alkylation of phenolic salts in solution produces the O-alkylation product in high yields. However, in certain protic solvents, C-alkylation of phenolic salts dominates in the conversion process. Phase-transfer catalyzed phenoxide dis-

* Corresponding author. Fax: (+886-3)4559373, e-mail: cehswu@ce.yzit.edu.tw

placement reactions have been carefully studied [11–14]. In their results, the O-alkylation product yield could be increased using phase-transfer catalysis, and the O-alkylations of nitrophenols and salicylaldehyde were particularly noteworthy since these phenols were otherwise cleanly alkylated only by special techniques. However, the study of reaction kinetics in a two-phase reaction has been limited. In the present work, the reaction kinetics in the preparation of 1-methylbenzyl phenyl ether in an organic solvent/alkaline solution with phase-transfer catalyst was studied.

2. Experimental

2.1. Materials

Phenol, solvents, tetra-*n*-butylammonium bromide and the other quaternary ammonium salts are all reagent grade chemicals. 1-Bromoethylbenzene was distilled under reduced pressure before use.

2.2. Procedure

The reactor used was a 250-ml three-neck Pyrex flask, serving the functions of agitating the solution, inserting the thermometer and condenser, taking samples, and feeding reactants. The reactor was submerged into a constant-temperature water bath in which the temperature could be controlled to within $\pm 0.02^\circ\text{C}$. To start a kinetic run, known quantities of potassium hydroxide, phenol, and tetra-*n*-butylammonium bromide were prepared and introduced into the reactor thermostated at the desired temperature. Measured quantities of 1-bromoethylbenzene, chlorobenzene and diphenyl ether (internal standard for HPLC), which were also maintained at the desired temperature, were then added to the reactor. An aliquot sample was withdrawn from the reaction solution at a selected time interval. The sample (0.5 ml) was immediately added to 1 ml dichloromethane/2 ml of diluted hydrochloric acid to quench the reaction. The phase separation time was less than 10 s. The

organic phase content was then analyzed quantitatively by HPLC using the method of internal standard.

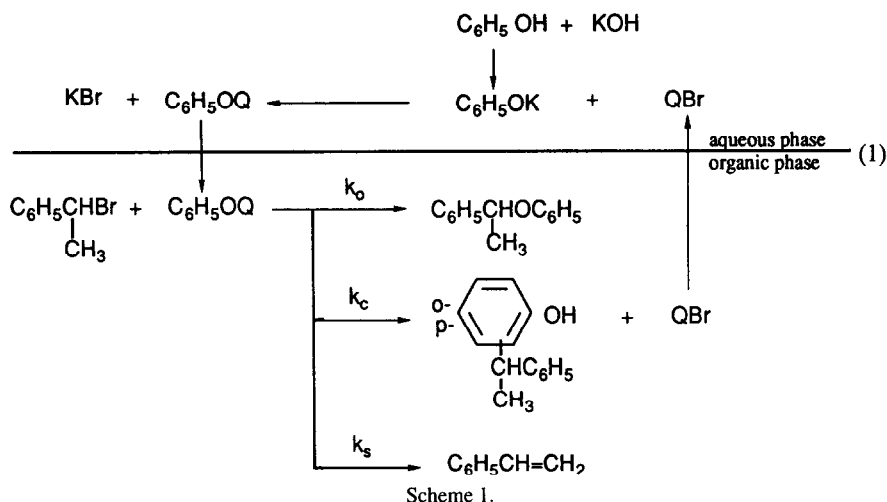
The accuracy of our analytical techniques was within 2–3% and most of the data could be reproduced well within 5% of the values reported in this work. The yields of O-arylation product were equal to the concentration of 1-methylbenzyl phenyl ether divided by the initial concentration of 1-bromoethylbenzene. They were calculated when the variation of the concentration of 1-methylbenzyl phenyl ether was less than 3%, and the concentration of 1-bromoethylbenzene was exhausted. The apparent reaction rate constant (k_{app}) was obtained by following in $[\text{RX}]$ vs. time and computed by the least-squares method (correlation coefficient > 0.99).

Liquid chromatography was carried out on a Shimadzu LC-10AD instrument, using a column packed with Inertsil 5 ODS (5 μm , Vercotech Inc). The eluent was $\text{CH}_3\text{CN}/\text{H}_2\text{O} = 3/1$, with a flow rate of 1.0 ml/min monitored at 268 nm (UV detector).

3. Kinetics of the two phase reaction

In this investigation, tetra-*n*-butylammonium bromide was used as a liquid–liquid phase-transfer catalyst. Potassium phenoxide was synthesized in situ directly by reacting phenol with potassium hydroxide in the aqueous phase. 1-Methylbenzyl phenyl ether was synthesized by reacting phenol with 1-bromoethylbenzene in an organic solvent and alkaline solution by liquid–liquid phase-transfer catalytic reaction. From Starks et al. (1994) [2] offering the classic diagram of phase-transfer catalytic cycle, the reaction scheme is as depicted in Scheme 1 where Q represents phase-transfer catalytic cation. 1-Methylbenzyl phenyl ether, styrene and a mixture of *o*- and *p*-1-phenylethylphenols were formed.

The arylations of phenoxide ion and phenol with 1-methylbenzyl alcohols were $\text{S}_{\text{N}}2$ -type substitution [15] and $\text{S}_{\text{N}}1$ -type substitution [10], respectively. Thus, the overall reaction rate



$(-r)_B$ for the case without adding phase-transfer catalyst as a promoter can be expressed as

$$\begin{aligned}
 (-r)_B &= [((-r)_o + (-r)_c + (-r)_s)_{\text{phO}^-} \\
 &\quad + ((-r)_o + (-r)_c + (-r)_s)_{\text{phOH}}]_B \\
 &= ((k_{o,B} + k_{c,B} + k_{s,B})_{\text{phO}^-} [\overline{\text{phO}^-}] \\
 &\quad + (k_{o,B} + k_{c,B} + k_{s,B})_{\text{phOH}}] [\overline{\text{RX}}] \quad (2)
 \end{aligned}$$

In the presence of PTC, the arylation of phenoxide ion comes from the contribution of the reaction with and without using PTC as a promoter. Thus, the total reaction rate $(-r)_B$, can be written as

$$(-r)_T = (-r)_{\text{PTC}} + (-r)_B \quad (3)$$

where $(-r)_{\text{PTC}}$ denotes the reaction rate which comes from the contribution with adding PTC to the reaction system, i.e.

$$\begin{aligned}
 (-r)_{\text{PTC}} &= [((-r)_o + (-r)_c + (-r)_s)]_{\text{PTC}} \\
 &= (k_{o,\text{PTC}} + k_{c,\text{PTC}} + k_{s,\text{PTC}}) [\overline{\text{phOQ}}] [\overline{\text{RX}}] \quad (4)
 \end{aligned}$$

A generalized approach to accurately describe the phase-transfer catalyzed reaction system involves using a pseudo-first order reaction [2].

$$-\frac{d[\overline{\text{RX}}]}{dt} = k_{\text{app}} [\overline{\text{RX}}] \quad (5)$$

where k_{app} is the apparent reaction rate constant. Substituting Eq. 2 and 4 into Eq. 5, k_{app} can be derived as follows:

$$\begin{aligned}
 k_{\text{app}} &= (k_{o,\text{PTC}} + k_{c,\text{PTC}} + k_{s,\text{PTC}}) [\overline{\text{phOQ}}] \\
 &\quad + (k_{o,B} + k_{c,B} + k_{s,B})_{\text{phO}^-} [\overline{\text{phO}^-}] \\
 &\quad + (k_{o,B} + k_{c,B} + k_{s,B})_{\text{phOH}} \quad (6)
 \end{aligned}$$

On the basis of experimental results (k_{app} values), the reactivity for PTC and blank reactions are analyzed.

4. Results and discussion

The phenoxide ion can be alkylated with other compounds to form a covalent bond at the oxygen or carbon atom in which O-alkylation and C-alkylation may both occur. In view of recent papers [6–10] for the synthesis of 1-methylbenzyl phenyl ether, the yield of the O-arylation product was generally below 60% in the absence of phase-transfer catalyst. The yield of O-arylation product was increased to 27% and then decreased to 11% in the present heterogeneous two-phase reaction system without adding phase-transfer catalyst (Fig. 1). The report by Kinoshita et al. [10] indicated that 1-methylbenzyl phenyl ether could be rearranged to *p*-, *o*-(1-phenylethyl)phenols by liberated hydrogen chloride in the organic phase. Hence, the experimental results reveal that the

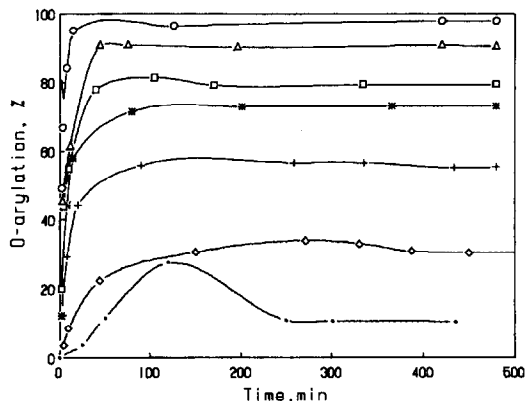


Fig. 1. Plot of the yield of O-arylation product vs. time on various amounts of $(\text{C}_4\text{H}_9)_4\text{NBr}$ (●) 0 g; (■) 0.35 g; (+) 1.05 g; (*) 2.1 g; (□) 3.5 g; (△) 5.25 g; (○) 7 g; $\text{C}_6\text{H}_5\text{Cl} = 50$ ml, $\text{KOH} = 0.25$ mol, aqueous phase = 50 ml, $\text{C}_6\text{H}_5\text{OH} = 53$ mmol, $1\text{-BrC}_2\text{H}_4\text{C}_6\text{H}_5 = 10.8$ mmol, 50°C .

small amount of phenol in the organic phase could react with 1-bromoethylbenzene by $\text{S}_{\text{N}}1$ -type substitution which liberated hydrogen chloride in this heterogeneous two-phase reaction system (Eq. 2). Moreover, sodium phenoxide exists usually in chlorobenzene as an ion pair and/or higher aggregates in the concentrated solution. Hence, the heterogeneous reaction leads to the formation of C-arylated product, more than that of O-arylated product.

Using tetra-*n*-butylammonium bromide as a liquid-liquid phase-transfer catalyst, the experimental results for studying the catalytic effects are shown in Fig. 1 and Fig. 2. The reaction was clearly enhanced by adding more catalyst and the apparent reaction rate constant was proportional to the amount of tetra-*n*-butylammonium bromide. Thus, the arylation follows second-order kinetics.

The O-alkylated yields of the PTC reaction compare favorably with those of more conventional methods, especially in critical cases where C-alkylation intervenes [11,12]. The yield of O-arylation product increases with an increasing amount of tetra-*n*-butylammonium bromide (more than 90%, Fig. 2). Moreover, 1-methylbenzyl phenyl ether was not rearranged to phenylethylphenol. No arylation of phenol and no side-reaction product (styrene) were observed in the presence of tetra-*n*-butylammonium bromide,

and no evidence was obtained from HPLC as phenol reacted with 1-bromoethylbenzene. When the amount of tetra-*n*-butyl ammonium bromide is more than 21.7 mmol, the yield of O-arylation product is found to be more than 98%. No C-arylation product was observed in this PTC reaction. The PTC-arylation of 1-bromoethylbenzene with phenoxide ion leads only to O-arylation because bulky quaternary cations activate the anion by increasing the distance separating cation from anion in the ion pair. However, the desired 1-methylbenzyl phenyl ether was obtained in excellent yield only when a stoichiometric or excess amount of ammonium salt was employed. Experimental results reflect that the arylations were best carried out using a stoichiometric or excess amount of quaternary ammonium salt, in order to avoid competition between the arylations of phenoxide ion and phenol (see Eq. 2). As noted above, Eq. 6 could be rewritten as

$$k_{\text{app}} = k_{\text{o,PTC}}[\overline{\text{phOQ}}] + (k_{\text{o,B}} + k_{\text{c,B}})[\overline{\text{phO}^-}] \quad (7)$$

Based on experimental results, $k_{\text{o,PTC}}[\overline{\text{phOQ}}]$ is more significant than $(k_{\text{o,B}} + k_{\text{c,B}})[\overline{\text{phO}^-}]$ when the amount of tetra-*n*-butylammonium bromide was equal to 21.7 mmol. The value of $k_{\text{o,PTC}} (= k_{\text{app}}/[\overline{\text{phOQ}}])$ using tetra-*n*-butylammonium bromide for phase transfer catalyst is 0.51 ($\text{mol/l}\cdot\text{min}$) $^{-1}$. The concentration of phOQ in the

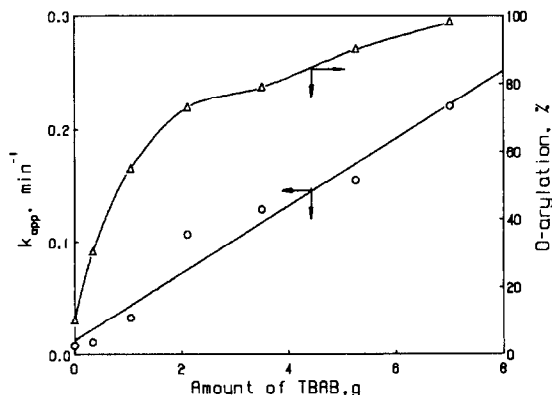


Fig. 2. Effect of $(\text{C}_4\text{H}_9)_4\text{NBr}$ on the yield of O-arylation product and apparent reaction rate constant: $\text{C}_6\text{H}_5\text{Cl} = 50$ ml, $\text{KOH} = 0.25$ mol, aqueous phase = 50 ml, $\text{C}_6\text{H}_5\text{OH} = 53$ mmol, $1\text{-BrC}_2\text{H}_4\text{C}_6\text{H}_5 = 10.8$ mmol, 50°C .

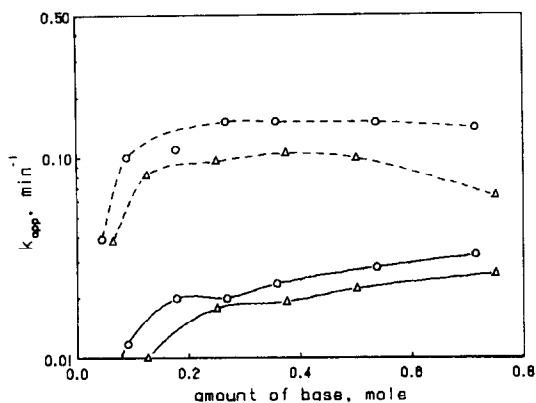


Fig. 3. Effect of base concentrations of NaOH (Δ) and KOH (\circ) on the apparent reaction rate constant (---) ($(C_4H_9)_4NBr = 6.5$ mmol; (—) ($(C_4H_9)_4NBr = 0$ mmol; $C_6H_5Cl = 50$ ml, aqueous phase = 50 ml, $C_6H_5OH = 53$ mmol, $1-BrC_2H_4C_6H_5 = 10.8$ mmol, $50^\circ C$).

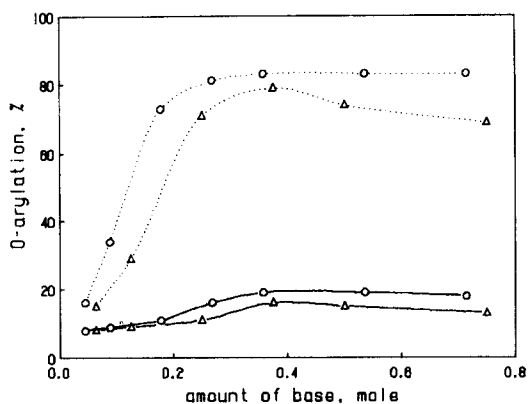


Fig. 4. Effect of concentrations of NaOH (Δ) and KOH (\circ) on the yield of O-arylation product, (---) ($(C_4H_9)_4NBr = 6.5$ mmol; (—) ($(C_4H_9)_4NBr = 0$ mmol; $C_6H_5Cl = 50$ ml, aqueous phase = 50 ml, $C_6H_5OH = 53$ mmol, $1-BrC_2H_4C_6H_5 = 10.8$ mmol, $50^\circ C$).

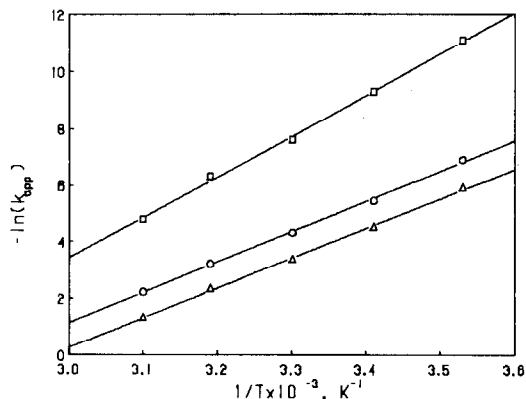


Fig. 5. Effect of temperatures on the apparent reaction rate constants for (\circ) ($(C_4H_9)_4NBr = 6.5$ mmol; (Δ) ($(C_4H_9)_4NBr = 21.7$ mmol; (\square) ($(C_4H_9)_4NBr = 0$ mmol; $C_6H_5Cl = 50$ ml, $KOH = 0.25$ mol, aqueous phase = 50 ml, $C_6H_5OH = 53$ mmol, $1-BrC_2H_4C_6H_5 = 10.8$ mmol, $50^\circ C$).

organic phase was measured by the extractive-titration method [16,17].

The effects of NaOH and KOH concentrations on the apparent reaction rate constant are illustrated in Fig. 3. The k_{app} values also increased to a maximum of 0.09 min^{-1} at 7 M. Similar to the above case for the effect of KOH, the k_{app} values were increased by increasing the concentration of KOH. In this case, the k_{app} values increased slightly when the concentration of NaOH or KOH increased without adding tetra-*n*-butylammonium bromide.

The report of Landini et al. (1982) [18] indicated that the capability of solvation between catalyst and water could be decreased by increasing the concentration of NaOH, and the substitution reactivity of $(n-C_4H_9)_4N^+ - OC_6H_5$ could be increased. Hence, the apparent reaction rate constant should be increased by increasing the free concentration of NaOH with respect to phenol. When the concentration of NaOH is more than 7 M, the aqueous solution is saturated, and a decrease in the apparent reaction rate constant is observed.

The effects of basis concentration on the yields of O-arylation product with and without the presence of tetra-*n*-butylammonium bromide are displayed in Fig. 4. The capability of solvation between catalyst $(n-C_4H_9)_4N^+ - OC_6H_5$ and water could be decreased by increasing the concentration of base. The yields of O-arylation product increased from 15 to 80% when the amount of base increased from 0.045 to 0.4 mol. The effect may be explained that the selective hydration of the oxygen of the phenoxide (higher electron density) decreases as the base concentration increases. As the oxygen of the phenoxide is less hydrated (less competition with Na^+ and OH^- for association with water molecules), the O-arylation alternative increases. Results in Fig. 3 and Fig. 4 indicate that the choice of potassium hydroxide enhances the reaction rate and the yield of O-arylation product. The results are consistent with that reported by Wu and Lai [19].

The temperature effect on the apparent reaction rate constant is shown in Fig. 5. The results show

Table 1

Effects of catalysts on the apparent rate constant and the yields of O-arylation products

PTC	k_{app}, min^{-1}	
	PTC = 21.7 mmol	PTC = 6.5 mmol
BTBAB	0.24 (99)	0.11 (74)
TBAI	0.23 (99)	0.11 (74)
TBAB	0.22 (98)	0.11 (74)
Aliq336	0.11 (40)	0.054 (28)
BTEAC	0.095 (33)	0.046 (23)
CTMAB	0.088 (28)	0.043 (20)
TEAC	0.087 (27)	0.042 (19)
TMAC	0.049 (18)	0.024 (13)

The values in parentheses are the yields of O-arylation product.

Reaction conditions: $\text{C}_6\text{H}_5\text{Cl} = 50 \text{ ml}$, $\text{KOH} = 0.25 \text{ mol}$, aqueous phase = 50 ml, $\text{C}_6\text{H}_5\text{OH} = 53 \text{ mmol}$, $1\text{-BrC}_2\text{H}_4\text{C}_6\text{H}_5 = 10.8 \text{ mmol}$, 50°C .

that the apparent reaction rate constant increases when the temperature is increased. The corresponding blank experiments without using the catalyst were also carried out in order to test the effect of the catalyst. The activation energy of the blank reaction was 28.6 kcal/mol. Upon addition of tetra-*n*-butylammonium bromide, a much faster reaction rate was obtained, and the activation energy decreased to 21.4 and 21 kcal/mol, corresponding to 6.5 mmol and 21.7 mmol of tetra-*n*-butylammonium bromide.

The functional groups of the quaternary cation generally affect the dissolution of the catalyst in the organic phase. Furthermore, the phase transfer of the anion will also affect the reaction rate in the two-phase reaction. Therefore, a proper choice of phase-transfer catalyst is rather crucial in promoting the reaction rate. The experimental results of the apparent rate constant and the yields of O-arylation product for different kinds of phase-transfer catalysts in the two-phase reaction system are shown in Table 1. The order of the reactivity for these phase-transfer catalysts is BTBAB > TBAI > TBAB > Aliq336 > BTEAC > CTMAB > TEAC > TMAC. The order of the yield of O-arylation product is BTBAB \approx TBAI \approx TBAB > Aliq336 > BTEAC > CTMAB > TEAC > TMAC. The O-arylated yield is favored in the PTC reaction. The yield of O-arylation prod-

Table 2

Effects of solvents on the apparent rate constant and the yields of O-arylation products

Solvent	Dielectric constant	k_{app}, min^{-1}	
		PTC = 21.7 mmol	PTC = 6.5 mmol
dichloromethane	9.08 (20°C)	0.30 (99)	0.14 (86)
chlorobenzene	5.6 (25°C)	0.22 (98)	0.11 (73)
toluene	2.37 (25°C)	0.20 (79)	0.091 (59)
cyclohexane	1.89 (20°C)	0.17 (72)	0.061 (54)
diethyl ether	4.33 (20°C)	0.11 (63)	0.049 (48)
benzene	2.28 (20°C)	0.088 (71)	0.046 (53)

The values in parentheses are the yield of O-arylation product.

Reaction conditions: solvent = 50 ml, $\text{KOH} = 0.25 \text{ mol}$, aqueous phase = 50 ml, $\text{C}_6\text{H}_5\text{OH} = 53 \text{ mmol}$, $1\text{-BrC}_2\text{H}_4\text{C}_6\text{H}_5 = 10.8 \text{ mmol}$, PTC = TBAB, 50°C .

uct decreases with increasing accessibility of quaternary ammonium cation [2]. The concentration of active catalyst in the organic phase, using BTEAC, CTMAB, CTMAB or TEAC was small so that its reactivity could not compete with that of ambident phenoxide ion. The significance of $k_{o,PTC}[\overline{\text{phOQ}}]$ is smaller than that of $(k_{o,B} + k_{c,B})[\overline{\text{phO}^-}]$ in Eq. 6.

Six kinds of solvents, including polar or non-polar, are examined for the sake of investigating the effects of the solvents on the apparent rate constant k_{app} and the yield of O-arylation product. The results are depicted in Table 2. The apparent reaction rate constants k_{app} of the PTC reaction for solvents with a higher dielectric constant are larger. The yields of O-arylation products were about 10% for solvents in the absence of tetra-*n*-butylammonium bromide. The yield of O-arylation product for solvents can be increased using tetra-*n*-butylammonium bromide in an organic solvent/alkaline solution. Using phase-transfer catalyst, phenoxide anion can be O-arylated in a solvent with a higher dielectric constant.

5. Conclusion

An improved process for the catalytic preparation of 1-methylbenzyl phenyl ether from phenol and 1-bromoethylbenzene with a liquid-liquid

phase-transfer catalyst in an organic solvent/alkaline solution was examined in this work. The advantages of the process are high ether yield (>98%) and the easy separation by distillation. The PTC-arylation led to O-arylation only and prevented the decomposition of 1-methylbenzyl phenyl ether. Quaternary ammonium cation accessibility, hydration and solvation effect were considered to optimize selectivity of alkylation of ambident nucleophiles. The best reaction conditions are suggested (i) the mole ratio of PTC (BTBAB used as a catalyst) to 1-bromoethylbenzene is more than 50%. (ii) the mole ratio of base (KOH) to phenol is more than 5.

6. Nomenclature

Aliq336	tricyltrimethylammonium chloride
BTBAB	benzyltributylammonium bromide
BTEAC	benzyltriethylammonium chloride
CTMAB	cetyltrimethylammonium bromide
Ind	tetrabromophenol phthalein ethyl ester potassium
k_{app}	apparent reaction rate constant, min^{-1}
k_c	rate constant for C-arylation, $(\text{mol}/\text{l}\cdot\text{min})^{-1}$
k_o	rate constant for O-arylation, $(\text{mol}/\text{l}\cdot\text{min})^{-1}$
k_s	rate constant for producing styrene, $(\text{mol}/\text{l}\cdot\text{min})^{-1}$
$(-r)_B$	reaction rate in the absence of PTC, $\text{mol}/\text{l}\cdot\text{min}^{-1}$
$(-r)_T$	overall reaction rate, $\text{mol}/\text{l}\cdot\text{min}^{-1}$
$(-r)_{PTC}$	reaction rate contribution when PTC is added, $\text{mol}/\text{l}\cdot\text{min}^{-1}$
RX	1-bromoethylbenzene
phO^-	phenoxide ion
PTC	phase-transfer catalyst
t	reaction time, min
TBAB	tetra- <i>n</i> -butylammonium bromide
TBAI	tetra- <i>n</i> -butylammonium iodide
TEAC	tetraethylammonium chloride

6.1. Superscript

species in the organic phase

6.2. Subscripts

B	reaction without using PTC
phO^-	arylation of phenoxide ion
phOH	arylation of phenol
PTC	reaction with presence of PTC
T	total amount

Acknowledgements

The authors thank the National Science Council, Taiwan, Republic of China for financial support under contract No. NSC 82-0113-E-155-051-T.

References

- [1] E.V. Dehmlow and S.S. Dehmlow, Phase Transfer Catalysis, Verlag Chemie, Weinheim, 1993.
- [2] C.M. Starks, C. Liotta and M. Halpern, Phase Transfer Catalysis, Fundamentals, Application and Industrial Perspective, Chapman & Hall, London, 1994.
- [3] W.P. Weber and G.W. Gokel, Phase Transfer Catalysis in Organic Syntheses, Springer Verlag, New York, 1977.
- [4] H.S. Kesling, Jr., US Pat. 4,514,576, (1985) (C.A. 110,22274q).
- [5] H.S. Kesling, Jr., US Pat. 4,518,806, (1985) (C.A. 110,71050x).
- [6] H. Hart and H.S. Eleuterio, J. Am. Chem. Soc., 76 (1954) 516.
- [7] K. Okamoto, H. Yamada, I. Nitta and H. Shingu, Bull. Chem. Soc. Jpn., 39 (1966) 299.
- [8] L.A. Paquette, R.P. Henzel and S.E. Wilson, J. Am. Chem. Soc., 94 (1972) 7780.
- [9] R.M. Parlman, US Pat. 4,299,996 (1981) (C.A. 96,51995t).
- [10] T. Kinoshita, T. Ueno, K. Ikai, M. Fujiwara and K. Okamoto, Bull. Chem. Soc. Jpn., 61 (1988) 3273.
- [11] E. D'Incan and P. Biout, Tetrahedron, 31 (1975) 159.
- [12] A. McKillop, J.C. Fiand and R.P. Hug, Tetrahedron, 30 (1974) 1379.
- [13] F. Montanari, S. Quici and P. Tundo, J. Org. Chem., 48 (1983) 199.
- [14] O.A. Reutov and A.C. Kurts, Russ. Chem. Rev. (Engl. Transl.), 46 (1977) 1040.

- [15] K. Okamoto, T. Kinoshita, Y. Oishi and T. Moriyama, *J. Chem. Soc., Perkin II*, (1977) 453.
- [16] T. Sakai, M. Tsubouchi, M. Nakagawa and M. Tanaka, *Anal. Chim. Acta*, 93 (1977) 357.
- [17] H.S. Wu and Y.K. Lin, *J. Chem. Eng. Jpn.*, 27 (1994) 818.
- [18] D. Landini, A. Maia and G. Podda, *J. Org. Chem.*, 47 (1982) 2264.
- [19] H.S. Wu and J.J. Lai, *J. Chin. I. Chem. Eng.*, 26 (1995) 277.