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Journal of Molecular Catalysis A: Chemical 153 (2000) 83–91

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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Phase-transfer catalyzed allylation of sodium phenoxide in a solid–liquid system

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Received 3 March 1999; received in revised form 15 May 1999; accepted 9 August 1999

Abstract

The kinetics for the O-allylation of sodium phenoxide with allyl bromide was investigated in the presence of phase-transfer catalyst in a solid–liquid system. The reaction was carried out in a stirred batch reactor under very mild operating conditions. The role of phase-transfer catalytic intermediate in the solid–liquid system was explored. Effects of various operating variables were performed. When the degree of agitation exceeded 200 rpm, the mass transfer resistance at the solid–liquid interface can be ignored. A kinetic model was proposed for the solid–liquid etherification and the experimental data were well described by the pseudo-first-order equation. The apparent activation energy was also obtained as 60.92 kJ mol^{-1} for tetra-*n*-butylammonium bromide (TBAB) as the catalyst. Experimental results also show that C-alkylation of sodium phenoxide with allyl bromide would not occur under the appropriate phase-transfer conditions.

Keywords: Phase-transfer catalysis; Solid–liquid system; Allylation; Sodium phenoxide; Kinetics

1. Introduction

The reaction rate between two mutually insoluble reactants was usually very slow. When applying a protic solvent in a severe condition for such a system, the conversion can be enhanced but generally accompanied with some unfavorable side-reactions. Such drawbacks can be overcome by using phase-transfer catalysis. The advantages of applying phase-transfer catalysts are to give rapid reaction rates and higher product selectivity under very mild reaction conditions. Numerous reactions have been investigated to explore the mechanisms and kinetics of phase-transfer catalysis especially for two-liquid system [1–4]. Nowadays, phase-transfer catalysis is widely applied in manufacturing pharmaceuticals, agricultural chemicals, perfumes, flavors, dyes and specialty polymers, and is extended to the pollution and environmental control processes.

When the reacting nucleophile is in a solid form with another reactant in the organic phase, the reaction system is called the solid–liquid phase-transfer catalysis (SL-PTC). Several reactions performed in the liquid–liquid system that might lead to severe unfavorable side-reactions can be carried out efficiently in a solid–liquid system. The catalysts used in SL-PTC include

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1381-1169/00/$ - see front matter
PII: S1381-1169(99)00304-0

tertiary amines, quaternary ammonium salts, diamines and crown ethers, etc. Two distinct mechanisms for SL-PTC, the heterogeneous solubilization and the homogeneous solubilization, were proposed by considering the solubility of solid salts in the organic phase [5]. Trace amount of water also plays an important role in SL-PTC. A thin aqueous layer called the 'omega phase' would be formed around the solid reactant to enhance the solubilization of solid reactant and the formation of catalytic intermediate. The catalytic intermediate was found to act as the key-reacting component in the solid–liquid phase-transfer reaction of dipotassium phthalate with benzyl bromide [6]. However, the behaviors of SL-PTC are still scarcely studied. A model reaction of allylation of sodium phenoxide [7] was used to investigate the characteristics of SL-PTC. The product, allyl phenyl ether, is used in the production of insecticides, herbicides, delation agent of coronary artery, dropping agent of blood pressure, tranquilizer and thermoplastic resins, etc.

In most studies on O-alkylation of phenolic salts in the protic solution, the C-alkylation of phenolic salts was also produced simultaneously. Kornblum et al. [7–9] concluded that the ratio of O-alkylation to (O + C)-alkylation for the synthesis of allylation product was small and varied with different solvents. Akabori et al. [10] applied crown ether as the phase-transfer catalyst to investigate the allylation of sodium phenoxide. In that study, the ratio of O-alkylation was improved, but along with a quite slow reaction rate. The allylation of phenol by using polyethylene glycol as the catalyst in a two-phase system was also reported to enhance the selectivity of $O/O+C$, but the reaction rate decreased with increasing polarity of organic solvent [11,12]. Wu and Lai [13,14] investigated the allylation of phenol in the two-phase system of organic solvent/alkaline solution in the presence of quaternary salts. They concluded that the O-alkylation was favored in the phase-transfer catalyzed reaction and the C-alkylation more sensitive for higher temperature. In the present study, the kinetics of sodium phenoxide with allyl bromide was investigated in the presence of tetra-*n*-butylammonium bromide (TBAB) in the solid–liquid system.

2. Experimental

2.1. Materials

Reagent sodium phenoxide with trihydrate ($C_6H_5ONa \cdot 3H_2O$, $PhONa \cdot 3H_2O$) from Merk is used as the solid reactant without further treatment. TBAB (Bu_4NBr, QBr), allyl bromide (C_3H_5Br, RBr), allyl phenyl ether (C_6H_5-OC_3H_5, PhOR, used as the standard in the analysis) and other reagents are all reagent-grade chemicals from Fluka, Lancaster and Aldrich Chemical. Tetra-*n*-butylammonium phenoxide ($PhOBu_4N$, PhOQ) was prepared from the aqueous reaction of tetra-*n*-butylammonium hydroxide with sodium phenoxide. The formed PhOQ was extracted by dichloromethane, and purified by separating the solvent, dried and then identified.

2.2. Catalytic measurement

Known quantities of phase-transfer catalyst and allyl bromide together with a definite quantity of diphenylmethane (used as the internal standard in the analysis) were added into the organic solvent dichlorobenzene and agitated in a 250 cm^3 three-neck batch reactor which was immersed in a constant-temperature water bath. For a batch run, a known quantity of sodium phenoxide was put into the reactor to start the phase-transfer reaction. The agitation speed and the reaction temperature were controlled at the desired values. During the reaction, 0.2 cm^3 of the organic sample was withdrawn at the chosen time and diluted into 4 cm^3 of acetonitrile. The concentrations of RBr, PhOQ and PhOR were measured with the internal standard method. The sample was analyzed with HPLC and a variable-wavelength UV detector at 254 nm. The eluent condition was set at a volumetric

ratio of methanol/acetonitrile/water to be 37/37/26. The flow rate was 1.0 $cm^3\ min^{-1}$. The column was the C-18 (5 μm) type.

3. The kinetic model

3.1. Independent reaction of PhONa with QBr

The formation of catalytic intermediate PhOQ plays an important role in the solid–liquid reaction system. The independent ion-exchange reaction is

$$\mathrm{PhONa(s) + QBr(org) \rightarrow PhOQ(org) + NaBr(s)}. \quad (1)$$

This reaction would involve the following steps.

(1) Dissolution of PhONa. The salt PhONa with trihydrate was used as the solid reactant. Since a trace of water was present in the solid reactant, the omega phase around the solid particle might be formed to enhance the solubilization of PhONa in organic solvent. Hence, the solid part of PhONa is in equilibrium with its soluble part. The expression is:

$$\mathrm{PhONa(s) \rightleftarrows PhONa(org)}. \quad (2)$$

(2) Reaction of PhONa with QBr. Phase-transfer catalyst QBr would react with the soluble parts of PhONa to form PhOQ in the solid–liquid interface. The film reaction is usually reversible and is written as

$$\mathrm{PhONa(org) + QBr(org) \overset{K_1}{\rightleftarrows} PhOQ(org) + NaBr(org)} \quad (3)$$

with

$$K_1 = \frac{C^*_{\mathrm{PhOQ}} C^*_{\mathrm{NaBr}}}{C^*_{\mathrm{PhONa}} C^*_{\mathrm{QBr}}}. \quad (4)$$

In Eq. (4), the superscript * represents the component concentration in the layer adjacent to the surface of the solid reactant.

(3) Mass transfer of PhOQ to the bulk phase. The formed PhOQ then transfers from the solid–liquid interface to the organic phase in which the solubility of PhOQ is limited. The expression is given as

$$V_{\mathrm{org}} \frac{\mathrm{d}C_{\mathrm{PhOQ}}}{\mathrm{d}t} = k_{\mathrm{m}} A_{\mathrm{s}} (C^*_{\mathrm{PhOQ}} - C_{\mathrm{PhOQ}}). \quad (5)$$

In Eq. (5), A_{s} denotes the surface area of solid particle and is gradually reduced during the progress of reaction. N_i denotes the number of moles of component i. Thus, at time t, A_{s} can be expressed as

$$A_{\mathrm{s}} = A_{\mathrm{s}0} \left(\frac{N_{\mathrm{PhONa},0} - N_{\mathrm{PhOQ}}}{N_{\mathrm{PhONa},0}} \right)^{2/3} = A_{\mathrm{s}0} \left(1 - q\bar{C}_{\mathrm{PhOQ}}\right)^{2/3} \quad (6)$$

$$\text{with } q = \frac{N_{\mathrm{QBr},0}}{N_{\mathrm{PhONa},0}} \text{ and } \bar{C}_{\mathrm{PhOQ}} = \frac{C_{\mathrm{PhOQ}}}{C_{\mathrm{QBr},0}}. \quad (7)$$

The mass transfer coefficient k_{m} is also dependent on the particle size. The mass transfer coefficient is inversely proportional to n power of the particle size, in which n is in the range of 0.25 to 1.0 from high degrees of agitation (high Reynolds numbers) to low degrees of agitation (low Reynolds numbers). Hence, k_{m} is expressed in a function of salt conversion as,

$$k_{\mathrm{m}} = k_{\mathrm{m}0} \left(\frac{N_{\mathrm{PhONa},0} - N_{\mathrm{PhOQ}}}{N_{\mathrm{PhONa},0}} \right)^{-n/3} = k_{\mathrm{m}0} \left(1 - q\bar{C}_{\mathrm{PhOQ}}\right)^{-n/3}. \quad (8)$$

Combining Eqs. (5), (6) and (8), we have

$$\frac{\mathrm{d}\bar{C}_{\mathrm{PhOQ}}}{\mathrm{d}t} = \alpha \left(1 - \beta \bar{C}_{\mathrm{PhOQ}}\right) \left(1 - q\bar{C}_{\mathrm{PhOQ}}\right)^{(2-n)/3} \quad (9)$$

$$\text{where } \beta = \frac{C_{\mathrm{QBr},0} C^*_{\mathrm{NaBr}}}{K_1 C^*_{\mathrm{PhONa}} C^*_{\mathrm{QBr}}} \text{ and } \alpha = \frac{k_{\mathrm{m}0} A_{\mathrm{s}0}}{\beta V_{\mathrm{org}}}. \quad (10)$$

Eq. (9), with the initial condition, at $t = 0$, $C_{\mathrm{PhOQ}} = 0$, can be numerically solved by introducing the parameters α and β.

3.2. The overall reaction of PhONa with RBr

By adding the organic substrate into the organic solvent, the overall reaction in solid–liquid phases is expressed as

$$\mathrm{PhONa(s)} + \mathrm{RBr(org)} \overset{\mathrm{QBr}}{\rightarrow} \mathrm{PhOR(org)} + \mathrm{NaBr(s)}. \quad (11)$$

The reactants, PhONa and QBr, conducted to form PhOQ, that then reacts with RBr to produce the desired product PhOR. This intrinsic reaction is

$$\mathrm{PhOQ(org)} + \mathrm{RBr(org)} \overset{k_{\mathrm{in}}}{\rightarrow} \mathrm{PhOR(org)} + \mathrm{QBr(org)}. \quad (12)$$

The intrinsic reaction is a bimolecular elementary reaction of second order, and the rate of change of PhOR is given as

$$\frac{\mathrm{d}C_{\mathrm{PhOR}}}{\mathrm{d}t} = k_{\mathrm{in}} C_{\mathrm{PhOQ}} C_{\mathrm{RBr}}. \quad (13)$$

By taking mass balance for R group, the above equation is rewritten in terms of the product yield as follows.

$$\frac{\mathrm{d}\overline{C}_{\mathrm{PhOR}}}{\mathrm{d}t} = k_{\mathrm{in}} C_{\mathrm{QBr},0} \overline{C}_{\mathrm{PhOQ}} \left(1 - \overline{C}_{\mathrm{PhOR}}\right) \quad (14)$$

where $\overline{C}_{\mathrm{PhOR}} = \dfrac{C_{\mathrm{PhOR}}}{C_{\mathrm{RBr},0}} = \text{yield of PhOR} = Y.$

The rate of change of PhOQ in the overall reaction is thus deduced as

$$\frac{\mathrm{d}\overline{C}_{\mathrm{PhOQ}}}{\mathrm{d}t} = \alpha\left(1 - \beta\overline{C}_{\mathrm{PhOQ}}\right)\left(1 - q\overline{C}_{\mathrm{PhOQ}}\right)^{(2-n)/3} - k_{\mathrm{in}} C_{\mathrm{RBr},0} \overline{C}_{\mathrm{PhOQ}} \left(1 - \overline{C}_{\mathrm{PhOR}}\right). \quad (15)$$

If the quantities of PhOQ were kept at near constant values after the induction period, the pseudo-first-order behavior would be observed. Therefore, Eq. (13) is simplified to the form

$$\frac{\mathrm{d}Y}{\mathrm{d}t} = k_{\mathrm{app}}(1 - Y), \quad (16)$$

where k_{app} is the apparent reaction rate constant with $k_{\mathrm{app}} = k_{\mathrm{in}} C_{\mathrm{QBr},0} \overline{C}_{\mathrm{PhOQ}}$.

Eq. (16) can be easily solved to give the pseudo-first-order rate constant k_{app} by plotting $-\ln(1 - Y)$ vs. t from the experimental data.

4. Results and Discussion

4.1. Behaviors of catalytic intermediate

Regarding the formation of PhOQ in SL-PTC, the independent experiments for solid PhONa reacting with QBr at different temperatures were performed. The experimental results are shown in Fig. 1. The near saturated concentrations of PhOQ were reached after about 20 min of operation. The difference of PhOQ at various reaction temperatures was not significant. This shows that the catalytic intermediate PhOQ can be formed from tetra-*n*-butylammonium salt reacted with PhONa even in a solid–liquid system. Transferred from the outside layer of the solid particle to the bulk organic phase, the produced PhOQ will then conduct the intrinsic reaction. The degree of agitation influences the mass transfer rate of PhOQ. By applying pseudo-first-order kinetics for different agitation

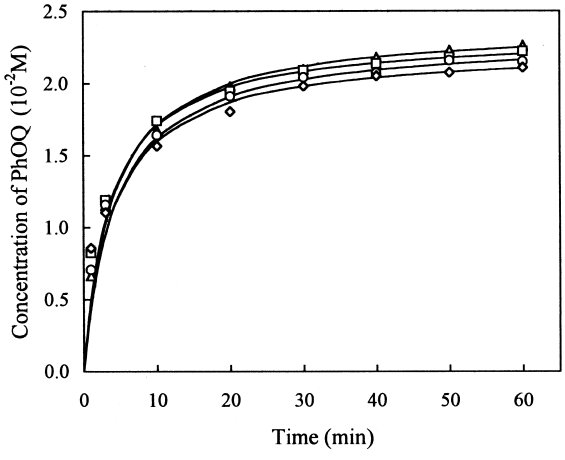

Fig. 1. Concentration of PhOQ for PhONa reacted with QBr. Operating conditions: dichlorobenzene, 50 cm^3; PhONa, 0.002 mol; TBAB, 0.002 mol; agitation speed, 350 rpm; temperature (°C): (△) 30 (□) 35 (○) 40 (◇) 45.

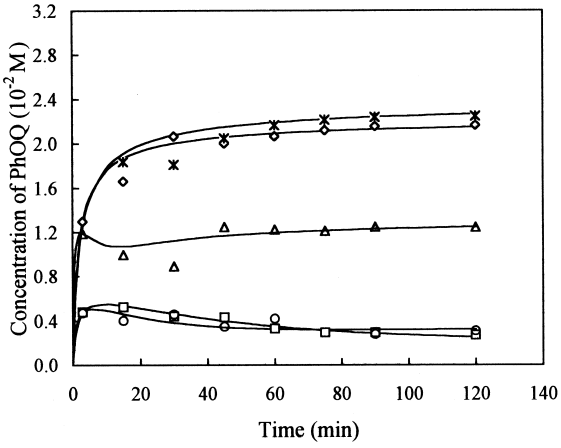

Fig. 2. Variation of PhOQ for different amounts of TBAB used. Operating conditions: temperature, 35°C; dichlorobenzene, 50 cm^3; RBr, 0.005 mol; PhONa, 0.01 mol; agitation speed, 350 rpm; f value: (□) 0.075 (○) 0.1 (△) 0.15 (◇) 0.2 (✱) 0.25.

speeds, the apparent rate constants for 100, 200, 350, 500 and 800 rpm were estimated as 0.015, 0.035, 0.038, 0.031 and 0.034 min^{-1}, respectively. The agitation effect is insignificant as the speed exceeding 200 rpm. Hence, the ion-exchange reaction and the mass transfer resistance between solid and liquid phases are not the limiting steps in the overall reaction.

To evaluate the effect of catalyst amounts, Different molar ratios of TBAB to PhONa (denoted as f) were investigated, and the product yield was less than 2% in 2 h of duration for $f = 0$ at 35°C. Increasing the catalyst usage up to $f = 0.2$, the yield of PhOR increased to 100% for 2 h of operation. In addition, the concentration of PhOQ did not increase for $f > 0.2$ due to its limiting solubility in dichlorobenzene. The overall reaction rate was thus increased not too much. Such phenomena can be explained by Fig. 2. It is seen that the concentration of PhOQ increased to a near constant value as increasing molar quantity of TBAB after induction period. However, the concentration of PhOQ for f equal to 0.25 was only slightly higher than that for $f = 0.2$. In this solid–liquid reaction system, too much catalyst is not appropriate for enhancing reaction rate. Pseudo-first-order kinetics can be well applied to describe the overall reaction. Moreover, the effect of induction period is more significant for lower quantity of catalyst used. The apparent rate constants as well as the product yields are shown in Table 1.

In principle, the reaction rate constant is not affected by the relative usage of reactants for an elementary reaction. In the present phase-transfer catalyzed system, several reaction and mass transfer steps were involved. The concentration of PhOQ in organic solvent was also dependent on the molar ratio of reactants, thus influencing the observed reaction rate. The yields as well as the profiles of PhOQ are shown in Figs. 3 and 4, respectively. By keeping constant usage of RBr, the yield decreased with increasing molar ratio of PhONa to RBr (denoted as M). These

Table 1
Effect of TBAB amounts and temperature on the apparent reaction rate constant[a]

Entry no.	Temperature (°C)	TBAB (mol)	$10^2 k_{app}$ (min^{-1})	Yield of PhOR (%)	
				at 0.5 h	at 2 h
1	35	0.00075	0.241	24.1	35.6
2	35	0.001	0.336	35.0	52.2
3	35	0.0015	1.402	47.2	84.9
4	35	0.0025	4.324	77.4	100
5	45	0.002	4.656	85.1	100
6	40	0.002	4.052	74.0	100
7	35	0.002	3.793	72.3	100
8	30	0.002	2.266	61.1	95.5
9	25	0.002	0.914	41.2	77.8

[a] Sodium phenoxide: 0.01 mol; allyl bromide: 0.005 mol; dichlorobenzene: 50 cm^3; agitation speed: 350 rpm.

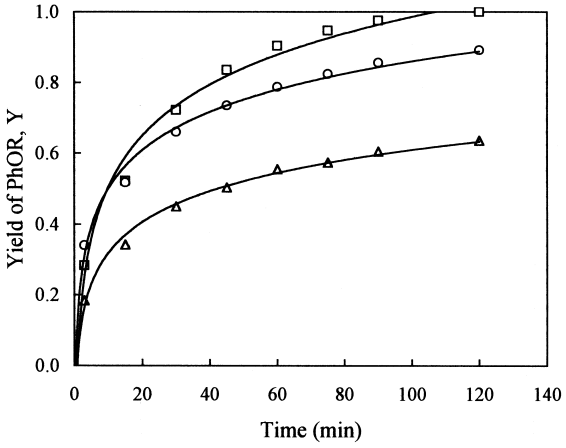

Fig. 3. Effect of different molar ratios of PhONa to RBr on the yield. Operating conditions: temperature, 35°C; dichlorobenzene, 50 cm^3; RBr, 0.005 mol; TBAB, 0.002 mol; agitation speed, 350 rpm; M value: (□) 2 (○) 3 (△) 4.

results are somewhat strange. However, such phenomena can be explained by the variation of concentration of PhOQ for various M. From the results in Fig. 4, the near equilibrium concentration of PhOQ decreased with increasing M. The PhOQ concentration in the organic phase increased from zero to an approximate constant value for $M = 2$. While for M equal to 3 or 4, the PhOQ concentration first increased from zero to a maximum value, then decreased to a near constant. Such declines of PhOQ were expected to result from the influence of extra solid PhONa. From the experimental observation, the PhONa fine particles would aggregate to form larger solid clusters for $M > 3$ during the agitated reaction. This leads to the effective surface area of PhONa particles reduced. The probability of contact of PhONa with TBAB as well as the mass transfer rate of PhOQ was then diminished in dichlorobenzene. Hence, the formation of PhOQ was inhibited due to the solid salt concentrated in the organic solvent. The lower PhOQ concentration in the organic phase caused to a lower intrinsic reaction rate for greater M. The rate-determining step was identified as the intrinsic reaction of PhOQ with RBr.

To further investigate the behaviors of formation of PhOQ in this solid–liquid system, the independent reaction of solid PhONa and TBAB in dichlorobenzene without the addition of RBr at different molar ratios PhONa to TBAB (denoted as r) were performed. The results are shown in Fig. 5. From the profiles of PhOQ vs. time, the PhOQ concentration decreased with increasing r-values by keeping a constant TBAB usage. At the condition of $r > 5$, the PhOQ concentration in dichlorobenzene increased to a

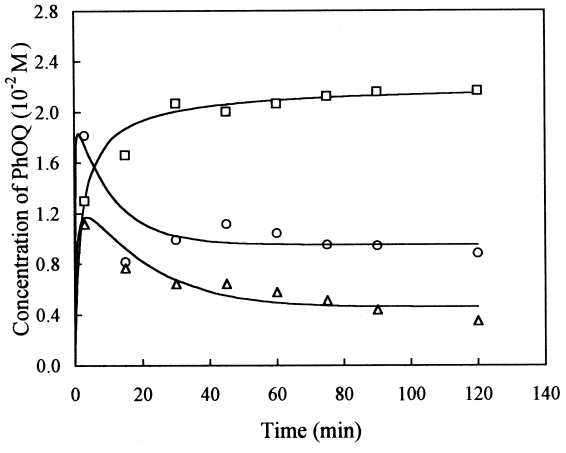

Fig. 4. Variation of PhOQ for different molar ratios of PhONa to RBr. Operating conditions as in Fig. 3; M value: (□) 2 (○) 3 (△) 4.

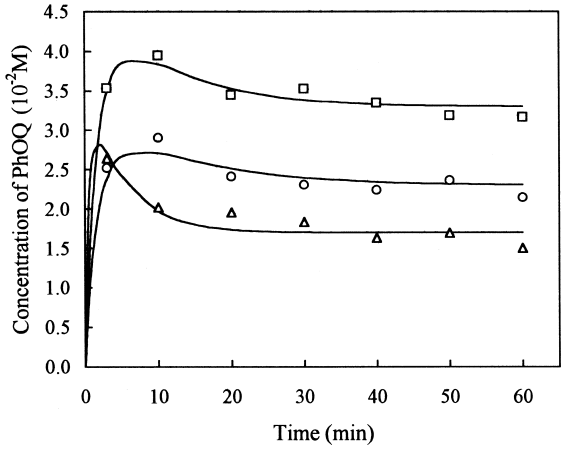

Fig. 5. Concentration of PhOQ for PhONa reacted with QBr. Operating conditions: dichlorobenzene, 50 cm^3; PhONa, 0.002 mol; TBAB, 0.002 mol; agitation speed, 350 rpm; r-value: (△) 5 (□) 7.5 (○) 10.

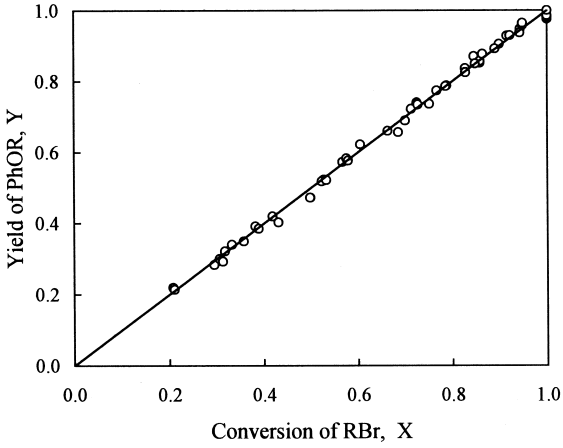

Fig. 6. Plot of yield of PhOR vs. conversion of RBr.

maximum then decreased to a near constant value. From the experimental observation, the initial fine particle of PhONa (with particle size in the range of 80–120 mesh) aggregated to finally form three larger clusters (with particle size about 10 mm) after 1 h of operation for the case of *r*-value equal to 10. Some of the already formed PhOQ was also adsorbed on the solid clusters. A greater reduction of PhOQ concentration in the dichlorobenzene solvent was thus observed, compared to the case of *r*-value equal to 5. The degree of aggregation of solid particles is believed to depend upon the relative usage of reactants and catalyst. This result strongly demonstrates that the PhONa aggregate retards the formation and transfer of PhOQ into the organic phase for greater molar ratio of PhONa to TBAB in the solid–liquid system.

4.2. Efficiency of phase-transfer catalyst

Experiments at different temperatures were performed to investigate the activation energy for TBAB in this solid–liquid phase-transfer reaction. The results are shown in Table 1. The yield increases as the temperature increases and follows the pseudo-first-order kinetics. The apparent activation energy for TBAB was obtained as 60.92 kJ mol^{-1} by applying the Arrhenius' equation, $k_{app} = A \exp(-E/RT)$, and the rate expression was correlated as $k_{app} = 6.058 \times 10^8 \exp(-60923/RT)$. The catalytic efficiency of TBAB was quite high with very mild operating conditions in the present solid–liquid system. Moreover, the C-alkylation of sodium phenoxide with allyl bromide was not observed in the experimental conditions of temperature below 45°C as described above. Fig. 6 shows the plot of the yield of PhOR vs. the conversion of RBr for the above reaction conditions. The quite consistency of conversion and yield demonstrates that no other side reactions, e.g., the C-allylation, were conducted for the above appropriate experimental conditions.

To identify the catalytic efficiency of catalysts, various phase-transfer catalysts with different cations and anions were performed. The tested catalysts were TBAB, tetra-*n*-butylammonium iodide (TBAI), tetra-*n*-butylphosphonium bromide (TBPB), tetra-*n*-butylammonium hydrogen sulfate (TBAHS), benzyltriethylammonium bromide (BTEAB), aliquat 336 and PEG

Table 2
Effect of different types of phase-transfer catalysts on the apparent reaction rate constant[a]

Entry no.	PTC (mol)	$10^2 k_{app}$ (min^{-1})	({O}/{O + C}) at 3.0 h	Yield of PhOR (%)	
				at 1.0 h	at 3.0 h
1	TBAB	0.527	0.783	31.1	66.0
2	TBPB	0.770	0.873	41.6	78.4
3	TBAI	0.698	0.891	48.3	74.9
4	TBAHS	0.515	0.824	35.0	62.2
5	BTEAB	0.064	0.378	5.1	11.7
6	Aliquat 336	0.481	0.775	38.4	63.9
7	PEG 1000	0.903	0.934	61.7	83.7

[a] Sodium phenoxide: 0.01 mol; allyl bromide: 0.01 mol; dichlorobenzene: 50 cm^3; phase-transfer catalyst: 0.001 mol; temperature: 50°C; agitation speed: 350 rpm.

1000. Unfortunately, at the higher temperature greater than 50°C, different degrees of C-allylation for various catalysts were observed. The pseudo-first-order rate constants, the degree of O-alkylation and the product yields are shown in Table 2. This might be due to the higher affinity for RBr with PhONa in another reaction route at temperature greater than 50°C. The better operating temperature would be expected below 45°C for this system. However, at a temperature of 50°C, the best performance of catalyst tested above was PEG 1000 with the least side-reaction and the highest reaction rate. The reactivity sequence was PEG 1000 > TBPB > TBAI > TBAB > TBAHS > aliquat 336 > BTEAB. The different reactivity for catalysts with the same tetra-*n*-butylammonium group exhibits that the lipophilic property of anion group in catalyst governs the formation of the catalytic intermediate. In addition, the reaction mechanism for using PEG 1000 in solid–liquid phase-transfer reaction would be expected to be different from that for quaternary onium catalyst. A future research work would be worthy to investigate the phenomena of PEG 1000 as the phase-transfer catalyst in the solid–liquid reaction system.

5. Conclusion

In the present work, the kinetics for the O-allylation of sodium phenoxide with allyl bromide to produce allyl phenyl ether in the solid–liquid phase-transfer conditions was investigated. The reactions were carried out in an isothermal stirred batch reactor. The role of phase-transfer catalytic intermediate in the solid–liquid system was explored. Effects of various operating variables were performed. A kinetic model was proposed to describe the overall reaction. The experimental data were well fitted by the pseudo-first-order equation. The apparent activation energy for TBAB was also obtained. Using the present reaction conditions, the side-reaction C-alkylation was not observed for the appropriate conditions. Various types of phase-transfer catalysts were also employed to compare their catalytic efficiency. This work provides an effective method for conducting allylation of sodium phenoxide and realizes the behavior of the catalytic intermediate.

6. Nomenclature

A	frequency factor in the Arrhenius equation
A_s	surface area of solid particles, dm^2
C_i	concentration of the *i*-component
$\overline{C}_{PhOQ}$	dimensionless concentration of PhOQ defined in Eq. (7)
$\overline{C}_{PhOR}$	dimensionless concentration of PhOR defined in Eq. (14)
E	apparent activation energy, J mol^{-1}
K_1	equilibrium constant for Eq. (4)
k_{app}	apparent reaction rate constant, min^{-1}
k_{in}	intrinsic reaction rate constant, mol dm^{-1} min^{-1}
k_m	mass transfer coefficient for PhOQ, dm min^{-1}
N_i	number of moles for component *i*
PhONa	sodium phenoxide
PhOQ	tetra-*n*-butylammonium phenoxide
PhOR	allyl phenyl ether
q	parameter defined in Eq. (7)
QBr	tetra-*n*-butylammonium bromide
R	gas constant
RBr	allyl bromide
t	time, min
X	conversion of allyl bromide
Y	yield of allyl phenyl ether
Greek Symbol	
α	parameter defined in Eq. (10)
β	parameter defined in Eq. (10)
Subscript	
0	initial condition

Acknowledgements

The authors acknowledge the financial support of the National Science Council, Taiwan, Republic of China (Grant No. NSC 88-2214-E-005-006).

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