Kinetics for etherification of sodium *o*-nitrophenoxide via third-liquid phase-transfer catalysis

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Abstract

The novel method for synthesizing *o*-nitrophenyl octyl ether from the etherification of sodium *o*-nitrophenoxide and 1-bromooctane was investigated via third-liquid phase-transfer catalysis (TLPTC). The volume of the third-liquid phase formed increases with increasing the amount of catalyst employed, and about 91.2% of tetrabutylammonium bromide (TBPB) was accumulated in the third-liquid phase by adding 0.07 mol of NaOH, leading to a higher reactivity. The product yield greater than 98% was obtained within 3 h of reaction using TBPB at 80 °C. The variations of the catalytic intermediate in the third-liquid phase during reaction were explored. The consumption rate of the catalytic intermediate increased with the increase of reaction rates. The enhancement factor (η) of the catalytic intermediate in third-liquid phase can be correlated as a linear function of the product yield (Y) in the organic phase as $\eta = \alpha_1 - \alpha_2 Y$. Based on the experimental observations, a kinetic model of pseudo-first-order was proposed to successfully describe the overall reaction with the apparent activation energy to be 23.32 kcal/mol for 0.003 mol of TBPB used. The interfacial phenomenon affected by catalytic intermediate and catalyst was also performed. The third-liquid phase-transfer catalysis is demonstrated as an effective method to synthesize specialty chemicals.
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Keywords: Third-liquid phase; Phase-transfer catalysis; Etherification; Interfacial tension; *o*-Nitrophenyl octyl ether

1. Introduction

For the reaction between two mutually insoluble reactants in organic synthesis, the rate is usually very slow merely by contacting the reactants in the interface, and a severe reaction condition is commonly applied, resulting in the difficulty of subsequent separation steps. In 1951, Jarrousse [1] found that the reaction rate could be improved by applying small amounts of quaternary ammonium salts in aqueous–organic systems under mild conditions. In 1971, Starks [2] conducted the nucleophilic substitution of sodium cyanide with *n*-octyl chloride by adding quaternary ammonium salts as the catalyst, and the reaction rate was greatly enhanced to obtain about 100% of product yield after several hours of reaction,

thus terming this type of reaction as phase-transfer catalysis. Nowadays, phase-transfer catalysis is widely applied in the synthesis of specialty chemicals, e.g. pharmaceuticals, flavors, dyes, perfumes, etc.

In 1984, Neumann and Sasson investigated the isomerization of allylanisole using polyethylene glycol as the catalyst in a toluene and aqueous KOH solution and observed a third-liquid phase formed between the aqueous and the organic phases [3]. Wang and Weng (1988) performed the reaction of benzyl chloride and sodium bromide using tetra-*n*-butylammonium bromide as the phase-transfer catalyst in liquid–liquid phases, and found that the overall reaction rate rapidly increased when the amount of catalyst exceeded some critical value, above which a viscous liquid phase concentrated with catalyst was insoluble in both aqueous and organic phases [4]. Mason et al. [5] investigated the elimination of phenethyl bromide to styrene using tetrabutylammonium

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bromide (TBAB) under phase-transfer conditions, and found that the third-liquid phase can only be formed under the conditions of using TBAB and 40% of aqueous NaOH solution. In 1994, Starks et al. [6] classified the third-liquid phase as the field of insoluble phase-transfer catalyst. Wang and Weng explored the effects of solvents and salts on the formation of a third-liquid phase for the reaction of *n*-butyl bromide and sodium phenolate, and concluded that the solvents of different polarities and the amount of NaOH were two important factors in the formation of a third-liquid phase, the distribution of catalyst and the reaction rate [7]. Ido et al. [8] investigated the formation of third-liquid phase by using tetrapentylammonium bromide as the catalyst and toluene as the solvent, and found that no formation of third-liquid phase was observed even by adding excess KBr, while formed by using dodecane as the solvent. Yadav and Reddy investigated the *n*-butoxylation of *p*-chloronitrobenzene (PCNB) using the base NaOH under tri-liquid phases conditions and the distribution of catalyst between organic and third-liquid phases indicated about 89% of total catalyst residing in the third-liquid phase [9].

In general, third-liquid phase-transfer catalysis (TLPTC) has the advantages of higher reaction rates and selectivity, easy separation of catalyst and product, mild reaction conditions, cheaper solvents and alkali compounds used, and easy reuse and recovery of catalyst, etc. [10,11]. For TLPTC, the catalytic intermediate in the third-liquid phase plays an important role in the multiphase reaction system; however, it lacked to be studied in the past literatures. The synthesis of *o*-nitrophenyl octyl ether, whose manufacturing method announced by Kaneko and Tanaka [12] was the reaction of nitrobenzenes and aldehydes catalyzed by Pd-C catalyst under 40–160 °C with varied side products formed, is investigated via third-liquid phase-transfer catalysis to obtain a higher reaction rate and selectivity in the present study. The formation of the third-liquid phase, the behaviors of the catalytic intermediate, the interfacial phenomenon, and the kinetics were all explored.

2. Experimental

The aqueous reactant *o*-nitrophenol sodium salt, the organic reactant 1-bromooctane, tetrabutylphosphonium bromide (TBPB), tetrabutylammonium bromide (TBAB), tetrabutylammonium iodide (TBAI), benzyl tributylammonium bromide (BTBAB), and tetrabutylammonium hydrogensulfate (TBAHS) were all purchased from ACROS and TCI, and were used without further treatments.

2.1. Synthesis of catalytic intermediate and product

Definite amounts of TBPB and *o*-nitrophenol sodium salt were dissolved and agitated in 20 cm^3 of de-ionized water to form tetrabutylphosphonium *o*-nitrophenoxide, that was then salted into the third-liquid phase. The third-liquid phase was taken and washed with 2 cm^3 of water three times to remove the unreacted aqueous reactant and catalyst. The red-gel type of catalytic intermediate, tetrabutylphosphonium *o*-nitrophenoxide was purified from the third-liquid phase and then identified. The ^{1}H NMR spectrum for standard tetrabutylphosphonium *o*-nitrophenoxide is shown in Fig. A.1.
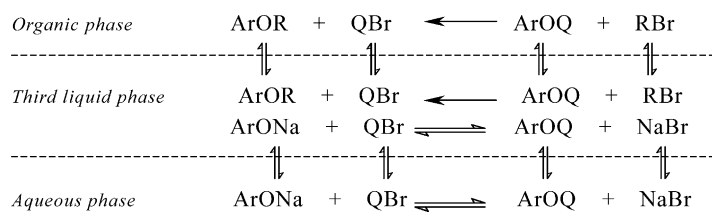
The product *o*-nitrophenyl octyl ether was synthesized as follows. An excess amount of sodium *o*-nitrophenoxide dissolving in 20 cm^3 of de-ionized water and 20 cm^3 of toluene solution containing 0.003 mol of TBPB and 0.01 mol of 1-bromooctane were agitated and reacted in a 250-cm^3 flask at 70 °C for 24 h. After the reaction, the product in the organic phase was separated and purified by liquid chromatography method and vacuum evaporation, and then identified. The boiling point and specific gravity of *o*-nitrophenyl octyl ether are 197–198 °C and 1.041, respectively. The ^{1}H NMR spectrum for standard *o*-nitrophenyl octyl ether is shown in Fig. A.2.

2.2. Third-liquid phase-transfer catalytic etherification

For kinetic analysis, definite amounts of aqueous reactant, sodium *o*-nitrophenoxide, sodium hydroxide, inorganic salt, and phase-transfer catalyst were added into 20 cm^3 of de-ionized water and toluene The solution was shaken for 10 min at 60 °C and 150 rpm to form the third-liquid phase. The volumes of the third-liquid, the aqueous, and the organic phases were measured. The three phases were then agitated at the desired speed in a 150-cm^3 reactor, which was immersed in a constant-temperature water bath, and controlled at the desired temperature. For a batch of run, known quantities of organic reactant 1-bromooctane and diphenylmethane (as the internal standard) were added into the reactor to start the phase-transfer reaction. During the reaction, 0.2 cm^3 of the organic sample or third-liquid phase was withdrawn at the chosen time. The amount of total catalyst *Q* in the third-liquid phase was determined by Volhard's method, and the organic sample was diluted into 4 cm^3 of acetonitrile to determine ArOQ and product with internal method using HPLC and a variable-wavelength UV detector at 254 nm. The elution conditions were set at a volumetric ratio of actonitrile/water to be 80/20. The flow rate is 1.0 cm^3 min^{-1} and the column is C18 (5 μm) type.

3. Kinetic model

The etherification reaction of aqueous sodium *o*-nitrophenoxide with 1-bromooctane was carried out under third-liquid phase-transfer catalytic conditions. The reaction scheme is shown as follows:

Organic phase	ArOR	+	QBr	⟵	ArOQ	+	RBr

Third liquid phase	ArOR	+	QBr	⟵	ArOQ	+	RBr
	ArONa	+	QBr	⇌	ArOQ	+	NaBr

Aqueous phase	ArONa	+	QBr	⇌	ArOQ	+	NaBr

The key step and reactant for the above reactions is the formation of catalytic intermediate (ArOQ), which is produced from the ion exchange reaction of sodium *o*-nitrophenoxide (ArONa) and phase-transfer catalyst (QBr), and the reaction and transfer steps included in the overall reaction are:

(1) formation of catalytic intermediate ArOQ from the reaction of ArONa and QBr;
(2) transfer and distribution of ArOQ between the aqueous and third-liquid phases;
(3) transfer and distribution of ArOQ between the third-liquid and organic phases;
(4) transfer and distribution of RBr from the organic into the third-liquid phase;
(5) intrinsic reaction of ArOQ with RBr in the third-liquid phase,

$$\text{ArOQ}_{(third)} + \text{RBr}_{(third)} \rightarrow \text{ArOR}_{(third)} + \text{QBr}_{(third)}$$
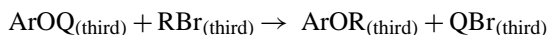
with rate constant k_2 and the reaction rate

$$\frac{dC_{ArOQ}^{third}}{dt} = -k_2 C_{RBr}^{third} C_{ArOQ}^{third}; \tag{1}$$

(6) intrinsic reaction of small amounts of ArOQ with RBr in the organic phase with rate constant k_1 and the reaction rate $\frac{dC_{ArOQ}^{org}}{dt}$:

$$\text{ArOQ}_{(org)} + \text{RBr}_{(org)} \rightarrow \text{ArOR}_{(org)} + \text{QBr}_{(org)};$$
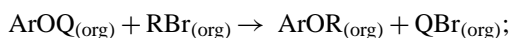
(7) transfer and distribution of QBr between the organic/third-liquid and the third-liquid/aqueous phases;
(8) transfer and distribution of product ArOR between the third-liquid and the organic phases.

From the experimental observations, the amount of ArONa in the third-liquid phase is only about 0.00234% of ArONa initially added; thus, the concentration of ArONa in third-liquid phase can be reasonably neglected. Moreover, the concentration of ArOQ in the aqueous phase can also be neglected because the catalyst in the aqueous phase is merely 1.5% of it initially added and the lipophilicity of ArOQ resulting in fast transport of it into the third-liquid phase when it is just formed. The product yield (Y) and the enhancement factor of catalytic intermediate (η) are defined on the basis of the initial concentration of ArONa, C_{ArONa}^0, as $Y = \frac{C_{ArOR}^{org}}{C_{ArONa}^0}$ and $\eta = \frac{C_{ArOQ}^{third}}{C_{ArONa}^0}$. From the experimental data, a linear relation of enhancement factor of catalytic intermediate in the third-liquid phase with the product yield was observed, i.e. $\eta = \alpha_1 - \alpha_2 Y$, implying that α_1 and α_2 are

approximately constant under specific reaction conditions. The physical meaning of α_1 represents the initial fraction of ArONa in the form of the catalytic intermediate, and the value of α_2 shows the consumption velocity of ArOQ on Y. The derivation of α_1 and α_2 as a function of system parameters is deduced in detail in Appendix B.

For a large excess usage of RBr relative to ArONa, the overall reaction rate for the present etherification would be the sum of ArOQ reacted with RBr in both third-liquid and organic phases; however, since the scale and variation of the concentration of ArOQ on reaction time in the organic phase are very small relative to that in the third-liquid phase, hence, the overall reaction is dominated by the intrinsic reaction of ArOQ and RBr in the third-liquid phase and the reaction rate in the organic phase can be neglected by applying the pseudo-steady-state-hypothesis as the following equation:

$$V^{third} \frac{dC_{ArOQ}^{third}}{dt} + V^{org} \frac{dC_{ArOQ}^{org}}{dt} \approx V^{third} \frac{dC_{ArOQ}^{third}}{dt} \tag{2}$$

Substituting $\eta = \alpha_1 - \alpha_2 Y$ into Eqs. (1) and (2), we have

$$\frac{d(\alpha_1 - \alpha_2 Y)}{dt} = -k_2 C_{RBr}^{third}(\alpha_1 - \alpha_2 Y) \tag{3}$$

From the experimental observations, the variation of the concentration of RBr in the third-liquid phase C_{RBr}^{third} versus time is so small as to be approximately constant; thus the apparent reaction rate constant is defined as $k_{app} = k_2 C_{RBr}^{third}$ and Eq. (3) becomes

$$\frac{d(\alpha_1 - \alpha_2 Y)}{dt} = -k_{app}(\alpha_1 - \alpha_2 Y) \tag{4}$$

Integrating Eq. (4) by using initial condition, $Y = 0$ at $t = 0$, it gives

$$-\ln(\alpha_1 - \alpha_2 Y) = k_{app}t - \ln\alpha_1, \quad or$$

$$-\ln(\eta) = k_{app}t - \ln\alpha_1 \tag{5}$$

By plotting η versus Y for each reaction condition, the parameters α_1 and α_2 are correlated and then substituted into Eq. (5) to obtain the apparent reaction rate constant k_{app} from the plot of $-\ln(\alpha_1 - \alpha_2 Y)$ versus t. The apparent activation energy can also be estimated by applying Arrhenius' equation, $k_{app} = A \exp(-E_{app}/RT)$.
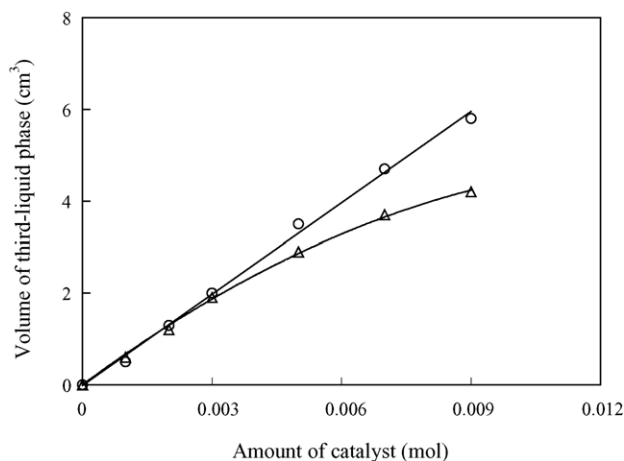
Fig. 1. Effect of PTC type on the formation of third-liquid phase: water $20\,cm^3$, toluene $20\,cm^3$, sodium o-nitrophenoxide 0.005 mol, NaOH 0.05 mol, temperature 80 °C; PTC: (○) TBPB; (△) TBAHS.

Fig. 2. Total Q^+ and ArOQ in the third-liquid phase for different amounts of TBPB: water $20\,cm^3$, toluene $20\,cm^3$, o-nitrophenoxide 0.005 mol, NaOH 0.05 mol, temperature 80 °C; TBPB: (○) total Q^+; (□) ArOQ.

4. Results and discussion

4.1. Formation of the third-liquid phase and the catalytic intermediate

The third-liquid phase formed by introducing phase-transfer catalysts, aqueous reactant, and inorganic salts exceeding the critical amounts has the volume almost less than $6\,cm^3$, as shown in Fig. 1. It shows that the volume of third-liquid phase increases linearly with increasing the amount of tetra-n-butylphosphonium bromide (TBPB) employed, but not linearly with tetra-n-butylammonium hydrogensulfate (TBAHS). This is due to TBAHS more hydrophilic than TBPB and much TBAHS would stay in the aqueous phase when the amount of TBAHS exceeds 0.005 mol. Table 1 shows that effect of different amounts of ArONa on the formation of third-liquid phase. It reveals that the volume of third-liquid phase increases with the increase of ArONa added, however, if ArONa is added too much, the precipitation of salts would occur. These results show that the third-liquid phase can be formed for either hydrophilic or hydrophobic type of PTC under the present conditions.

Fig. 2 shows the variation of total catalyst Q and catalytic intermediate ArOQ in the third-liquid phase for different amounts of TBPB employed. From the results, almost all of Q in the third-liquid phase was in the form of ArOQ when

the usage of TBPB was less than 0.005 mol of ArONa used. This fact shows that the active catalyst in the third-liquid phase is ArOQ. Table 1 also shows the amounts of ArOQ in the third-liquid phase increases with increasing the quantity of ArONa, and above 84% of catalyst Q is in the form of ArOQ when the amount of ArONa is greater than 0.005 mol.

The addition of NaOH would also affect the formation of the third-liquid phase and the amount of ArOQ in the third-liquid phase. When the quantity of NaOH used was in the range of 0–0.07 mol, the amount of ArOQ in the third-liquid phase increased with increasing NaOH, due to salting out effect in the aqueous phase, as shown in Table 2. When 0.07 mol of NaOH was employed, 91.2% of PTC in the form of ArOQ was concentrated in the third-liquid phase. The rate of reaction would thus be greatly enhanced.

4.2. Etherification via third-liquid phase-transfer catalysis

Since the reaction mainly carried out in the third-liquid phase, the organic reactant 1-bromooctane would transfer into the third-liquid phase to react with the catalytic intermediate, which is produced from the reaction of sodium o-nitrophenoxide and TBPB, the amounts of 1-bromooctane and PTC would affect the concentration of ArOQ in the

Table 1
ArOQ in third-liquid phase for different amounts of ArONa before reaction

ArONa (mol)	Volume of third-liquid phase (mL)	ArOQ in third-liquid phase (mmol)
0.001	1.3	0.765
0.002	1.7	1.564
0.005	2.0	2.539
0.008	2.2	2.564
0.01	2.4	2.568

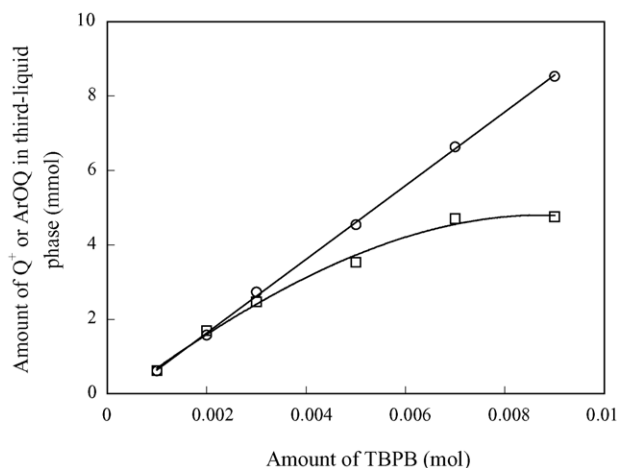Operating conditions: water 20 mL; toluene 20 mL; NaOH 0.05 mol; TBPB 0.003 mol; temperature 80 °C.

Table 2
Effect of NaOH on ArOQ formed in the third-liquid phase before reaction

NaOH (mol)	ArOQ (mmol)	ArOQ/TBPB added (%)
0	1.837	61.2
0.01	2.236	74.5
0.03	2.496	83.2
0.05	2.539	84.6
0.07	2.735	91.2

Operating conditions: water $20\,cm^3$; toluene $20\,cm^3$; sodium o-nitrophenoxide 0.005 mol; TBPB 0.003 mol; temperature 80 °C.
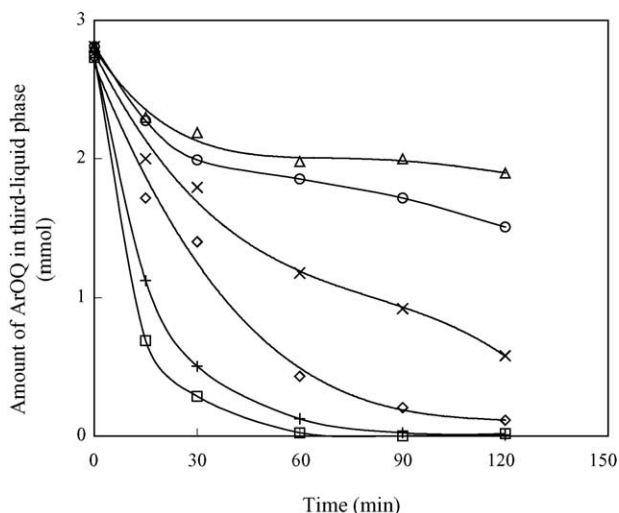
Fig. 3. Effect of 1-bromooctane on ArOQ in the third-liquid phase: toluene 20 mL, water 20 mL, TBPB 0.003 mol, NaOH 0.05 mol, o-nitrophenol sodium salt 0.005 mol, temperature 80 °C, 400 rpm, 1-bromooctane: (△) 0.0025; (○) 0.005; (×) 0.01; (◇) 0.02; (+) 0.04; (□) 0.07.

Fig. 5. C_{ArOQ}^{third}, C_{RBr}^{third} and C_{ArOQ}^{org} vs. reaction time: water 20 cm^3, toluene 20 cm^3, sodium o-nitrophenoxide 0.005 mol, NaOH 0.05 mol, TBPB 0.003 mol, 1-bromooctane 0.02 mol, temperature 80 °C, agitation speed 400 rpm: (◇) C_{ArOQ}^{third}; (○) C_{RBr}^{third}; (△) C_{ArOQ}^{org}.

third-liquid phase. Fig. 3 shows that the variation of ArOQ in the third-liquid phase for various amounts of 1-bromooctane used. It is obvious that ArOQ is gradually consumed and quickly decreases with reaction time for large excess usage of 1-bromooctane relative to that of ArONa. This demonstrates that the catalytic intermediate in the third-liquid phase is the key-reactant of the etherification. Fig. 4 depicts the variation of ArOQ in the third-liquid phase for different temperatures and reveals that a faster reaction rate at a higher temperature consumes ArOQ much more rapidly than at a lower temperature. This shows that the importance of formation of ArOQ at a high concentration is significant to conduct the etherification of sodium o-nitrophenoxide.

Fig. 4. Catalytic intermediate in the third-liquid phase vs. time for different temperatures: water 20 cm^3, toluene 20 cm^3, sodium o-nitrophenoxide 0.005 mol, NaOH 0.05 mol, TBPB 0.003 mol, 1-bromooctane 0.02 mol, agitation speed 400 rpm; temperature: (□) 40 °C; (◇) 60 °C; (●) 70 °C; (○) 80 °C; (△) 90 °C.

Based on the variation of ArOQ in the third-liquid phase on reaction time, a kinetic model is proposed to describe the third-liquid phase-transfer catalyzed etherification. Fig. 5 shows the variations of C_{ArOQ}^{org}, C_{ArOQ}^{third} and C_{RBr}^{third} on reaction time. It is seen that C_{ArOQ}^{org} and its variation is relatively very small with respect to C_{ArOQ}^{third}; hence, the effect of C_{ArOQ}^{org} on the overall reaction can be neglected and the intrinsic reaction is verified to mainly conduct in the third-liquid phase. Moreover, the variation of C_{RBr}^{third} on time is small and approximately constant, compared to that of C_{ArOQ}^{third}; therefore, the apparent reaction rate constant can be expressed as $k_{app} = k_2 C_{RBr}^{third}$. The correlations of typical experimental data are shown in Fig. 6(a). By expressing the enhancement factor of ArOQ as a function of the product yield, the parameters α_1 and α_2 can be correlated, and the pseudo-first-order apparent reaction rate constant can be obtained from the plot of Fig. 6(b). This shows that the proposed kinetic model can be applied to describe the present reaction system successfully.

The resistance of mass-transfer between phases may influence the overall reaction rate. For the conditions of water 20 cm^3, toluene 20 cm^3, sodium o-nitrophenoxide 0.005 mol, NaOH 0.05 mol, TBPB 0.003 mol, and 1-bromooctane 0.02 mol at 80 °C, the apparent reaction rate constant (k_{app}) was 0.0191 min^{-1} without agitation, but increased to be 0.024 min^{-1} and kept almost constant when the agitation speed was greater than 200 rpm, implying that the effect of mass-transfer resistance between phases can be neglected for agitation speed exceeding 200 rpm.

Fig. 7 shows the product yields for different phase-transfer catalysts, and exhibits that almost 100% of yield can be obtained using TBPB as the catalyst under the appropriate conditions. TBPB behaved the highest catalytic activity among the tested catalysts, due to its much higher reactivity with
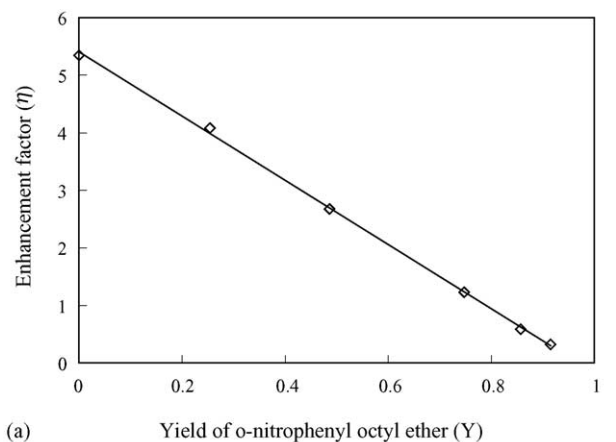
(a)

Yield of o-nitrophenyl octyl ether (Y)

(b)

Time (min)
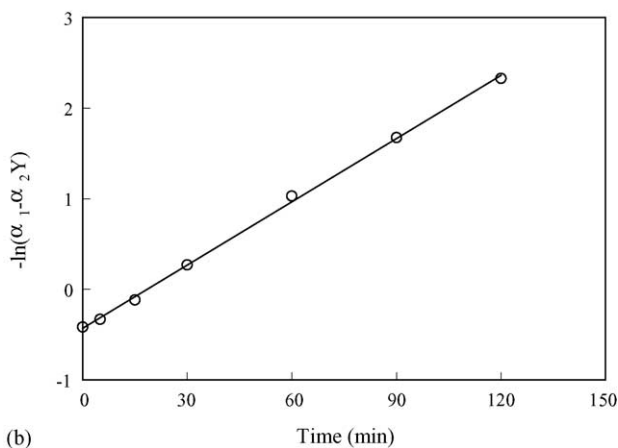
Fig. 6. (a and b) Plot of enhancement factor vs. product yield and correlation of k_{app}: water $20\,cm^3$, toluene $20\,cm^3$, sodium *o*-nitrophenoxide 0.005 mol, NaOH 0.05 mol, TBPB 0.003 mol, 1-bromooctane 0.02 mol, temperature $80\,^\circ C$, agitation speed 400 rpm.

Time (min)
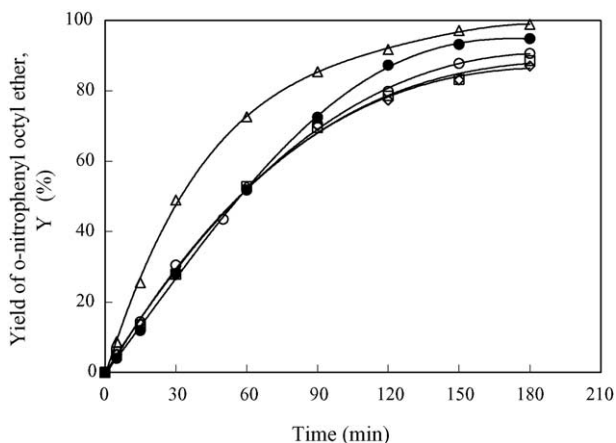
Fig. 7. Product yield vs. reaction time for different catalysts: water $20\,cm^3$, toluene $20\,cm^3$, sodium *o*-nitrophenoxide 0.005 mol, NaOH 0.05 mol, PTC 0.003 mol, 1-bromooctane 0.02 mol, temperaure $80\,^\circ C$, agitation speed 400 rpm; PTC: ($\triangle$) TBPB; ($\bullet$) TBAI; ($\bigcirc$) TBAHS; ($\square$) BTBAB; ($\diamond$) TBAB.

Amount of TBPB (mol)
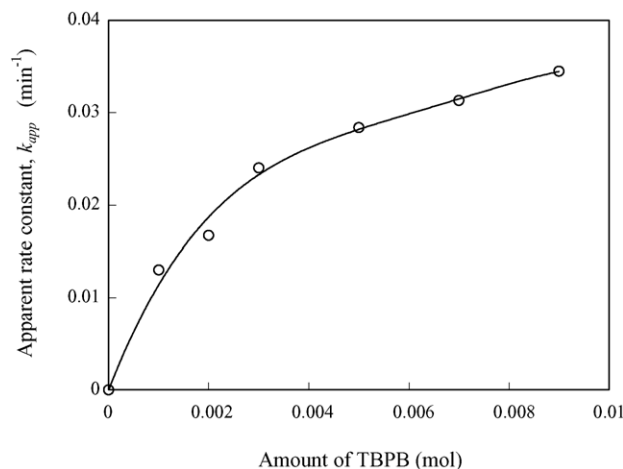
Fig. 8. Effect of amounts of TBPB on the apparent reaction rate constant: water $20\,cm^3$, toluene $20\,cm^3$, sodium *o*-nitrophenoxide 0.005 mol, NaOH 0.05 mol, TBPB 0.003 mol, 1-bromooctane 0.02 mol, temperature $80\,^\circ C$, agitation speed 400 rpm.

the aqueous reactant. Fig. 8 shows the variation of apparent reaction rate constant for different amounts of TBPB employed. Without the addition of TBPB, there was no third-liquid phase formed and no product was observed before 120 min of duration with the system being liquid–liquid type. By adding 0.001 mol of TBPB, $0.5\,cm^3$ of third-liquid phase was formed, and k_{app} was $0.013\,min^{-1}$ and increased with increasing the amount of TBPB.

Fig. 9(a) shows that greater product yields were obtained for higher temperatures. Using the concentration of ArOQ detected in the third-liquid phase and the product yield at the chosen sampling time, the linear plot of the enhancement factor of ArOQ with product yield can be obtained. The parameter α_1 represents the initial amount of ArOQ when the third-liquid phase is formed, and the parameter α_2 means the consumption rate of ArOQ in the third-liquid phase during the reaction. At a higher reaction rate, the value of α_2 is higher than it at a lower rate. Using the estimated values of α_1 and α_2, the plot of $-\ln(\alpha_1 - \alpha_2 Y)$ versus t gives the apparent reaction rate constants at different temperatures, as shown in Fig. 9(b). The rate constants k_{app} estimated are $2.83 \times 10^{-4}\,min^{-1}$ for $40\,^\circ C$, $2.60 \times 10^{-3}\,min^{-1}$ for $60\,^\circ C$, $9.20 \times 10^{-3}\,min^{-1}$ for $70\,^\circ C$, $2.40 \times 10^{-2}\,min^{-1}$ for $80\,^\circ C$, and $4.27 \times 10^{-2}\,min^{-1}$ for $90\,^\circ C$. The apparent activation energy can be obtained by using Arrhenius' equation as 23.32 kcal/mol.

4.3. Interfacial characteristics of tri-liquid phases

The interfacial tension between phases reflects the characteristics of the third-liquid phase, and can reveal whether the transport of ingredients between phases is easy or not. Fig. 10 shows the variation of interfacial tension between organic/third-liquid phases as well as third-liquid/aqueous phases for different NaOH introduced. It is seen that the interfacial tension between third-liquid/aqueous phases increases with increasing the amount of NaOH; hence, the
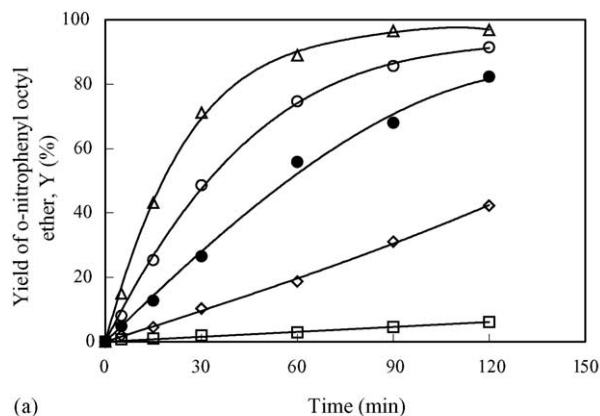
(a)
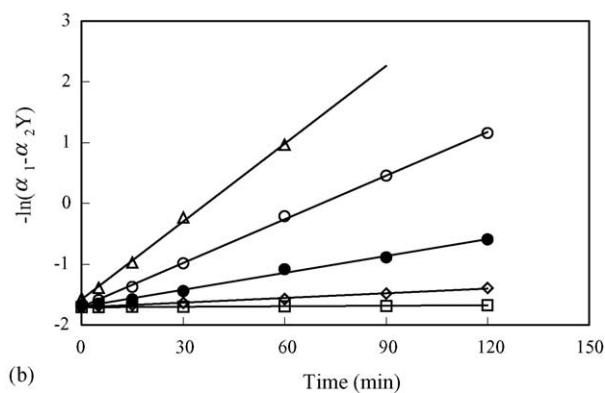
(b)

Fig. 9. (a and b) Product yield and $-\ln(\alpha_1 - \alpha_2 Y)$ vs. reaction time for different reaction temperatures: water $20\,cm^3$, toluene $20\,cm^3$, sodium o-nitrophenoxide 0.005 mol, NaOH 0.05 mol, TBPB 0.003 mol, 1-bromooctane 0.02 mol, agitation speed 400 rpm; tempeature: ($\square$) 40 °C; ($\diamond$) 60 °C; ($\bullet$) 70 °C; ($\bigcirc$) 80 °C; ($\triangle$) 90 °C.

main resistance for transport dominates in the aqueous phase side. Fig. 11 is the interfacial tension for various amounts of ArONa, and shows that the interfacial tension between third-liquid/aqueous phases reduces when the usage of aque-
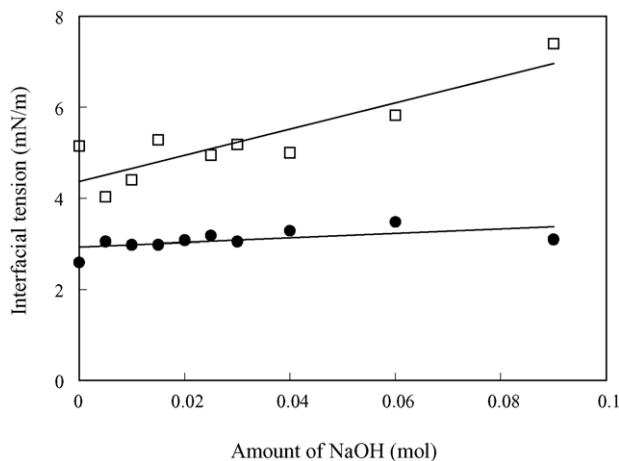
Fig. 10. Effect of NaOH on the interfacial tension: toluene 20 mL, water 20 mL, TBPB 0.003 mol, 2-nitrophenol sodium salt 0.005 mol, 1-bromooctane 0.02 mol: ($\bullet$) organic/third-liquid interface; ($\square$) third-liquid/aqueous interface.
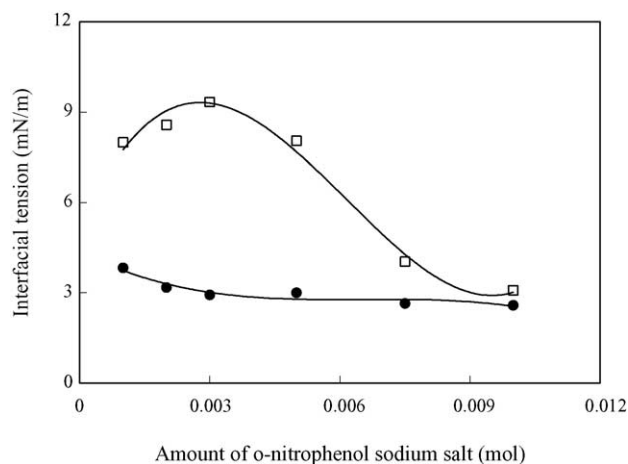
Fig. 11. Interfacial tension using different amounts of sodium o-nitrophenoxide: water $20\,cm^3$, toluene $20\,cm^3$, NaOH 0.05 mol, TBPB 0.003 mol; interface: ($\square$) third-liquid/aqueous; ($\bullet$) organic/third-liquid.
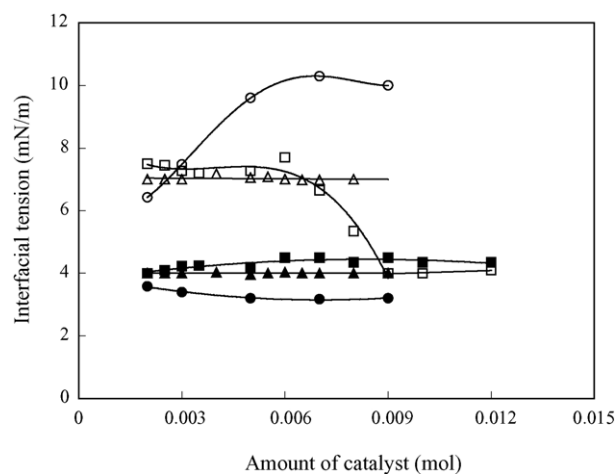

Fig. 12. Interfacial tension using different phase-transfer catalysts: water $20\,cm^3$, toluene $20\,cm^3$, sodium o-nitrophenoxide 0.005 mol, NaOH 0.05 mol; interface: interfacial tention for third-liquid/aqueous phases: ($\bigcirc$) TBPB; ($\square$) TBAHS; ($\triangle$) TBAB; interfacial tension for organic/third-liquid phases: ($\bullet$) TBPB; ($\blacksquare$) TBAHS; ($\blacktriangle$) TBAB.

ous reactant exceeds 0.003 mol. This exhibits that increasing the aqueous reactant can promote the formation of catalytic intermediate, leading to the resistance of transport gradually diminished. Fig. 12 shows the effects of different phase-transfer catalysts on the interfacial tension of third-liquid/aqueous phases and organic/third-liquid phases, and also demonstrates that the main resistance of transport exists in the aqueous side for the present tri-liquid system.

5. Conclusion

The novel method for synthesizing o-nitrophenyl octyl ether was investigated via third-liquid phase-transfer catalysis. The behaviors of catalytic intermediate in third-liquid phase and the interfacial characteristics between phases were

explored. The consumption rate of the catalytic intermediate in third-liquid phase increased with the increase of reaction rates. A kinetic model was successfully used to describe the overall reaction. The third-liquid phase-transfer catalysis is demonstrated as an effective method to synthesize specialty chemicals.

Acknowledgement

Appendix A. ^{1}H NMR spectrum of compounds

A.1. *Standard o-nitrophenyl octyl ether*

The ^{1}H NMR spectrum for *o*-nitrophenyl octyl ether used as the standard is shown in Fig. A.1.

A.2. *Standard tetra-n-butylphosphonium o-nitrophenoxide*

The ^{1}H NMR spectrum for the catalytic intermediate, tetra-*n*-butylphosphonium 2-nitrophenoxide used as the standard is shown in Fig. A.2.
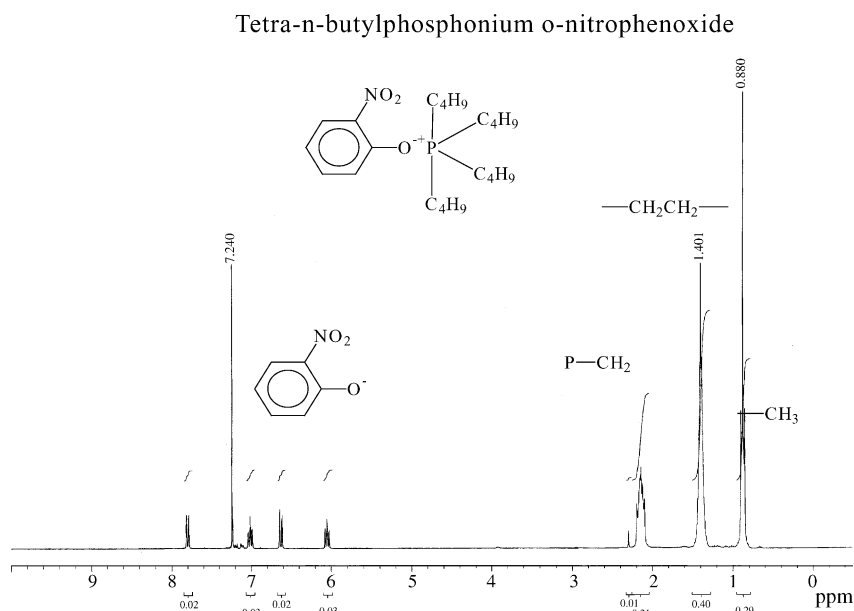
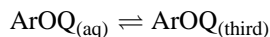Fig. A.1. ^{1}H NMR spectrum of standard tetra-*n*-butylphosphonium *o*-nitrophenoxide.
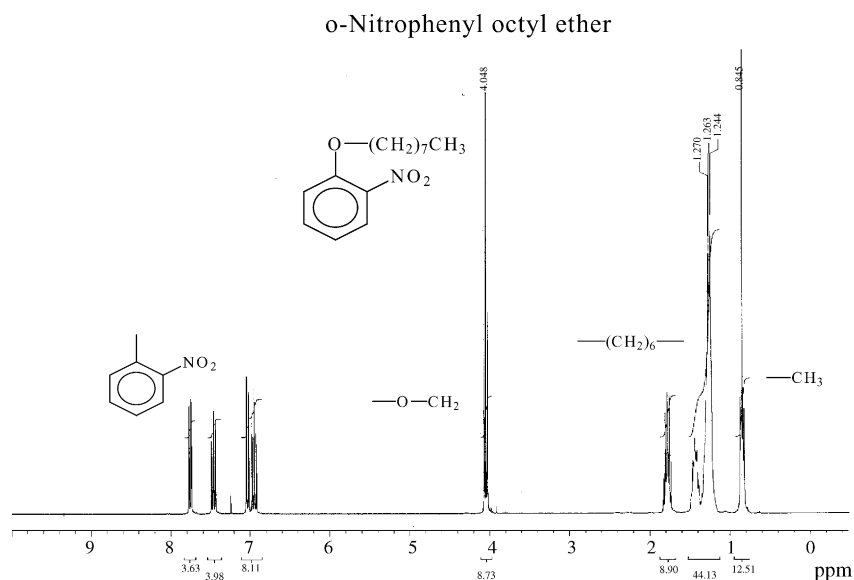
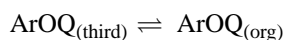Fig. A.2. ^{1}H NMR spectrum of standard *o*-nitrophenyl octyl ether.

Appendix B. Derivation of physical meaning of α_1 and α_2

The distribution of ArOQ between aqueous and the third-liquid phases is

$$ArOQ_{(aq)} \rightleftharpoons ArOQ_{(third)}$$

with distribution coefficient K_{ArOQ}^{aq}, as defined in $K_{ArOQ}^{aq} = \frac{C_{ArOQ}^{third}}{C_{ArOQ}^{aq}}$.

The distribution of ArOQ between the third-liquid and organic phases is

$$ArOQ_{(third)} \rightleftharpoons ArOQ_{(org)}$$

with distribution coefficient K_{ArOQ}^{org}, as defined in $K_{ArOQ}^{org} = \frac{C_{ArOQ}^{third}}{C_{ArOQ}^{org}}$.

The distribution of RBr between organic and the third-liquid phases is
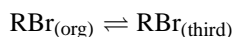
$$RBr_{(org)} \rightleftharpoons RBr_{(third)}$$

with distribution coefficient K_{RBr}^{org}, as defined in $K_{RBr}^{org} = \frac{C_{RBr}^{third}}{C_{RBr}^{org}}$.

The distributions of QBr between the third-liquid, organic and aqueous phases are $K_{QBr}^{org} = \frac{C_{QBr}^{third}}{C_{QBr}^{org}}$ and $K_{QBr}^{aq} = \frac{C_{QBr}^{third}}{C_{QBr}^{aq}}$.

The distribution of ArOR between the third-liquid and organic phases is $K_{ArOR}^{org} = \frac{C_{ArOR}^{third}}{C_{ArOR}^{org}}$.

Taking mass balance for the aqueous reactant ArONa yields,

$$V^{aq}C_{ArONa}^0 = V^{aq}(C_{ArONa}^{aq} + C_{ArOQ}^{aq})$$
$$+ V^{third}(C_{ArOQ}^{third} + C_{ArOR}^{third} + C_{ArONa}^{third})$$
$$+ V^{org}(C_{ArOQ}^{org} + C_{ArOR}^{org}) \quad (6)$$

Substituting the distribution equations of ArOQ and ArOR into Eq. (6) gives,

$$V^{aq}(C_{ArONa}^0 - C_{ArONa}^{aq}) = V^{third}(C_{ArOQ}^{third} + K_{ArOR}^{org}C_{ArOR}^{org})$$
$$+ V^{org}\left(\frac{C_{ArOQ}^{third}}{K_{ArOQ}^{org}} + C_{ArOR}^{org}\right) \quad (7)$$

The concentration of ArOQ in the third-liquid phase can thus be obtained from Eq. (7) as

$$C_{ArOQ}^{third} = \frac{V^{aq}(C_{ArONa}^0 - C_{ArONa}^{aq})}{V^{third} + (V^{org}/K_{ArOQ}^{org})}$$
$$- \frac{V^{third}K_{ArOR}^{org} + V^{org}}{V^{third} + (V^{org}/K_{ArOQ}^{org})}C_{ArOR}^{org} \quad (8)$$

Substituting the definitions of η and Y into Eq. (8), the relationship of η and Y is then obtained as in Eq. (9) and used to correlate the experimental data,

$$\eta = \frac{C_{ArOQ}^{third}}{C_{ArONa}^0} = \frac{V^{aq}(C_{ArONa}^0 - C_{ArONa}^{aq})}{(V^{third} + (V^{org}/K_{ArOQ}^{org}))C_{ArONa}^0}$$
$$- \frac{V^{third}K_{ArOR}^{org} + V^{org}}{V^{third} + (V^{org}/K_{ArOQ}^{org})}Y$$
$$= \alpha_1 - \alpha_2 Y \quad (9)$$

where

$$\alpha_1 = \frac{V^{aq}(C_{ArONa}^0 - C_{ArONa}^{aq})}{(V^{third} + (V^{org}/K_{ArOQ}^{org}))C_{ArONa}^0} \quad \text{and}$$

$$\alpha_2 = \frac{V^{third}K_{ArOR}^{org} + V^{org}}{V^{third} + (V^{org}/K_{ArOQ}^{org})}$$

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