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Rate enhancement effect of third liquid phase on dibenzyl ether production in solid–liquid–liquid phase transfer catalytic system

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Abstract

To investigate the effect of polyethylene glycol (PEG) as a phase transfer catalyst (PTC) for a solid–liquid reaction, dibenzyl ether synthesis from benzyl chloride and benzyl alcohol in organic phase by using solid KOH. A third phase containing the catalyst PEG was formed when dodecane was used as an organic phase. Benzyl alcohol reactants and KOH were dissolved into the third phase. PEG, KOH and benzyl alcohol were combined to produce the alcoxide type complex in the third phase. The complex was transferred into the organic phase. Then, the reaction between the complex and benzyl chloride took place in the organic phase. The reaction rate of this system without water was nearly eight times higher than that of the PTC system with water. Furthermore, the amount of KOH could be reduced by this solid (KOH)–liquid (catalyst)–liquid (organic solvent) system. The difference of the reaction rate was explained by the variation of the base strength of the third phase containing the catalyst. The base strength in the system without water was higher than that in the system with water, which results in the higher concentration of the complex.

Keywords: Phase transfer catalyst; Solid–liquid reaction; Catalyst activity; Third liquid phase; Symmetrical ether synthesis

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1. Introduction

Phase transfer catalysis, a technique to bring the reactants in two immiscible phases together by adding a phase transfer agent, has been employed in the production of fine chemicals and pharmaceuticals in the last few decades [1].

In general, phase transfer catalyst (PTC) can be divided into two major classes: liquid–liquid two-phase PTC (abbreviated as LL-PTC) and solid–liquid two-phase PTC (abbreviated as SL-PTC) [2]. In the case of SL-PTC without an aqueous phase, the nucleophile is in a solid form and the other reactants stay in the organic phase. SL-PTC has certain advantages over LL-PTC: (1) separation of products from reactants and recovery of catalyst become easy; (2) side reactions can be suppressed to avoid the decompositions of reactants or products by water. However, SL-PTC often suffers from slower reaction rates, possibly because the dissolution of the sparingly soluble solid into the organic phase limits the kinetics of the reaction [3].

In the case of LL-PTC, if PTC cannot be dissolved in either organic or aqueous phase, the third phase may appear as a middle liquid phase between organic and aqueous phases. Then, this system becomes liquid–liquid–liquid three-phase PTC (abbreviated as LLL-PTC). Once the third phase with rich PTC appears, the reaction rate increases dramatically [4,5].

If the solid phase can be solved into the third liquid phase with PTC even without water, the reaction rate is expected to be enhanced significantly. This system,

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Nomenclature

$C_{A,org.}$	concentration of benzyl chloride in organic phase (mol/m^3 org.)
$C_{A,0}$	feed concentration of benzyl chloride in organic phase (mol/m^3 org.)
$C_{B,org.}$	concentration of benzyl alcohol in organic phase (mol/m^3 org.)
$C_{B,0}$	feed concentration of benzyl alcohol in organic phase (mol/m^3 org.)
k_{obs}	ether production rate constant (s^{-1})
t	reaction time (min)
$V_{org.}$	volume of organic phase (m^3)
V_{third}	volume of third phase (m^3)
$y_{i,org.}$	dimensionless concentration of benzyl chloride, benzyl alcohol and dibenzyl ether (–)

Greek letters

ξ_{KOH}	dimensionless concentration of potassium hydroxide in the aqueous phase (–)
ω	concentration of PEG based on the volume of organic phase mP/$V_{org.}$ (mol/m^3 org.)

Subscripts

A	benzyl chloride
B	benzyl alcohol
R	dibenzyl ether

therefore, becomes solid–liquid–liquid three-phase PTC (abbreviated as SLL-PTC).

Dibenzyl ether is synthesized from benzyl chloride and benzyl alcohol:

$$\begin{array}{ccccccc} C_6H_5CH_2Cl & + & C_6H_5CH_2OH & \underset{PTC}{\overset{KOH}{\rightarrow}} & (C_6H_5CH_2)_2O & + & HCl \\ (A) & & (B) & & (R) & & \\ (org., third) & & (org., third, aq.) & & (org., third) & & (aq.) \end{array} \quad (1)$$

This reaction usually progress via the intermediate alcoxide as shown later. In this study, polyethylene glycol (PEG) in the liquid state under the reaction condition is used as PTC, which dissolves the solid-state KOH as well as benzyl chloride and benzyl alcohol even without water. It is expected that the alcoxide is formed by the reaction between KOH and benzyl alcohol in the third phase. Then, dibenzyl ether is produced from the alcoxide and benzyl chloride.

The product, dibenzyl ether is a kind of symmetrical ether and is used in several commercial processes such as a carrier in dyeing, solvent in organic chemistry as well as perfumes. However, up to now, no attempt succeeded in this kind of symmetrical ether synthesis applying the third liquid PTC system.

In general, PEG and their many derivatives have been extensively investigated as PTCs and are used in many commercial processes [6]. Comparing to the quaternary ammonium salts, which are usually employed as PTC, PEG are inexpensive, thermally stable in the presence of strong bases, nontoxic, easily biodegradable.

In this study, the reaction rate and the base strength in the three kinds of PTC systems, that is, LL-PTC, LLL-PTC and SLL-PTC, were measured, and the formation of the intermediate alkoxide was also investigated in each system.

2. Experimental

2.1. Materials

For the three reaction systems, PEG with the molecular weight of 3000 (abbreviated as PEG3000) was used as PTC if without special description. It is commercially available from Wako Pure Chemical Industries and was not further purified.

Dodecane and toluene were used as the organic phase solvents, respectively. All the chemicals were of analytical grade.

2.2. Analysis of samples

The concentration of reactants and products in the organic phase was analyzed using a gas chromatograph (GC353B of GL Sciences with a capillary column of 30 m × 0.25 mm) with flame ionization detector.

2.3. Procedure for reaction rate measurements

All of the reactions were carried out at 323 K. Both of the initial concentration of benzyl chloride and benzyl alcohol were 200 mol/m^3 org., the amount of KOH added to the system vary in different systems will be indicated, respectively, in Section 3.

2.3.1. LL-PTC and LLL-PTC

The experiments were conducted in the same way as the previous paper except for tetradecane employed as the inter-standard [7].

2.3.2. SLL-PTC

Dodecane, PEG3000, benzyl alcohol and the inter-standard in the liquid state were charged into the batch reactor with KOH in the solid state. The reactor was placed in a constant-temperature (323 K) water bath, benzyl chloride dissolved in dodecane was added finally and the kinetic run was started. The stirring rate was 1000 rpm.

3. Results and discussion

3.1. The formation and volume of third phase

3.1.1. Condition of forming third liquid phase

Fig. 1 shows the third liquid phase volume (V_{third}) with different two solvents (toluene and dodecane) by using PEG3000 as PTC and also gives the effect of KOH concentration in the aqueous phase on the third volume. The value of ξ_{KOH} represents the dimensionless concentration of KOH in the aqueous phase. When the aqueous phase is saturated with KOH (1.76×10^4 mol/m^3 aq.), ξ_{KOH} equals unity.

When toluene (a weak polar organic solvent) was used as an organic solvent, no third liquid appeared over the all range of ξ_{KOH} because PTC was dissolved in the organic phase.

However, in the case of dodecane (a nonpolar organic solvent) was used as an organic phase, the third phase is formed. However, at higher ξ_{KOH}, the third liquid phase disappeared and the solidification occurred. The solidification phenomena were also observed by Jin et al. [7,8] and Mason et al. [9]. The phenomenon can be explained rationally by the dehydration of third phase, resulting in its precipitation.

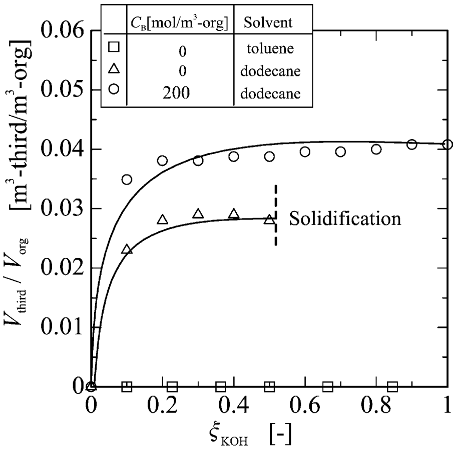

Fig. 1. Effect of the organic solvent on the formation of third liquid phase and effect of KOH concentration in the aqueous phase on the third phase volume (PEG3000, $\omega = 10$ mol/m^3 org.).

With the addition of benzyl alcohol, the volume of third phase increased and the solidification was not observed because the alcohol moderated the properties of the third phase which could prevent its solidification.

3.1.2. Effect of benzyl alcohol concentration on third liquid phase volume

Fig. 2 shows the effect of benzyl alcohol concentration on the volume of the third phase.

When water is present, KOH is dissolved into water (LLL-PTC system). As the concentration of benzyl alcohol $C_{B,0}$ is increased, the volume of the third phase increases.

When water is absent, KOH exists in the solid state (SLL-PTC system). Two liquid phases (organic and PTC-rich phases) are formed and the volume of PTC-rich phase is increased with the concentration of benzyl alcohol. The PTC-rich phase is named as the third phase.

These results suggest that substantial quantity of benzyl alcohol may be dissolved into the third phase during the reaction.

3.2. Three PTC systems formations

The above experiments show three kinds of system appeared as follows.

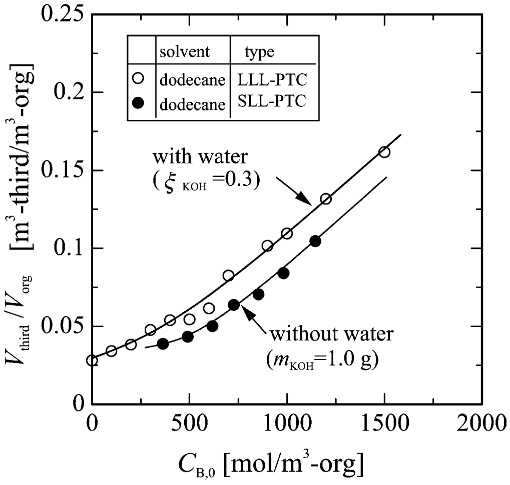

Fig. 2. Effect of benzylalcohol concentration on the volume of third phase in LLL-PTC and SLL-PTC systems (PEG3000, $\omega = 10\,\text{mol/m}^3$ org.).

(1) *LL-PTC*. When toluene was used as the organic solvent, PEG3000 and benzyl alcohol were dissolved in the organic phase, and KOH was dissolved in the aqueous phase. Therefore, the system has two liquid phases.

(2) *LLL-PTC*. When dodecane was used as the organic solvent, benzyl alcohol was slightly dissolved in the organic phase. The third liquid phase was formed when PEG3000 were used as the PTC. The system has three liquid phases. The volume of the third phase depends both on the KOH concentration in the aqueous phase and benzyl alcohol initial concentration added to the system.

(3) *SLL-PTC*. If water was absent, PEG3000 existed as the liquid phase (PTC-rich phase) at the reaction conditions. The reactants and the product were dissolved in both the organic and PTC-rich phases. KOH existed in the pellet (3 mm in diameter, 1.5 mm in length) as added. Therefore, solid (KOH)–liquid (PEG3000)–liquid (dodecane) could be formed.

3.3. Reaction rates in LL-PTC, LLL-PTC and SLL-PTC system

3.3.1. Time course of LLL-PTC and SLL-PTC

Equal concentrations of benzyl chloride and benzyl alcohol were added to the reactor and the variations of the concentrations of benzyl chloride (A), benzyl alcohol (B) and the ether (R) with time were measured. Figs. 3 and 4 show their concentration profiles in LLL-PTC and SLL-PTC systems, respectively.

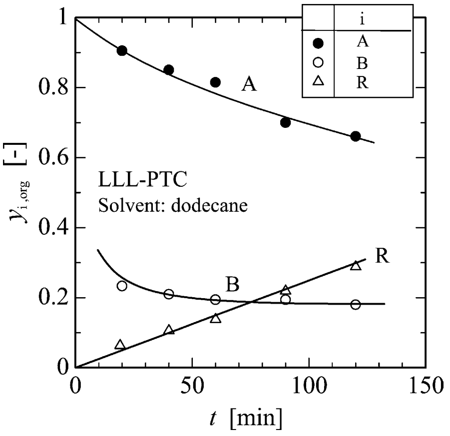

Fig. 3. Time course of reactants and product in LLL-PTC system (PEG3000, $\omega = 10\,\text{mol/m}^3$ org., $\xi_{KOH} = 0.3$, $C_{A,0} = C_{B,0} = 200\,\text{mol/m}^3$ org.).

Although the initial concentrations of both reactants are stoichiometrically the same in Figs. 3 and 4, the decrease of B in the organic phase is much greater than that of A. This may be explained by the dissolution of B into the third phase and the formation of the intermediate, alkoxide, from B and KOH as

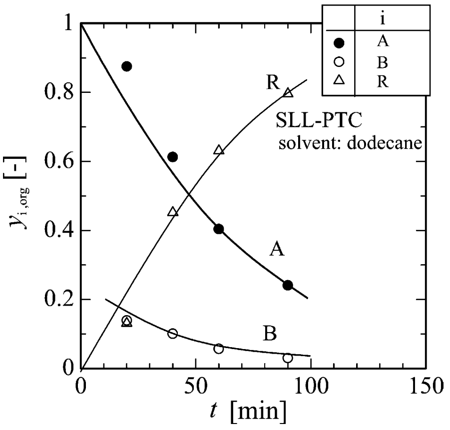

Fig. 4. Time course of reactants and product in SLL-PTC system (PEG3000, $\omega = 10\,\text{mol/m}^3$ org., $C_{A,0} = C_{B,0} = 200\,\text{mol/m}^3$ org., $m_{KOH} = 1.0\,\text{g}$).

explained later in Section 3.5. Therefore, The dimensionless concentration of benzyl alcohol in the organic phase, $y_{\mathrm{B,org.}}$ at $t = 0$ becomes much lower than unity. On the other hand, the dimensionless concentration of benzyl chloride in the organic phase, $y_{\mathrm{A,org.}}$ at $t = 0$ is the unity. This means that benzyl chloride cannot be dissolved into the third phase and remains in the organic phase. The reaction may occur in the organic phase.

The observed rate constant, k_{obs} (s^{-1}) was determined from the slope of the plots between $y_{\mathrm{R,org.}}$ vs. t at the initial stage of Figs. 3 and 4. Observed reaction constants k_{obs} were measured in three systems by varying the amount of KOH. The results are shown in Fig. 5. The mass of KOH shown in gram on the abscissa is the amount of KOH added in the reactor for the case of SLL-PTC system. In the cases of LL-PTC and LLL-PTC systems, both volumes of the organic solvent and water added to the system were 50 cm^3. Therefore, $\xi_{\mathrm{KOH}} = 1$, that is, the saturated concentration of KOH (1.76×10^4 mol/m^3 aq.) corresponds to 65 g.

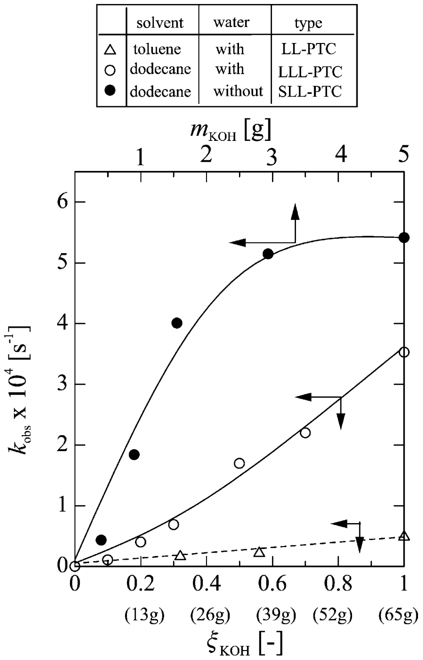

Fig. 5. Dependence of k_{obs} on the KOH concentration in LL-PTC, LLL-PTC and SLL-PTC systems (PEG3000, $\omega = 10$ mol/m^3 org., $C_{\mathrm{A,0}} = C_{\mathrm{B,0}} = 200$ mol/m^3 org.).

3.3.2. Comparison between LL-PTC and LLL-PTC

In Fig. 5, the reaction rates in both systems were increased with the increase of the concentration of KOH in the aqueous phase, ξ_{KOH}. However, the reaction rate in LLL-PTC was higher by about eight times than that in LL-PTC. This rate enhancement of LLL-PTC may be explained by the higher concentration of the intermediate, alcoxide, in the third liquid phase. The highest reaction rate was obtained by the saturated KOH in the aqueous phase due to the least water concentration in the third phase at $\xi_{\mathrm{KOH}} = 1$ as previous papers [7,8].

3.3.3. Comparison between LLL-PTC and SLL-PTC

As shown in Fig. 5, the reaction rate in SLL-PTC was about twice higher than that in LLL-PTC even if the amount of KOH added in the reactor was decreased to one-thirteenth. These may be attribute to the increase of base strength of the third phase. In detail, PEG3000 has such a ring as crown ether, which corporate with [OH^-] easily and lead to a high catalytic activity. In our previous studies [7], the base strength of third phase and the catalytic activity increased with the decrease of the water concentration in the third phase. In SLL-PTC system, since the water was absent, the almost naked OH^- causes the increase of base strength resulting in the increase of alcoxide concentration and then the reaction rate increases.

3.4. Base strength in the LLL-PTC and SLL-PTC

The base strength of the third liquid phase containing catalyst was determined in LLL-PTC and SLL-PTC systems. The indicators with different pK_{a} values were employed in order to explore the base strength of each case in the experiments. Fig. 6 shows the results in the same conditions as Fig. 5. The marks (triangle and circle) indicate the highest pK_{a} values which the indicator's color turned in the third liquid phase.

In the case of LLL-PTC, at $0 < \xi_{\mathrm{KOH}} < 0.3$, only the 2,4-dinitroaniline's color was changed. It means that the third phase shows a weak base property. At $0.3 < \xi_{\mathrm{KOH}} < 0.5$, the base strength increases, and at $\xi_{\mathrm{KOH}} > 0.5$, the base strength is in the range of $17.2 < \mathrm{p}K_{\mathrm{a}} < 18.4$.

In the case of SLL-PTC, the base strength of SLL-PTC shows a higher value as $18.4 < \mathrm{p}K_{\mathrm{a}} < 22.3$ than that of the LLL-PTC. This increase may attribute

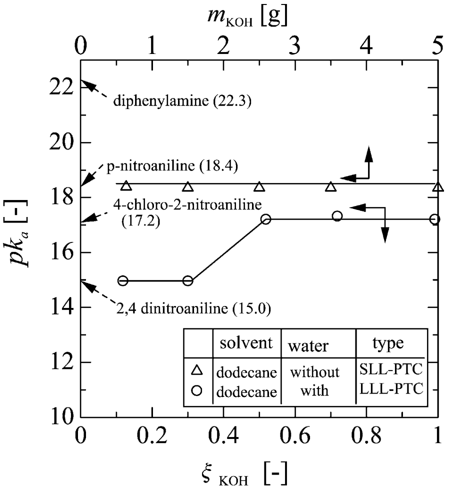

Fig. 6. Base strength variation in LLL-PTC and SLL-PTC systems (PEG3000, $\omega = 10\,\text{mol/m}^3$ org., $C_{A,0} = C_{B,0} = 200\,\text{mol/m}^3$ org.).

to the water absence in this system, that is, the OH^- becomes naked and then the base strength is increased.

The base strength of the organic phase was also measured in the cases of LLL-PTC and SLL-PTC. The indicator of 2,4-dinitroaniline did not change in any cases. Therefore, the catalyst PEG3000 does not exists in the organic phase.

3.5. *Formation of intermediate, alkoxide*

As described in our pervious paper [10], two-step process is required in the traditional Williamson ether synthesis.

Step 1. Potassium alkoxide synthesis from alcohol and metal potassium:

$$2ROH + 2K \rightarrow 2ROK + H_2 \tag{2}$$

Step 2. Ether synthesis from potassium alkoxide and alkyl halide:

$$ROK + R'X \rightarrow ROR' + KX \tag{3}$$

In such technique, metal potassium is consumed and potassium halide is released as the waste. However, in the presence of PTC, the process can be simplified as one-step process. Here, the alkoxide roles as an intermediate in the sequence reaction. Thus, the formation of the potassium alkoxide is also the crucial factor determining the reaction rate. Correspondingly, it is worth to exploring the formation of the alkoxide. Benzyl alcohol concentration in the organic phase was measured with time for three cases as follows.

3.5.1. *In the case without catalyst*

When KOH is absent ($\xi_{KOH} = 0$), the fraction of benzyl alcohol (B) in the organic phase is 0.57, the rest is dissolved in the aqueous phase. However, all of the alcohol exists in the organic phase at $\xi_{KOH} > 0.4$. This is due to the salting out effect by KOH. These results imply that alkoxide cannot be formed in the absence of PTC.

3.5.2. *In the case of LLL-PTC system*

When PEG3000 presents in the system, $y_{B,org.}$ decreases with the increase in ξ_{KOH} as shown in Fig. 7. This implies the formation of the alkoxide in the third phase because $1 - y_{B,org.}$ indicates the fraction of the alkoxide in the third phase. This is because the PEG3000 has such a ring structure as crown ether, which corporate with $[OH^-]$ easily and lead to a high catalytic activity [11]. This explanation will be described in Section 3.6 (Fig. 9).

It is necessary to point out that the phase separation is difficult at $\xi_{KOH} = 0$ because of foaming formation. However, this obstacle is overcome at $\xi_{KOH} = 0.01$.

After 20 min, $y_{B,org.}$ becomes constant at any ξ_{KOH}, which shows alkoxide's formation is reversible reaction.

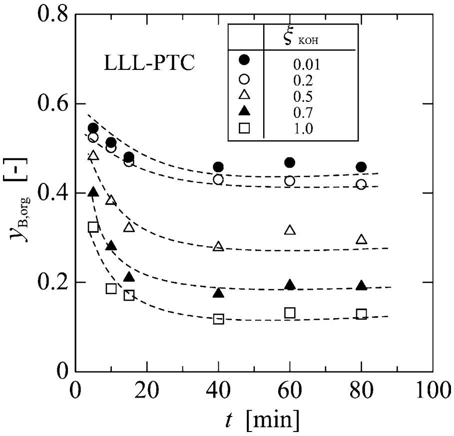

Fig. 7. Time course of benzyl alcohol in organic phase for different KOH concentrations in aqueous phase with catalyst in LLL-PTC system (PEG3000, $C_{A,0} = C_{B,0} = 200\,\text{mol/m}^3$ org., $\omega = 10\,\text{mol/m}^3$ org.).

3.5.3. *In the case of SLL-PTC system*

The same experiments were conducted under the condition of SLL-PTC system. The results are shown in Fig. 8. As the amount of KOH increases, the decrease of $y_{\mathrm{B,org.}}$ is more significant with time. Alkoxide' formation reaches the constant value after 40 min. Therefore, alcoxide formation reaction is also reversible.

The higher alkoxide' formation in SLL-PTC than that in LLL-PTC of Fig. 7 may be due to the formation of the naked base attribute to the absence of water as described in Section 3.4 (Fig. 6).

3.6. *Reaction mechanism of SLL-PTC system without water*

Fig. 9 shows the reaction mechanism in SLL-PTC system. Solid KOH is dissolved into the third phase with rich PEG. The complex, PEG–KOH is formed by the reaction of Eq. (6) in Fig. 9. As shown in the

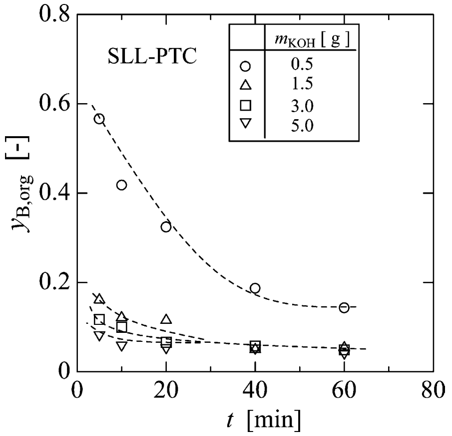

Fig. 8. Time course of benzyl alcohol in organic phase for different KOH amounts with catalyst in SLL-PTC system (PEG3000, $C_{\mathrm{A},0} = C_{\mathrm{B},0} = 200\,\mathrm{mol/m^3}$ org., $\omega = 10\,\mathrm{mol/m^3}$ org.).

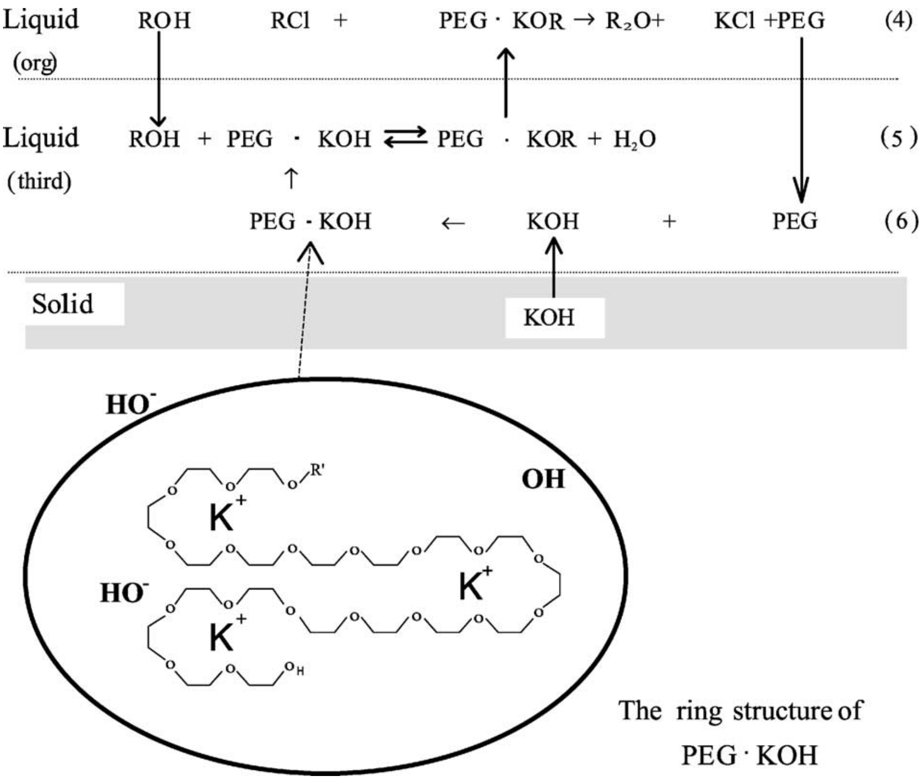

Fig. 9. Reaction mechanism in SLL-PTC system.

lower part of Fig. 9, PEG, that is, $(HO(CH_2CH_2O)_nH$, where $n > 3$) has such a ring structure-like crown ether [11]. This ring structure in SLL-PTC may be the same as that in LL-PTC or LLL-PTC. However, SLL-PTC has the highest base strength because water is absent. Thus, the complex formed by Eq. (6) has the naked OH^- ion which has a strong catalytic activity.

The complex in the third phase becomes the alcoxide type complex, PEG·KOR by the reaction of Eq. (5) with benzyl alcohol, ROH which is transferred from the organic phase. The complex PEG·KOR is transferred into the organic phase as it has a high lipophilicity.

Benzyl chloride, RCl in the organic phase reacts with this complex and produces dibenzyl ether by the reaction of Eq. (4). The isolated PEG in the organic phase returns to the third phase.

4. Conclusions

When PEG with molecular weight of 3000 (PEG3000) was employed as a PTC, dibenzyl ether was synthesized from benzyl chloride and benzyl alcohol by means of two liquid phases (LL-PTC), three liquid phases (LLL-PTC) as well as solid–liquid–liquid phases (SLL-PTC). The following conclusions are obtained:

(1) In the case of water existence, the third liquid (PTC-rich phase) was formed when dodecane was used as an organic solvent and was not formed when toluene was used as an organic solvent.

(2) Once the third liquid phase was formed (LLL-PTC), the reaction rate is much higher than that of the two liquid–liquid phase (LL-PTC) system.

(3) KOH amount could be reduced by solid (KOH)–liquid (PTC)–liquid (organic solvent) system without water (SLL-PTC) and the reaction rate is higher than that of three liquid phase system (LLL-PTC).

(4) The difference of the reaction rate is explained by the base strength of the third phase containing PTC. The base strength in SLL-PTC is higher than that in LLL-PTC, which results in higher concentration of the intermediate, alkoxide.

(5) The reaction mechanism for SLL-PTC system without water is formulated by Eqs. (4)–(6).

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