

Phase-transfer catalytic reaction of dibromo-*o*-xylene and 1-butanol in two-phase solution

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Abstract

A reaction of dibromo-*o*-xylene and 1-butanol to synthesize diether compound was carried out under two-phase phase-transfer catalysis (PTC) conditions. Mono-bromo-substituted product (*o*-bromomethyl 1-butanoxymethyl benzene) and dibromo-substituted product (*o*-di(1-butanoxymethyl)benzene) are both produced from the reaction. Rational reaction mechanism and kinetic model were built up by considering the reaction in aqueous and organic phase, the mass transfer of catalysts between two phases and the phase equilibrium of the catalysts between two phases. The concentration of the active catalyst, identified by instruments, was measured during the reaction. The two apparent rate constants and the two intrinsic rate constants in the organic phase were both obtained via experimental data and the technique of the parameter estimation. Effects of agitation, amount of water, catalysts, amount of tetrabutylammonium bromide (TBAB) catalyst, amount of potassium hydroxide, organic solvents and the temperature on the conversion and the rate constants were investigated in detail. The results are explained satisfactorily of the interaction between the reactants and the environmental species. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Many organic chemicals are required to synthesize by reacting two immiscible reactants existing in different phases. However, the essential condition for the occurring of reaction is the collision of molecules in each other. Reactions of two immiscible reactants are thus confined locally to the interface of the two phases. Conventional methods to improve the reactions from these two immiscible solutions are to increase the agitation speed, to elevate the temperature of reaction, and to use the cosolvents, such as protic solvent or aprotic solvent [1]. Nevertheless, these

efforts are limited because of the technique restriction, solvation of solvent with reactant, side reaction at high temperature, and the cost of solvents. Therefore, the problems of synthesizing organic chemicals from two immiscible reactants cannot be solved until the development of phase-transfer catalysis (PTC) [2].

For this, the technique of PTC has then extensively been applied in the synthesis of organic chemicals via substitution, displacement, condensation, elimination, Ylide-mediated reaction, redox, and polymerization. The most advantages of using PTC technique to synthesize organic chemicals are the enhancement of reaction rate, carrying out the reaction at moderate conditions, obtaining high selectivity of main product and high conversion of reactant [3–6]. Types of reactions, such as liquid–liquid [6], solid–liquid [7],

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gas–liquid [8] and liquid–solid–liquid (triphasic catalysis) [9] are broadly carried out to obtain the desired products.

Ether, one of the high additive-value chemicals, is extensively applied to various industries for the additives of petroleum chemicals and extractants [10,11]. In this work, a diether which can be synthesized from the reaction of dibromo-*o*-xylene and alcohol in an alkaline solution of KOH and organic solvent two-phase medium was carried out under PTC conditions. Two sequential substitutions of bromides from dibromo-*o*-xylene proceed in the organic phase, i.e. mono-bromo-substituted and dibromo-substituted product are obtained due to the two competitive reactions in the organic phase. Using 1-butanol as the aqueous phase reactant, the conditions for searching a condition of high yield of *o*-bromomethyl 1-butanoxymethyl benzene or *o*-di(1-butanoxymethyl)benzene are obtained. Rational mechanism of the alkylation via PTC was proposed and the reaction kinetic was obtained. The model of the reaction in which a pseudo-steady-state hypothesis (PSSH) is assumed, was developed. The two apparent rate constants and the concentration of the active catalyst (tetrabutylammonium butanoxide, $(C_4H_9)_4N^+ - OC_4H_9$, QOR, Q^+ : $(C_4H_9)_4N^+$; R: C_4H_9) are obtained from experiments. Two intrinsic rate constants (k_1 and k_2) of the organic phase reactions are searched via parameter estimation.

2. Experimental

2.1. Materials

All reagents, including dibromo-*o*-xylene, *o*-bromomethyl 1-butanoxymethyl benzene, *o*-di(1-butanoxymethyl)benzene, 1-butanol, chlorobenzene, toluene, xylene, dibutyl ether, potassium hydroxide, tetrabutylammonium bromide (TBAB) and other reagents for synthesis were guaranteed grade (G.R.) chemicals.

2.2. Procedures

2.2.1. Synthesis of dibromo-substituted product (*o*-di(1-butanoxymethyl)benzene)

Measured quantities of dibromo-*o*-xylene (5 g), 1-butanol (10 g), potassium hydroxide (10 g) and

TBAB (0.2 g) were dissolved in 20 ml of chlorobenzene and 20 ml of water at 50 °C. The mixed solution was uniformly agitated to start the reaction. After 3 h of reaction, the solution was separated and the portion of the organic solution was washed by an alkaline solution at least five times to remove TBAB. The solution was concentrated by a vacuum evaporator. *o*-Di(1-butanoxymethyl)benzene of 98% purity was obtained.

2.2.2. Synthesis of mono-bromo-substituted product, *o*-bromomethyl 1-butanoxymethyl benzene

Same reaction conditions as indicated in Section 2.2.1 are used to synthesize the products. After 20 min of reaction, the solution was separated by a separatory funnel. The organic solution was purified through extraction and vacuum evaporation. A mixed solution product of *o*-bromomethyl 1-butanoxymethyl benzene and *o*-di(1-butanoxymethyl)benzene was separated through an adsorption column (adsorbent: 70–23 mesh silica gel, eluent: *n*-hexane/dichloromethane, $v/v = 75/25$). The mono-bromo-substituted product in *n*-hexane/dichloromethane was concentrated by vacuum evaporation. A product of mono-bromo-substituted product, *o*-bromomethyl 1-butanoxymethyl benzene of 98% purity was obtained.

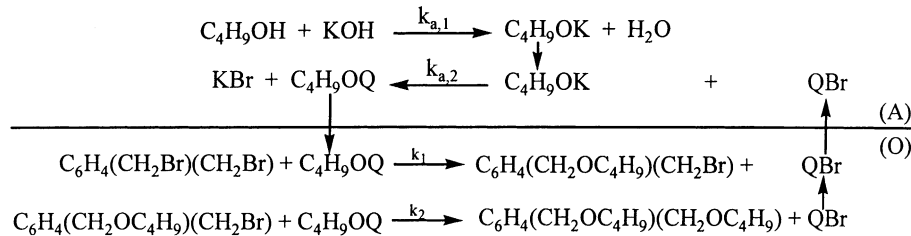
2.2.3. Kinetics of the two-phase reaction

The reactor was a 150 ml three-necked Pyrex flask, serving the purposes of agitating the solution, inserting the thermometer, taking samples, and feeding the feed. Known quantities of 1-butanol, potassium hydroxide were completely dissolved in water. The solution was put into the reactor which was submerged into a well controlled temperature water bath. Then, measured quantities of TBAB and dibromo-*o*-xylene were added to the solution and agitated to start the reaction. The sample (0.5 ml), which was withdrawn from the reactor at each time interval, was put into the test tubes containing 4 ml of water and 4 ml of solvent. The samples were analyzed from dibromo-*o*-xylene, *o*-bromomethyl 1-butanoxymethyl benzene and *o*-di(1-butanoxymethyl)benzene. The product was identified by GC mass for molecular weight, IR and NMR (1H NMR and ^{13}C NMR) for functional groups. The content of the reactant (dibromo-*o*-xylene), and the product (*o*-bromomethyl 1-butanoxymethyl benzene and

o-di(1-butanoxymethyl)benzene) were measured by HPLC. The analyzing conditions are: Shimadzu, system controller—SCL 10AVP, detector—SPD-M10AVP, pump—LC 10-ATVP.

3. Reaction mechanism and kinetic model

As stated, the reaction of dibromo-*o*-xylene and 1-butanol was catalyzed by TBAB, or QBR in an alkaline solution of KOH/organic solvent two-phase medium. Two products, mono-bromo-substituted, *o*-bromomethyl 1-butanoxymethyl benzene, and dibromo-substituted product, *o*-di(1-butanoxymethyl)benzene are obtained in the organic phase. The reaction mechanism is proposed as



The mechanism is formulated on the basis of Starks' extraction model. An active catalyst $\text{C}_4\text{H}_9\text{OQ}$ (or QOR), which is organic-soluble species, was produced from the aqueous solution by reacting catalyst QBr and potassium butanoxide ($\text{C}_4\text{H}_9\text{OK}$). Then, $\text{C}_4\text{H}_9\text{OQ}$, which transfers to the organic phase, reacts with organic phase reactant dibromo-*o*-xylene to produce two products. QBr, which transfers from the organic phase, prepares for regeneration in the aqueous phase.

Based on the experimental data, no by-products were produced. Therefore, the total moles of the two products equal to the consumption of dibromo-*o*-xylene reactant. Several independent experiments were carried out to identify the reaction mechanism. First, no reaction of dibromo-*o*-xylene and 1-butanol in the absence of TBAB or QBr and KOH. In the second experimental run, the active catalyst (QOR) was synthesized by reacting 1-butanol (50 mmol), TBAB (10 mmol) and KOH (100 mmol) in a 10 ml of water and 50 ml of chlorobenzene. After separating the organic phase from aqueous phase, we found that the active catalyst (QOR) exists in the

organic phase. Then, dibromo-*o*-xylene (30 mmol) was added to the portion of organic phase solution. *o*-Bromomethyl 1-butanoxymethyl benzene and *o*-di(1-dibutanoxymethyl)benzene were produced after 1 h of reaction. This experiments confirm that the reaction is catalyzed by TBAB catalyst and the active catalyst produced from the aqueous phase exist in the organic phase.

Based on the proposed mechanism, the material balance of each species can be written as

$$\begin{aligned}
 \frac{d[\text{QOR}]_o}{dt} = & K_{\text{QOR}} A \left(\frac{[\text{QOR}]_a - [\text{QOR}]_o}{M_{\text{QOR}}} \right) \\
 & - k_1 [\text{Ar}(\text{CH}_2\text{Br})_2]_o [\text{QOR}]_o \\
 & - k_2 [\text{Ar}(\text{CH}_2\text{Br})(\text{CH}_2\text{OR})]_o [\text{QOR}]_o
 \end{aligned} \quad (1)$$

$$\begin{aligned}
 \frac{d[\text{QOR}]_a}{dt} = & k_{a,2} [\text{ROK}]_a [\text{QBr}]_a \\
 & - K_{\text{QOR}} A f \left(\frac{[\text{QOR}]_a - [\text{QOR}]_o}{M_{\text{QOR}}} \right)
 \end{aligned} \quad (2)$$

$$\begin{aligned}
 \frac{d[\text{QBr}]_o}{dt} = & k_1 [\text{Ar}(\text{CH}_2\text{Br})_2]_o [\text{QOR}]_o \\
 & + k_2 [\text{Ar}(\text{CH}_2\text{Br})(\text{CH}_2\text{OR})]_o [\text{QOR}]_o \\
 & - K_{\text{QBr}} A ([\text{QBr}]_o - M_{\text{QBr}} [\text{QBr}]_a)
 \end{aligned} \quad (3)$$

$$\begin{aligned}
 \frac{d[\text{QBr}]_a}{dt} = & K_{\text{QBr}} A ([\text{QBr}]_o - M_{\text{QBr}} [\text{QBr}]_a) \\
 & - k_{a,2} [\text{ROK}]_a [\text{QBr}]_a
 \end{aligned} \quad (4)$$

The rate of consuming the dibromo-*o*-xylene reactant and producing the two products are

$$\frac{d[\text{Ar}(\text{CH}_2\text{Br})_2]_o}{dt} = -k_1 [\text{Ar}(\text{CH}_2\text{Br})_2]_o [\text{QOR}]_o \quad (5)$$

$$\begin{aligned} & \frac{d[\text{Ar}(\text{CH}_2\text{Br})(\text{CH}_2\text{OR})]_o}{dt} \\ &= k_1[\text{Ar}(\text{CH}_2\text{Br})_2]_o[\text{QOR}]_o \\ & \quad - k_2[\text{Ar}(\text{CH}_2\text{Br})(\text{CH}_2\text{OR})]_o[\text{QOR}]_o \end{aligned} \quad (6)$$

$$\begin{aligned} & \frac{d[\text{Ar}(\text{CH}_2\text{OR})_2]_o}{dt} \\ &= k_2[\text{Ar}(\text{CH}_2\text{Br})(\text{CH}_2\text{OR})]_o[\text{QOR}]_o \end{aligned} \quad (7)$$

$$\begin{aligned} [\text{QOR}]_o = \frac{Q_o}{V_o} \left\{ \left(1 + \frac{1}{fM_{\text{QOR}}} \right) + (1 + fM_{\text{QOR}}) \frac{\{k_1[\text{Ar}(\text{CH}_2\text{Br})_2]_o + k_2[\text{Ar}(\text{CH}_2\text{Br})(\text{CH}_2\text{OR})]_o\}}{k_{a,2}} [\text{ROK}]_a \right. \\ \left. + \left[\frac{1}{K_{\text{QBr}A}} + \frac{1}{fK_{\text{QOR}A}} \right] \{k_1[\text{Ar}(\text{CH}_2\text{Br})_2]_o + k_2[\text{Ar}(\text{CH}_2\text{Br})(\text{CH}_2\text{OR})]_o\} \right\}^{-1} \end{aligned} \quad (12)$$

The subscript “a” and “o” represent the characteristics of the species in the aqueous and organic phase, respectively. The nomenclature of the species are QOR: $(\text{C}_4\text{H}_9)_4\text{N}^+\text{OC}_4\text{H}_9^-$; QBr: $(\text{C}_4\text{H}_9)_4\text{N}^+\text{Br}^-$; $\text{Ar}(\text{CH}_2\text{Br})_2$: *o*- $\text{C}_6\text{H}_4(\text{CH}_2\text{Br})_2$; $\text{Ar}(\text{CH}_2\text{Br})(\text{CH}_2\text{OR})$: *o*- $\text{C}_6\text{H}_4(\text{CH}_2\text{Br})(\text{CH}_2\text{OR})$; $\text{Ar}(\text{CH}_2\text{OR})_2$: *o*- $\text{C}_6\text{H}_4(\text{CH}_2\text{OR})_2$.

The *f* denotes the volume ratio of organic phase and aqueous phase. M_{QOR} and M_{QBr} are the distribution coefficient of QOR and QBr, between two phases, respectively. The total amount of catalyst Q_o , and the initial amount of 1-butanol E_o are

$$Q_o = V_o([\text{QOR}]_o + [\text{QBr}]_o) + V_a([\text{QOR}]_a + [\text{QBr}]_a) \quad (8)$$

and

$$E_o = V_o([\text{QOR}]_o + 2[\text{Ar}(\text{CH}_2\text{Br})_2]_{o,0} - [\text{Ar}(\text{CH}_2\text{Br})_2]_o) + V_a([\text{ROK}]_a + [\text{QOR}]_a) \quad (9)$$

The initial conditions of the species are

$$\begin{aligned} t = 0, \\ [\text{QBr}]_{o,0} = [\text{QOR}]_{o,0} = [\text{QOR}]_{a,0} = [\text{ROK}]_{a,0} = 0, \\ [\text{QBr}]_{a,0} = Q_o, [\text{Ar}(\text{CH}_2\text{Br})_2]_o = [\text{Ar}(\text{CH}_2\text{Br})_2]_{o,0}, \\ [\text{Ar}(\text{CH}_2\text{Br})(\text{CH}_2\text{OR})]_{o,0} = [\text{Ar}(\text{CH}_2\text{OR})_2]_{o,0} = 0 \end{aligned} \quad (10)$$

In this study, $[\text{QOR}]_o$ and $[\text{QBr}]_o$ keep at constant values in using large excess amount of 1-butanol. Thus, the PSSH is applied, i.e.

$$\frac{d[\text{QOR}]_a}{dt} = \frac{d[\text{QOR}]_o}{dt} = \frac{d[\text{QBr}]_a}{dt} = \frac{d[\text{QBr}]_o}{dt} = 0 \quad (11)$$

Combining Eqs. (1)–(4) and (11), the concentration of QOR in organic phase is obtained

Define the Damkohler numbers D_a and the dimensionless variables, R_1 and R_2 as

$$D_{a,\text{QOR},1} = \frac{k_1[\text{Ar}(\text{CH}_2\text{Br})_2]_o}{K_{\text{QOR}A}} \quad (13)$$

$$D_{a,\text{QOR},2} = \frac{k_2[\text{Ar}(\text{CH}_2\text{Br})(\text{CH}_2\text{OR})]_o}{K_{\text{QOR}A}} \quad (14)$$

$$D_{a,\text{QBr},1} = \frac{k_1[\text{Ar}(\text{CH}_2\text{Br})_2]_o}{K_{\text{QBr}A}} \quad (15)$$

$$D_{a,\text{QOR},2} = \frac{k_2[\text{Ar}(\text{CH}_2\text{Br})(\text{CH}_2\text{OR})]_o}{K_{\text{QBr}A}} \quad (16)$$

$$R_1 = \frac{k_1[\text{Ar}(\text{CH}_2\text{Br})_2]_o}{k_{a,2}[\text{ROK}]_a} \quad (17)$$

$$R_2 = \frac{k_2[\text{Ar}(\text{CH}_2\text{Br})(\text{CH}_2\text{OR})]_o}{k_{a,2}[\text{ROK}]_a} \quad (18)$$

The concentration of ROK in aqueous phase was calculated from Eq. (9). The Damkohler number denotes the rate of organic phase reaction to the mass transfer rate of catalyst. R_1 and R_2 represent the ratio of the reaction rate in the organic phase to the reaction rate in the aqueous phase. Thus, Eq. (12) reduces to

$$[\text{QOR}]_o = \frac{Q_o}{V_o} \left\{ \frac{(1 + (1/fM_{\text{QOR}})) + (1 + fM_{\text{QOR}})(R_1 + R_2) + (D_{a,\text{QBr},1} + D_{a,\text{QBr},2}) + (D_{a,\text{QOR},1} + D_{a,\text{QOR},2})}{f} \right\}^{-1} \quad (19)$$

In general, the rate of acid–base neutralization and the rate of ion-exchange are all rapid. Thus, R_1 and R_2 are small. Further, we found that $[QOR]_o$ keeps at a constant value after 1 min or slow PTC reaction. Therefore, the Damkohler number, such as $D_{a,QOR,1}$, $D_{a,QOR,2}$, $D_{a,QBr,1}$ and $D_{a,QBr,2}$ are all small. For this, Eq. (19) is simplified to

$$[QOR]_o = \frac{Q_o}{V_o} \frac{fM_{QOR}}{1 + fM_{QOR}} \quad (20)$$

In applying the PSSH approach, Eqs. (5) and (6) are written as

$$\frac{d[Ar(CH_2Br)_2]_o}{dt} = -k_{app,1}[Ar(CH_2Br)]_o \quad (21)$$

$$\begin{aligned} \frac{d[Ar(CH_2Br)(CH_2OR)]_o}{dt} &= k_{app,1}[Ar(CH_2Br)_2]_o \\ &\quad - k_{app,2}[Ar(CH_2Br)(CH_2OR)]_o \end{aligned} \quad (22)$$

$$\frac{d[Ar(CH_2OR)_2]_o}{dt} = k_{app,2}[Ar(CH_2Br)(CH_2OR)]_o \quad (23)$$

where

$$k_{app,1} = k_1[QOR]_o \quad (24)$$

$$k_{app,2} = k_2[QOR]_o \quad (25)$$

The solution of Eqs. (21)–(23) are

$$\ln \left(1 - \frac{[Ar(CH_2Br)_2]_o}{[Ar(CH_2Br)_2]_{o,0}} \right) = -k_{app,1}t \quad (26)$$

$$\begin{aligned} \frac{[Ar(CH_2Br)(CH_2OR)]_o}{[Ar(CH_2Br)_2]_{o,0}} &= -\frac{k_{app,1}}{k_{app,2} - k_{app,1}} [e^{-k_{app,1}t} - e^{-k_{app,2}t}] \end{aligned} \quad (27)$$

$$\begin{aligned} \frac{[Ar(CH_2OR)_2]_o}{[Ar(CH_2Br)_2]_{o,0}} &= 1 + \frac{1}{k_{app,2} - k_{app,1}} [k_{app,1} \exp(-k_{app,2}t) \\ &\quad - k_{app,2} \exp(-k_{app,1}t)] \end{aligned} \quad (28)$$

The value of $k_{app,1}$ was obtained from the slope of the straight line by plotting $\ln(1 - X)$ versus t .

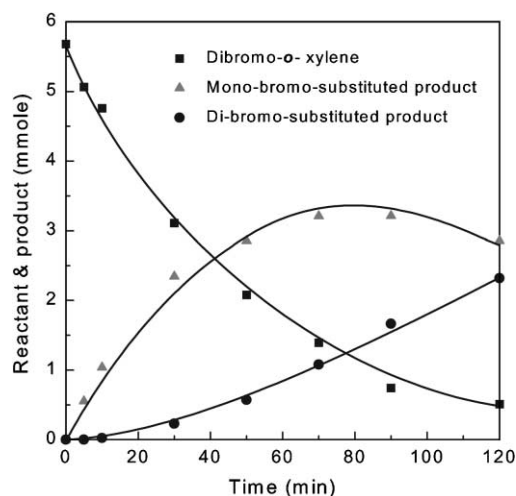


Fig. 1. Distribution of reactant, mono-bromo-substituted product and dibromo-substituted product during the reaction period; 5.68 mmol of dibromo-*o*-xylene, 15 ml of water, 20 ml of toluene, 40 mmol of 1-butanol, 44.63 mmol of KOH, 0.621 mmol of TBAB catalyst, 50 °C, 800 rpm.

Then, $k_{app,2}$ was obtained from Eq. (27) based on the experimental value. Therefore, k_1 and k_2 values are calculated from Eqs. (24) and (25) in measuring the concentration of QOR in the organic phase experimentally.

The time required for a maximum concentration of the first product is obtained from Eq. (27), i.e.

$$t_{max} = \frac{\ln(k_{app,2} - k_{app,1})}{k_{app,2} - k_{app,1}} = \frac{\ln(k_2/k_1)}{(k_2 - k_1)[QOR]_o} \quad (29)$$

For example, t_{max} is calculated as 79.4 min, which is very consistent with the experimental value (80 min) with $k_{app,1} = 2.08 \times 10^{-3}$ and $k_{app,2} = 6.89 \times 10^{-4} \text{ min}^{-1}$. The results are given in Fig. 1.

4. Results and discussion

In this work, two bromides on the *o*-position of dibromo-*o*-xylene were sequentially substituted by alkoxides under PTC conditions. The two reaction rates of these two bromide-substitution steps are almost the same order due to the effect of the stereo-hindrance for the second bromo-substitution. Therefore, the magnitude of these two intrinsic rate

constants of the reactions in the organic phase are the same order.

4.1. Effect of agitation speed

In the two-phase reaction, mass transfer resistance is an important factor in affecting the reaction rate. In general, either the organic or aqueous solution can disperse in smaller droplet size by agitation the two-phase solution. Hence, the contact area of the interface between continuous and dispersion phase increases with the increase of the agitation speed. Further, the mass transfer coefficient also highly dependent on the flow condition (e.g. agitation speed). Hence, the mass transfer rate increases with the increase of the agitation speed. In this work, the conversion does not significantly change for agitation speed larger than 400 rpm in which the mass transfer resistance keeps at a constant value. For agitation speed less than 400 rpm, both mass transfer and reaction resistance are the important roles in determining the reaction rate. Fig. 2 shows the two apparent rate constants on the agitation speed. The increase rate in $k_{app,1}$ is larger than that in $k_{app,2}$. The reason is that chemical reaction of the first bromo-substitution is still larger than that of the second bromo-substitution due to the effect

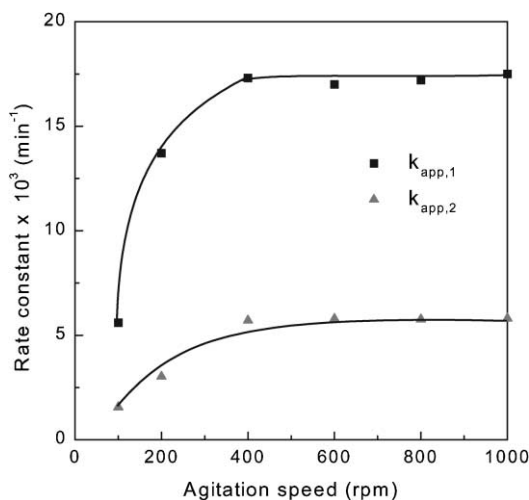


Fig. 2. Effect of the agitation speed on the two apparent rate constants of reaction in the organic phase; 5.68 mmol of dibromo-*o*-xylene, 20 ml of water, 20 ml of toluene, 40 mmol of 1-butanol, 44.63 mmol of KOH, 0.621 mmol of TBAB catalyst, 50 °C.

of the stereo-hindrance. Thus, the effect of agitation speed on the reaction is significantly within 400 rpm.

4.2. Effect of the amount of water

In general, the concentration of KOH, distribution of active catalyst QOR between two phases and the organic–aqueous interfacial area are all affected by the amount of water. As stated in Section 4.1, the mass transfer resistance is neglected or keeps at a constant value for the agitation speed larger than 400 rpm. Thus, the reaction rate does not increase with the increase of the amount of water increasing the interfacial area. Two main points in affecting the rate due to the change of the amount of water are cited. First, solvation of QOR with water is increased by increasing the amount of water. Hence, the activity of QOR decreases by increasing the amount of water. Second, the concentration of KOH is decreased with the increasing of the amount of water. For this, the partition coefficient ($\alpha = [\text{QOR}]_o/[\text{QOR}]_a$) decreases, which is influenced by the alkalinity of the solution. Therefore, the reaction rate is decreased by increasing the amount of water.

The reaction follows pseudo-first-order rate law. As expected, the conversion is decreased with the increase in the amount of water. Fig. 3 depicts the

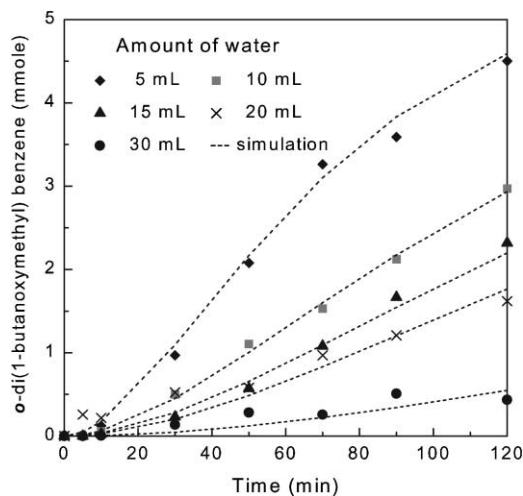


Fig. 3. Effect of the amount of water on the yield of *o*-di(1-butanoxymethyl)benzene; 5.68 mmol of dibromo-*o*-xylene, 20 ml of water, 20 ml of toluene, 40 mmol of 1-butanol, 44.63 mmol of KOH, 0.621 mmol of TBAB catalyst, 50 °C, 800 rpm.

results obtained from the experiments and the simulation value in using Eq. (28). The yield of dibromo-substituted product from experiments is consistent with the predicted value.

4.3. Effect of catalysts

In general, there is no universal rule to guide in selecting an appropriate catalyst except determined from experiments. The reason is that different reactions need various catalysts to enhance the rates and to promote the yields. In this work, seven chemicals, such as: TBAB, tetrabutylammonium hydrogensulfate (TBAHS), tetrabutylammonium iodide (TBAI), tetraethylammonium bromide (TEAB), 4-(tributylammonium) propansulfate (QSO₃), polyoxyethylene (20) sorbitan monostearate (TW80) and tricaprilylmethylammonium chloride (aliquat 336) were employed to examine their activities. Comparing the results for TBAB, TBAHS and TBAI, the order of the reactivity of these anions is $I^- > Br^- > HSO_4^-$; and the results for aliquat 336, TBAI, TBAHS, TBAB and TEAB, the order of the reactivity of these cations is: aliquat 336 > TBAI (TBAB, TBAHS) > TEAB. These results indicate that the reactivity of quaternary salt increases with the increase of the total carbon number in alkyl group of the cation. TEAB, which is more soluble in water, does not have high reactivity. QSO₃ has difficulty dissociating with cation (Q⁺) and anion (HSO₃⁻ or SO₃⁻²) due to the covalent bond between cation and anion. Therefore, the reaction of QSO₃ and ROK is low. In studying the influence of PTC catalysts, the results indicate that the reactions follow pseudo-first-order rate law for all these seven catalysts. Furthermore, high selectivity of the main product is obtained and no by-products are observed during or after the reaction. Table 1 depicts the two apparent rate constants for these seven catalysts in which aliquat 336 performs high reactivity.

4.4. Effect of organic solvents

In this work, Starks' extraction mechanism is employed to explain the reaction characteristics. The two bromo-substituted products were synthesized in the organic solution. For this, the organic solvents, such as: chlorobenzene, toluene, *p*-xylene, and dibutyl ether were employed to investigate their polarities

Table 1

Effect of catalyst on the apparent rate constant^a

Catalyst	$k_{app,1}$ (10^{-3} min^{-1})	$k_{app,2}$ (10^{-3} min^{-1})
Aliquat 336	22.6	8.25
TBAI	14.6	4.8
TBAB	12.2	3.17
TBAHS	10.8	2.71
TW80	5.2	1.52
QSO ₃	3.4	1.08
TEAB	1.7	0.87

^a 5.68 mmol of dibromo-*o*-xylene, 20 ml of toluene, 20 ml of water, 35.7 mmol of KOH, 20 mmol of 1-butanol, 500 rpm, 60 °C, 0.621 mmol of PTC.

on the synthesis of these two products. We found that the conversion of dibromo-*o*-xylene is increased with the polarity of the organic solvent, except dibutyl ether. The reason is that dibromo-*o*-xylene possesses two bromomethylene groups ($-CH_2Br$) of the dipole moment. The formation of dipole-dipole force τ_{dd} from polar solvent and two bromomethylene groups is favorable for the apart of bromide from methylene group. Hence, it is favorable for RO⁻ to attack bromide for a low activation energy E_a in the S_N2 nucleophilic substitution. As shown in Fig. 4, the results indicate that the reaction follows pseudo-first-order law in using these organic solvents. Also, as shown in

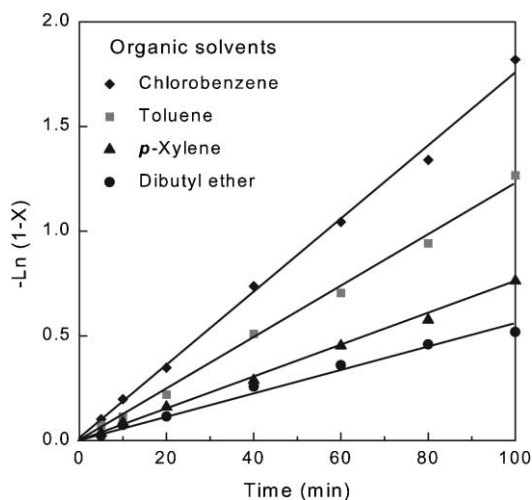


Fig. 4. Effect of the organic solvents on the conversion of dibromo-*o*-xylene; 5.68 mmol of dibromo-*o*-xylene, 20 ml of water, 20 ml of organic solvent, 20 mmol of 1-butanol, 35.70 mmol of KOH, 0.621 mmol of TBAB catalyst, 50 °C, 500 rpm.

Table 2
Effect of organic solvent on the apparent rate constant^a

Organic solvent	ϵ	$k_{app,1}$ (10^{-3} min^{-1})	$k_{app,2}$ (10^{-3} min^{-1})
Chlorobenzene	5.71 (20 °C)	17.7	6.02
Toluene	2.39 (20 °C)	12.2	3.17
<i>p</i> -Xylene	2.26 (20 °C)	7.51	2.08
Dibutyl ether	3.06 (25 °C)	5.60	1.55

^a 5.68 mmol of dibromo-*o*-xylene, 20 ml of organic solvent, 20 ml of water, 35.7 mmol of KOH, 20 mmol of 1-butanol, 0.621 mmol of TBAB, 500 rpm, 60 °C.

Table 2, the conversion of dibromo-*o*-xylene in using dibutyl ether is lower than that in toluene or *p*-xylene, although dibutyl ether possesses high polarity. The reason is probably due to the active lone pair electrons on the oxygen atom on dibutyl ether. Solvation of QOR with dibutyl ether decrease the reactivity.

4.5. Effect of temperature

Fig. 5 show the effect of temperature on the reaction. It is obvious that the conversion is increased with the increase of temperature. The reaction, which is a type of endothermic, follows pseudo-first-order rate law. The first apparent rate constant $k_{app,1}$, which is sensitive to temperature, is larger than the second apparent rate constant. The two activated energies,

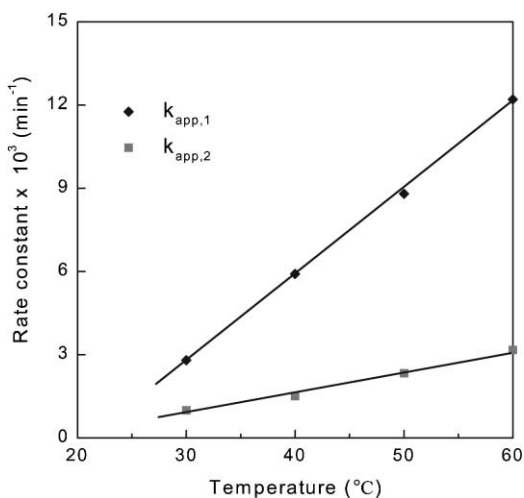


Fig. 5. Effect of temperature on the two apparent rate constants of the reaction in the organic phase; 5.68 mmol of dibromo-*o*-xylene, 20 ml of water, 20 ml of organic solvent, 20 mmol of 1-butanol, 35.70 mmol of KOH, 0.621 mmol of TBAB catalyst, 500 rpm.

E_{a1} and E_{a2} obtained from the slope of the straight line by plotting $\ln(k_{app})$ versus $1/T$, are 40.19 and 32.63 kJ/mol, respectively. The reason is that the free electrons of the dibromo-*o*-xylene are increased after the substitution of $^-OC_4H_9$ by Br^- ion. Thus, E_{a1} is larger than E_{a2} . Furthermore, the two $-CH_2Br$ groups are in an *o*-position. The probability of colliding *o*-bromomethyl 1-butanoxymethyl benzene with butanoxide is low due to stereo-hindrance. Therefore, the value of $k_{app,1}$ is larger than that of $k_{app,2}$. The comparison of the simulation result which obtained from Eq. (28) for the di-substitution product *o*-di(1-butanoxymethyl)benzene and the experimental results are given in Fig. 6. Very consistent results are obtained.

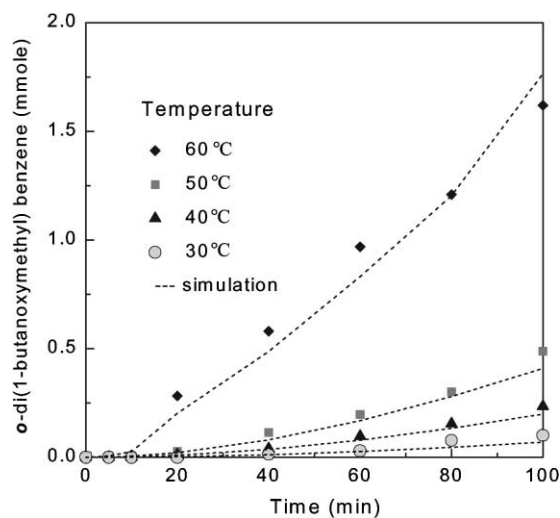


Fig. 6. Effect of temperature on the yield of *o*-di(1-butanoxymethyl)benzene; 5.68 mmol of dibromo-*o*-xylene, 20 ml of water, 20 ml of organic solvent, 20 mmol of 1-butanol, 35.70 mmol of KOH, 0.621 mmol of TBAB catalyst, 500 rpm.

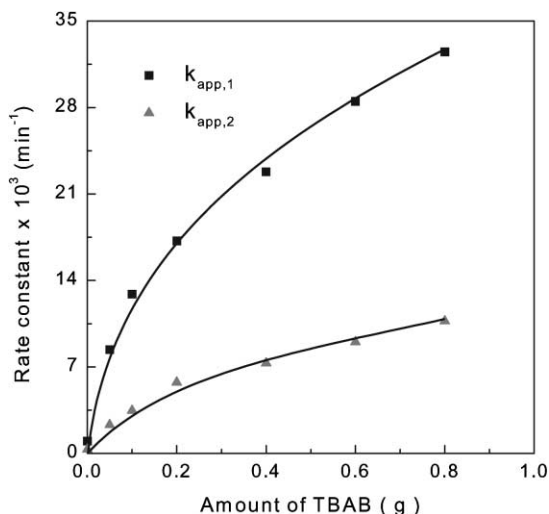


Fig. 7. Effect of the amount of TBAB catalyst on the two apparent rate constants; 5.68 mmol of dibromo-*o*-xylene, 20 ml of water, 20 ml of organic solvent, 40 mmol of 1-butanol, 44.63 mmol of KOH, 0.621 mmol of TBAB catalyst, 50 °C, 800 rpm.

4.6. Effect of the amount of TBAB catalyst

The effect of the amount of TBAB catalyst on the two apparent rate constants is shown in Fig. 7. The reaction follows pseudo-first-order rate law. In the absence of TBAB catalyst, only 10.6% conversion of dibromo-*o*-xylene is obtained after 2 h of reaction. Nevertheless, the conversion is increased to 63.2% after 2 h of reaction when 0.05 g of TBAB catalyst is added. The conversion (or the reaction rate) is increased with the increase of the amount of catalyst. As shown in Fig. 7, the two apparent rate constants, $k_{app,1}$ and $k_{app,2}$ are highly dependent on the amount of TBAB catalyst.

4.7. Effect of the amount of potassium hydroxide

In principle, the concentration of KOH (alkalinity) affects the distribution of the active catalyst QOR between the two phases. The hydration number of QOR is decreased by increasing the concentration of alkaline. Hence, the reaction rate is increased by increasing the concentration of KOH. Second, the solubility of alcohol dissolving in aqueous solution is also increased with the increase of the KOH concentration. Third, only active catalyst can formed from

the reaction of alcohol and the phase-transfer catalyst in the presence of KOH. The reason is that the alkoxide is difficult to apart from the hydrogen by bromide ion, i.e. the covalent bond of the alkoxide and hydrogen is strong, not easy to be dissociated. The formation of alkoxide is highly dependent on the KOH concentration in the aqueous solution.

The experimental results indicate that the reaction follows pseudo-first-order rate law, in which the rate is increased with the increase of the amount of KOH. The corresponding apparent rate constants, $k_{app,1}$ and $k_{app,2}$ are depicted in Fig. 8. The value of $k_{app,1}$, which is sensitive to the amount of KOH, is larger than that of $k_{app,2}$. After 2 h of reaction, the conversion is low (only 42%) when equal molar concentration (1 g of KOH) is used. The reason is that the distribution of the active catalyst QOR, α_{QOR} is small in using small amount of KOH. Hence the reaction rate is low. The conversions of dibromo-*o*-xylene are 79.5 and 98.5% when 2.5 and 4.0 g of KOH are used, respectively. This result reflects that the rate is highly dependent on the amount of KOH. This argument is re-confirmed from the conversion of 79.5 and 98.5% in using 2.5 and 4.0 g of KOH, respectively. Fig. 9 shows the comparison of the experimental results and the expected value

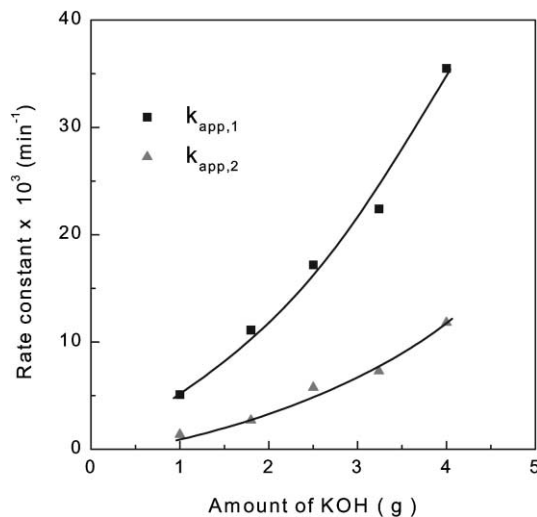


Fig. 8. Effect of the amount of KOH on the two apparent rate constants of reaction in the organic phase; 5.68 mmol of dibromo-*o*-xylene, 20 ml of water, 20 ml of organic solvent, 40 mmol of 1-butanol, 0.621 mmol of TBAB catalyst, 50 °C, 800 rpm.

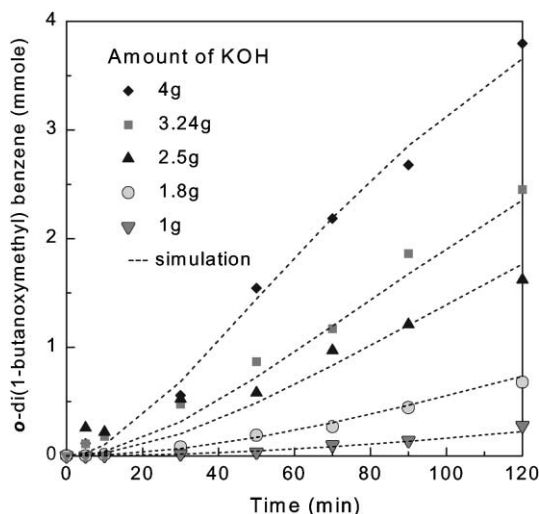


Fig. 9. Effect of the amount of KOH on the yield of *o*-di(1-butanoxymethyl)benzene; 5.68 mmol of dibromo-*o*-xylene, 20 ml of water, 20 ml of organic solvent, 40 mmol of 1-butanol, 35.70 mmol of KOH, 0.621 mmol of TBAB catalyst, 50 °C, 500 rpm.

for the yield of *o*-di(1-butanoxymethyl)benzene. The experimental data are very consistent with the predicted results. Within the range of 1–4 g of KOH, the reaction rate (and the conversion) is increased with the increase of the amount of KOH in the aqueous solution. For further increase in the amount of KOH larger than 4 g, the reaction solution becomes viscous and thick. Under this situation, quaternary ammonium salts decompose and lose its activity due to Hoffmann elimination.

5. Conclusion

In this work, the phase-transfer catalytic reaction in synthesizing diether was successfully carried out from the reaction of 1-butanol and dibromo-*o*-xylene in an alkaline solution of KOH/organic solvent two-phase medium. Two products, mono-bromo-substituted product and dibromo-substituted product were both obtained. For a rather short time of reaction, it is favorable to obtain a mono-bromo-substituted product due to the sequential reaction of the two bromide-substitution. The first apparent rate constant is larger than the second apparent rate constant of the

organic phase reaction. The reaction is not influenced by the agitation speed larger than 400 rpm. Due to the effect of solvation and the concentration of the species, the reaction rate is decreased by increasing the amount of water. In this work, a high reactivity is obtained by choosing an organic-soluble aliquat 336 as the phase-transfer catalyst. Also, the reaction is increased with the polarity of the organic solvent, the amount of KOH and catalyst. A kinetic model was built to find the intrinsic rate constants of the reactions in the organic phase.

Acknowledgements

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