

Kinetic model for synthesizing 4,4'-diethanoxy biphenyl by phase transfer catalysis

Maw-Ling Wang^{a,*}, Yao-Hsuan Tseng^b

^a Department of Chemical Engineering, Tung Hai University, Taichung, Taiwan 407, ROC

^b Department of Chemical Engineering, National Chung Cheng University, Chiayi, Taiwan 621, ROC

Received 26 November 2001; received in revised form 18 January 2002; accepted 16 February 2002

Abstract

The reaction between 4,4'-biphenol (HO(Ph)₂OH) and bromoethane (C₂H₅Br) was first carried out to synthesize 4,4'-diethanoxy biphenyl in an organic solvent/alkaline solution of NaOH two-phase medium under phase transfer catalytic condition. Rational reaction mechanism and kinetic model were built up by considering the reactions from which two sites of nucleophiles on a molecule attacked the organic phase reactant. The mass transfer and the phase equilibrium of the catalysts between two phases were constructed by the two-film theory. In this system, two active catalysts (QO(Ph)₂OQ produced from the aqueous phase, and QO(Ph)₂OR produced from the organic phase) were proposed to synthesize in using tetrabutylammonium bromide (TBAB or QBr) as the regenerated catalyst. The first active catalyst 4,4'-di-tetrabutylammonium biphenoxide ((C₄H₉)₄N⁺–OC₆H₄C₆H₄O^{–2}–N⁺(C₄H₉)₄, QO(Ph)₂OQ), could be identified, whereas the second active catalyst *p*-(tetrabutylammonium phenoxy) alkanoxy benzene ((C₄H₉)₄N⁺–OC₆H₄C₆H₄O^{–2}–C₂H₅, QO(Ph)₂OR) was not detected during the reaction. The first apparent constant of the organic phase reaction was obtained via experimental data. Effect of agitation, temperature, amount of water, organic solvents, catalysts, amount of TBAHS catalyst, amount of sodium hydroxide and volume of alkaline solution on the reaction rate and the conversion were investigated in detail. The results were explained satisfactorily by considering the interaction between the reactants and the environmental species.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Phase transfer catalysis; 4,4'-Biphenol; Bromoethane; Active catalyst; Kinetic model

1. Introduction

Many organic chemicals are synthesized from the reaction of two immiscible reactants existing in different phases. However, the essential condition for the occurrence of such a reaction is the collision of molecules confined locally to the interface of the two phases. The problem was not solved until Jarrouse [1] found the two-phase reaction that was enhanced by adding a small catalytic quantity of a quaternary ammonium salt. Since then, the use of quaternary salt as

a phase transfer catalyst in the two-phase reaction to synthesize specialty chemicals was extensively studied [2–4]. Today, phase transfer catalysis (PTC) is considered to possess a great potential in industrial-scale application because of the mild reaction temperature.

4,4'-Dialkanoxy biphenyl (RO(Ph)₂OR), one of the high additive-value ethers, is extensively applied to various liquid-crystal chemicals [5]. The well-known Williamson and alkoxymercuration–demercuration methods are the conventional ways to synthesize such ethers. These two methods cannot be used to synthesize 4,4'-diethanoxy biphenyl (C₂H₅O(Ph)₂OC₂H₅) because the reactant (4,4'-biphenol, HO(Ph)₂OH) is

* Corresponding author.

sparingly soluble in the organic solvent. Chemists also used some other methods to synthesize 4,4'-diethanoxy biphenyl. Among those methods, one is the homogeneous reaction in which the reactant and bromoalkane are dissolved in benzene at high temperature and reflux for a long time, whereas the other is the Suzuki reaction which uses the palladium compound ($\text{Pd}(\text{PPh}_3)_4$) to catalyze *p*-alkoxy bromobenzene and *p*-alkoxy dihydroxyboryl benzene and reflux for several hours [6–8]. Nevertheless, the desired product yield rate is low due to the production of a large amount of byproducts at reflux temperature. However, the PTC can synthesize 4,4'-dialkanoxy biphenyl easily under mild condition [9].

In this work, the reaction of 4,4'-biphenol and bromoalkane in an alkaline solution of NaOH and organic solvent two-phase medium to synthesize 4,4'-diethanoxy biphenyl was first carried out under PTC condition. Two substitution steps of bromide from bromoalkane are proceeded in the organic solvent in which two sites of nucleophiles on a molecule attack the organic phase reactant. Two active catalysts, 4,4'-di-tetrabutylammonium biphenoxide ($(\text{C}_4\text{H}_9)_4\text{N}^+-\text{OC}_6\text{H}_4\text{C}_6\text{H}_4\text{O}^{2-}-\text{N}^+(\text{C}_4\text{H}_9)_4$, $\text{QO}(\text{Ph})_2\text{OQ}$) produced from aqueous phase, and *p*-(tetrabutylammonium phenoxy) alkanoxy benzene ($(\text{C}_4\text{H}_9)_4\text{N}^+-\text{OC}_6\text{H}_4\text{C}_6\text{H}_4\text{O}^--\text{C}_2\text{H}_5$, $\text{QO}(\text{Ph})_2\text{OR}$) produced from organic phase, were obtained using tetrabutylammonium bromide (TBAB or QBr) as the regenerated catalyst. Using bromoethane as the organic phase reactant, the conditions for a high yield of 4,4'-diethanoxy biphenyl are obtained. For its high reactivity, the second active catalyst was not detected in the organic phase. Rational mechanism of the alkylation via PTC was proposed and the reaction kinetics was obtained. The model of the reaction in which a pseudo steady-state hypothesis (PSSH) is developed from which the first apparent rate constant $k_{\text{app},1}$ is obtained from experiments and the second apparent rate constant $k_{\text{app},2}$ is not determined.

2. Experimental

2.1. Materials

All reagents, including bromoethane, 4,4'-biphenol, toluene, chlorobenzene, *p*-xylene, dibutyl ether, TBAB, tetrabutylammonium hydrogensulfate

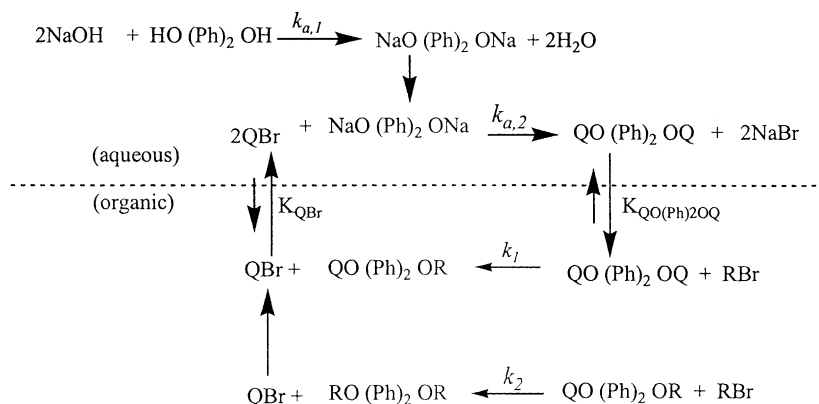
(TBAHS), tetrabutylammonium iodide (TBAI), tetrabutylammonium chloride (TBAC), tetraethylammonium bromide (TEAB), benzyltriethylammonium bromide (BTEAB), 4-(tributylammonium) propan-sultan (a zwitterion, $(\text{C}_4\text{H}_9)_3\text{N}^+(\text{CH}_2)_3\text{SO}_3^-$; QSO_3), sodium hydroxide, biphenyl, 4,4'-diethanoxy biphenyl, and other reagents for synthesis were guaranteed grade (GR) chemicals.

2.2. Procedures

- (A) *Synthesis of 4,4'-diethanoxy biphenyl product* ($\text{H}_5\text{C}_2\text{OC}_6\text{H}_4\text{C}_6\text{H}_4\text{OC}_2\text{H}_5$, $\text{RO}(\text{Ph})_2\text{OR}$). Measured quantities of 4,4'-biphenol (3 g), bromoethane (10 ml), sodium hydroxide (15 g) and TBAHS (0.1 g) were dissolved in 20 ml of chlorobenzene and 30 ml of water at 65 °C. The mixed solution was uniformly agitated to start the reaction. After 1 h of reaction, the solution was separated and the portion of the organic solution was washed by an alkaline solution of NaOH at least six times to remove TBAHS. The solution was concentrated by a vacuum evaporator. 4,4'-Diethanoxy biphenyl of 90% purity was obtained. A bright white crystalline product of 99% purity was obtained using the method of recrystallization in ethanol.
- (B) *Synthesis of active catalyst* ($\text{QO}(\text{Ph})_2\text{OQ}$). To synthesize the active catalyst, measured quantities of sodium hydroxide (10 g) and 4,4'-biphenol (3 g) were dissolved in water (20 ml) at 50 °C. Then, TBAB (5 g) was introduced to the reactor. The solution mixture was rapidly agitated for 10 min producing a white precipitate of the active catalyst ($\text{QO}(\text{Ph})_2\text{OQ}$). The solid content was then filtered and washed with the alkaline solution of NaOH several times to remove TBAB catalyst. The extracted solid was then dried in a vacuum oven at 60 °C, and the white powder thus obtained was identified as 4,4'-di-tetrabutylammonium biphenoxide ($\text{QO}(\text{Ph})_2\text{OQ}$) by H-NMR (NMR data (400 MHz, CDCl_3): $\delta = 7.4\text{--}7.0$ (d, 8H, biphenyl group), $\delta = 3.31\text{--}3.40$ (t, 16H, $-\text{CH}_2$), $\delta = 1.59\text{--}1.81$ (m, 16H, $-\text{CH}_2$), $\delta = 1.40\text{--}1.49$ (m, 16H, $-\text{CH}_2$), $0.97\text{--}1.04$ (dd, 24H, $-\text{CH}_3$)).
- (C) *Kinetics of the two-phase reaction*. The reaction was carried out in a 150 ml three-necked Pyrex flask, serving the purposes of agitating

the solution, inserting thermometer, taking samples, and feeding the feed. Known quantities of 4,4'-biphenol and sodium hydroxide were completely dissolved in water. The solution was put into the reactor, which was submerged into a well-controlled temperature water bath within

product, 4,4'-diethanoxy biphenyl, was detected in the organic reaction. The mono-tetrabutylammonium-substituted product, *p*-(tetrabutylammonium phenoxy) ethanoxy benzene or 4,4'-ethanoxy phenoxy phenol ($\text{HO}C_6\text{H}_4C_6\text{H}_4\text{OC}_2\text{H}_5$) was not observed in the HPLC analysis procedure. The reaction mechanism is proposed as



$\pm 0.1^\circ\text{C}$. Then, measured quantities of TBAHS, biphenyl (internal standard) and bromoethane 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 at 4°C . The samples were analyzed from 4,4'-biphenol, 4,4'-diethanoxy biphenyl and 4,4'-di-tetrabutylammonium biphenoxide. The product was identified by GC-mass for molecular weight, IR and NMR (^1H -NMR and ^{13}C -NMR) for functional groups. The contents of 4,4'-diethanoxy biphenyl and 4,4'-di-tetrabutylammonium biphenoxide were measured by HPLC (Shimadzu, system controller SCL 10AVP, Detector SPD M10AVP, Pump 10 ATVP). The elution concentration of acetonitrile changed with time at 1.3 ml/min total flow rate.

3. Reaction mechanism and kinetic model

As stated, the reaction of bromoethane and 4,4'-biphenol was catalyzed by TBAB or QBr in an alkaline solution of NaOH/organic solvent two-phase medium. Only di-tetrabutylammonium-substituted

The mechanism is formulated on the basis of Starks' extraction model. The first active catalyst $\text{QO}(\text{Ph})_2\text{OQ}$, which is organic-soluble, was produced from the aqueous solution by reacting the catalyst QBr and 4,4'-di-sodium biphenoxide ($\text{NaO}(\text{Ph})_2\text{ONa}$). Then, this organic-soluble active catalyst $\text{QO}(\text{Ph})_2\text{OQ}$, which transfers to the organic phase, reacts with the organic phase reactant bromoethane to produce the second active catalyst, $\text{QO}(\text{Ph})_2\text{OC}_2\text{H}_5$, *p*-(tetrabutylammonium phenoxy) ethanoxy benzene which is not detected in the HPLC analysis procedure because of its high activity. QBr then transfers from the organic phase and prepares for regeneration in the aqueous phase.

Based on the experimental data, no byproducts were produced. Therefore, the total moles of 4,4'-diethanoxy biphenyl is two times of the consumption of bromoethane reactant. Several independent experiments were carried out to identify the reaction mechanism. First, no reaction of bromoethane and 4,4'-biphenol was observed in the absence of tetrabutylammonium salt and NaOH. 4,4'-Biphenol was hardly dissolved in pure water and in the organic solvent. The reaction was actually catalyzed by adding quaternary ammonium salt in the presence of NaOH solution. In the second run, the first active catalyst ($\text{QO}(\text{Ph})_2\text{OQ}$) was synthesized by reacting

4,4'-biphenol, tetrabutylammonium salt, NaOH solution and chlorobenzene. After separating the organic phase from aqueous phase, the first active catalyst was detected in the organic phase. Then, bromoethane was added to the portion of organic phase solution. 4,4'-Diethanoxy biphenyl was produced after 30 min of reaction. The experiments confirm that the reaction is catalyzed by TBAB and the first active catalyst produced from the aqueous phase exists in the organic phase.

Based on the proposed mechanism and two-film theory, the material balance of each species is written as

$$\begin{aligned} \frac{d[\text{QO}(\text{Ph})_2\text{OQ}]_o}{dt} &= K_{\text{QO}(\text{Ph})_2\text{OQ}} \\ &\times A \left([\text{QO}(\text{Ph})_2\text{OQ}]_a - \frac{[\text{QO}(\text{Ph})_2\text{OQ}]_a}{M_{\text{QO}(\text{Ph})_2\text{OQ}}} \right) \\ &- k_1[\text{RBr}]_o[\text{QO}(\text{Ph})_2\text{OQ}]_o \end{aligned} \quad (1)$$

$$\begin{aligned} \frac{d[\text{QO}(\text{Ph})_2\text{OQ}]_a}{dt} &= k_{a,2}[\text{NaO}(\text{Ph})_2\text{ONa}]_a[\text{QBr}]_a^2 - K_{\text{QO}(\text{Ph})_2\text{OQ}}A f \\ &\times \left([\text{QO}(\text{Ph})_2\text{OQ}]_a - \frac{[\text{QO}(\text{Ph})_2\text{OQ}]_a}{M_{\text{QO}(\text{Ph})_2\text{OQ}}} \right) \end{aligned} \quad (2)$$

where “*f*” denotes the volume ratio of the organic phase to the aqueous phase. $M_{\text{QO}(\text{Ph})_2\text{OQ}}$ and M_{QBr} are the distribution coefficients of $\text{QO}(\text{Ph})_2\text{OQ}$ and QBr , between two phases, respectively.

$$\begin{aligned} \frac{d[\text{QBr}]_o}{dt} &= k_1[\text{RBr}]_o[\text{QO}(\text{Ph})_2\text{OQ}]_o \\ &+ k_2[\text{QO}(\text{Ph})_2\text{OR}]_o[\text{RBr}]_o \\ &- K_{\text{QBr}}A([\text{QBr}]_o - M_{\text{QBr}}[\text{QBr}]_a) \end{aligned} \quad (3)$$

$$\begin{aligned} \frac{d[\text{QBr}]_a}{dt} &= K_{\text{QBr}}A([\text{QBr}]_o - M_{\text{QBr}}[\text{QBr}]_a) \\ &- 2k_{a,2}[\text{NaO}(\text{Ph})_2\text{ONa}]_a[\text{QBr}]_a^2 \end{aligned} \quad (4)$$

where $K_{\text{QO}(\text{Ph})_2\text{OQ}}$ and K_{QBr} are the overall mass transfer coefficients of $\text{QO}(\text{Ph})_2\text{OQ}$ and QBr , respectively, A is the interfacial area between two phases.

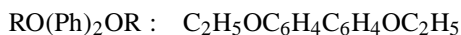
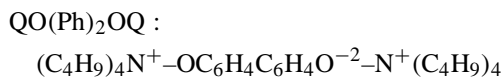
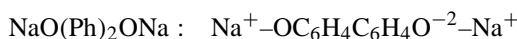
The rate of consuming the bromoethane reactant, and the rate of producing the second active catalyst and the product 4,4'-diethanoxy biphenyl are

$$\begin{aligned} \frac{d[\text{RBr}]_o}{dt} &= -k_1[\text{RBr}]_o[\text{QO}(\text{Ph})_2\text{OQ}]_o \\ &- k_2[\text{RBr}]_o[\text{QO}(\text{Ph})_2\text{OR}]_o \end{aligned} \quad (5)$$

$$\begin{aligned} \frac{d[\text{QO}(\text{Ph})_2\text{OR}]_o}{dt} &= k_1[\text{RBr}]_o[\text{QO}(\text{Ph})_2\text{OQ}]_o \\ &- k_2[\text{RBr}]_o[\text{QO}(\text{Ph})_2\text{OR}]_o \end{aligned} \quad (6)$$

$$\frac{d[\text{RO}(\text{Ph})_2\text{OR}]_o}{dt} = k_2[\text{RBr}]_o[\text{QO}(\text{Ph})_2\text{OR}]_o \quad (7)$$

The subscripts “a” and “o” represent the characteristics of the species in the aqueous and organic phase, respectively. The nomenclatures of the species are defined as:



The total initial amount of catalyst Q_0 added is

$$\begin{aligned} Q_0 &= V_o(2[\text{QO}(\text{Ph})_2\text{OQ}]_o + [\text{QO}(\text{Ph})_2\text{OR}]_o \\ &+ [\text{QBr}]_o) + V_a(2[\text{QO}(\text{Ph})_2\text{OQ}]_a + [\text{QBr}]_a) \end{aligned} \quad (8)$$

The initial conditions of the species are

$$\begin{aligned} t = 0, [\text{QBr}]_{o,0} &= [\text{QO}(\text{Ph})_2\text{OQ}]_{o,0} \\ &= [\text{QO}(\text{Ph})_2\text{OQ}]_{a,0} = [\text{QO}(\text{Ph})_2\text{OR}]_{o,0} \\ &= [\text{NaO}(\text{Ph})_2\text{ONa}]_{a,0} = 0, \quad [\text{QBr}]_{a,0} \\ &= Q_0, \quad [\text{RBr}]_o \\ &= [\text{RBr}]_{o,0}, \quad [\text{RO}(\text{Ph})_2\text{OR}]_{o,0} = 0 \end{aligned} \quad (9)$$

The subscript “0” denotes the condition of species at zero time. In this study $[\text{QBr}]_o$ and $[\text{QO}(\text{Ph})_2\text{OQ}]_o$

keep at constant values in using large excess amount of 4,4'-biphenol. It is reasonable to assume that $[\text{QO}(\text{Ph})_2\text{OQ}]_o$ keeps at a constant value because the activity of $\text{QO}(\text{Ph})_2\text{OR}$ is higher than that of $\text{QO}(\text{Ph})_2\text{OQ}$. Thus, by considering $\text{C}_2\text{H}_5\text{Br}$ as a limiting component, the PSSH is applied, i.e.

$$\begin{aligned} \frac{d[\text{QO}(\text{Ph})_2\text{OQ}]_a}{dt} &= \frac{d[\text{QO}(\text{Ph})_2\text{OQ}]_o}{dt} \\ &= \frac{d[\text{QO}(\text{Ph})_2\text{OR}]_o}{dt} = \frac{d[\text{QBr}]_a}{dt} \\ &= \frac{d[\text{QBr}]_o}{dt} = 0 \end{aligned} \quad (10)$$

Combining Eqs. (1)–(4) and (10), the concentration of QBr in organic phase and aqueous phase, and the concentration of the first active catalyst in the aqueous phase are

$$[\text{QBr}]_a = \left\{ \frac{fk_1[\text{RBr}]_o[\text{QO}(\text{Ph})_2\text{OQ}]_o}{k_{a,2}[\text{NaO}(\text{Ph})_2\text{ONa}]_a} \right\}^{1/2} \quad (11)$$

$$\begin{aligned} [\text{QBr}]_o &= \frac{M_{\text{QBr}}}{K_{\text{QBr}A}} \left(\frac{fk_1[\text{RBr}]_o[\text{QO}(\text{Ph})_2\text{OQ}]_o}{k_{a,2}[\text{NaO}(\text{Ph})_2\text{ONa}]_a} \right)^{1/2} \\ &+ \frac{2k_1[\text{RBr}]_o[\text{QO}(\text{Ph})_2\text{OQ}]_o}{K_{\text{QBr}A}} \end{aligned} \quad (12)$$

$$\begin{aligned} [\text{QO}(\text{Ph})_2\text{OQ}]_a &= \left(\frac{1}{M_{\text{QO}(\text{Ph})_2\text{OQ}}} + \frac{k_1[\text{RBr}]_o}{K_{\text{QO}(\text{Ph})_2\text{OQ}A}} \right) \\ &\times [\text{QO}(\text{Ph})_2\text{OQ}]_o \end{aligned} \quad (13)$$

Combining Eqs. (8) and (11)–(13), the concentration of $\text{QO}(\text{Ph})_2\text{OQ}$ in organic phase is

$$\begin{aligned} \frac{Q_0}{V_o} &= [\text{QO}(\text{Ph})_2\text{OQ}]_o \left(2 + \frac{2k_1[\text{RBr}]_o}{K_{\text{QBr}A}} + \frac{2}{fM_{\text{QO}(\text{Ph})_2\text{OQ}}} + \frac{2k_1[\text{RBr}]_o}{fk_{\text{QO}(\text{Ph})_2\text{OQ}A}} \right) + [\text{QO}(\text{Ph})_2\text{OR}]_o \\ &+ [\text{QO}(\text{Ph})_2\text{OQ}]_o^{1/2} \left\{ \frac{M_{\text{QBr}}}{K_{\text{QBr}A}} \left(\frac{fk_1[\text{RBr}]_o}{k_{a,2}[\text{NaO}(\text{Ph})_2\text{ONa}]_a} \right)^{1/2} + \left(\frac{k_1[\text{RBr}]_o}{fk_{a,2}[\text{NaO}(\text{Ph})_2\text{ONa}]_a} \right)^{1/2} \right\} \end{aligned} \quad (14)$$

In general, the rate of acid–base neutralization and the rate of ion-exchange are all rapid. Thus, the aqueous phase rate constant $k_{a,2}$ is larger than the organic phase rate constant k_1 . Further, $[\text{QO}(\text{Ph})_2\text{OQ}]_o$ is found to maintain at a constant value after 1 min of reaction. Therefore, both $K_{\text{QBr}A}$ and $K_{\text{QO}(\text{Ph})_2\text{OQ}A}$ are larger than $k_1[\text{RBr}]_o$. The concentration of $\text{QO}(\text{Ph})_2\text{OR}$ is very close to zero because the activity of $\text{QO}(\text{Ph})_2\text{OR}$

is much higher than that of $\text{QO}(\text{Ph})_2\text{OQ}$. For this, Eq. (14) is simplified to

$$[\text{QO}(\text{Ph})_2\text{OQ}]_o = \frac{Q_0}{2V_o} \frac{fM_{\text{QO}(\text{Ph})_2\text{OQ}}}{1 + fM_{\text{QO}(\text{Ph})_2\text{OQ}}} \quad (15)$$

Combining Eqs. (6) and (9), and applying PSSH approach, Eq. (5) can be written as

$$\begin{aligned} \frac{d[\text{RBr}]_o}{dt} &= -k_{\text{app},1}[\text{RBr}]_o - k_2[\text{QO}(\text{Ph})_2\text{OR}]_o[\text{RBr}]_o \\ &= -2k_{\text{app},1}[\text{RBr}]_o \end{aligned} \quad (16)$$

$$k_2[\text{QO}(\text{Ph})_2\text{OR}]_o = k_1[\text{QO}(\text{Ph})_2\text{OQ}]_o = k_{\text{app},1} \quad (17)$$

in which $k_{\text{app},1}$ is the rate coefficient of pseudo first-order reaction

$$\begin{aligned} k_{\text{app},1} &= k_1[\text{QO}(\text{Ph})_2\text{OQ}]_o \\ &= \frac{k_1fM_{\text{QO}(\text{Ph})_2\text{OQ}}}{1 + fM_{\text{QO}(\text{Ph})_2\text{OQ}}} \frac{Q_0}{2V_o} \end{aligned} \quad (18)$$

The conversion of bromoethane is defined as X ,

$$X = 1 - \frac{[\text{C}_2\text{H}_5\text{Br}]_o}{[\text{C}_2\text{H}_5\text{Br}]_{o,0}} \quad (19)$$

where $[\text{C}_2\text{H}_5\text{Br}]_{o,0}$ is the initial concentration of $\text{C}_2\text{H}_5\text{Br}$ (RBr). Then, Eq. (16) can be expressed as

$$\ln(1 - X) = -2k_{\text{app},1}t \quad (20)$$

According to Eq. (18), the value of $k_{\text{app},1}$ is obtained from the rate coefficient of the first reaction in the organic phase and the distribution coefficient of $\text{QO}(\text{Ph})_2\text{OQ}$ between two phases. However, $k_{\text{app},1}$ is

obtained experimentally from the slope of the straight line by plotting $\ln(1 - X)$ vs. time.

4. Results and discussion

In this work, there are two $\text{S}_{\text{N}}2$ reactions in the organic phase, one is bromoethane attacked by

QO(Ph)₂OQ, and the other is bromoethane attacked by QO(Ph)₂OR. Only the first active catalyst QO(Ph)₂OQ and the final product RO(Ph)₂OR were observed in the organic phase. This result indicates that the activity of QO(Ph)₂OR, which is not detected in the organic phase, is greater than that of QO(Ph)₂OQ. Unfortunately, the QO(Ph)₂OR cannot be prepared under this two-phase reaction, and the HO(Ph)₂OR is also unavailable to synthesize QO(Ph)₂OR. The reason for the different activities can be explained by two factors and one similar reaction system. First, there are two positive charges on the two ends of Q⁺-O(Ph)₂O⁻²-⁺Q molecule and only one positive charge on one end of Q⁺-O(Ph)₂OR molecule. Therefore, the electron-withdrawing capability of QO(Ph)₂OQ is stronger than that of QO(Ph)₂OR. Second, the stereo hindrance due to the molecule radius of QO(Ph)₂OQ is much bigger than QO(Ph)₂OR. Wang and Chang [10] pointed out that reactivity of ethanoxy butanol (C₂H₅OC₂H₄OH) is much higher than 1-butanol (C₄H₉OH) in PTC alkylation system. It obviously depicts that the active agent of ether alcohol, QOR-OR', is more active than the active agent of normal alcohol, QOR.

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 the aqueous solution can be dispersed in smaller droplet size by agitating the two-phase solution. Hence, the contact area of interface between continuous and dispersion phase increases with the increase in the agitation speed. The mass transfer coefficient is also highly dependent on the flow condition (e.g., agitation speed). Hence, the mass transfer rate increases with the increase in the agitation speed. Fig. 1 shows the dependence of the apparent rate constant on the agitation speed. For agitation speed less than 250 rpm, both mass transfer and reaction resistance are important in determining the reaction rate. In this work, the reaction rate does not significantly change for agitation speed larger than 250 rpm. The mass transfer resistances of the active catalyst between the two phases are the same for agitation speed between 250 and 1000 rpm. Further increase the agitation speed, the conversion is not affected by the agitation speed greater than

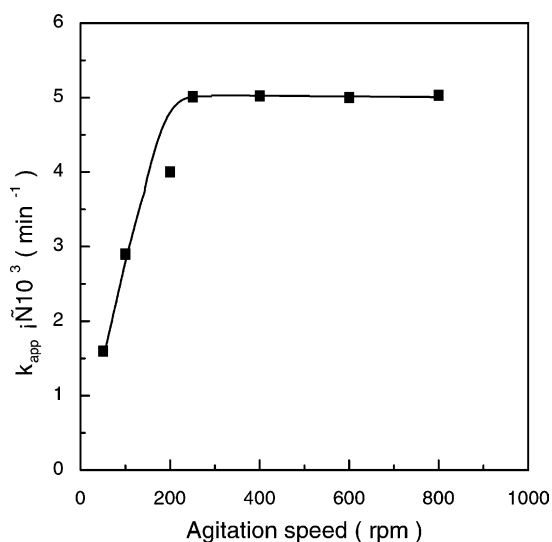


Fig. 1. Effect of the agitation speed on the apparent rate constant in the organic phase; 10 g of sodium hydroxide, 10 ml of water, 5.37 mmol of 4,4'-biphenol, 0.59 mmol of TBAHS, 4 mmol of bromoethane, 50 ml of chlorobenzene, 50 °C.

250 rpm. Therefore, the agitation speed was kept at 500 rpm in the following experiments to obtain the kinetic data. Hence, it is obvious that the reaction in organic phase is the rate-controlling step for agitation speed larger than 250 rpm under this set of conditions. However, this threshold value will be changed with change in the reaction parameters. For example, the surface tension of the two-phase is decreased by increasing temperature and adding surfactants (ex: dodecyltrimethylammonium bromide, cationic surfactant). The maximum two-phase mass transfer rate will be reached under lower agitation speed.

4.2. Effect of temperature

Fig. 2 shows the effect of temperature on the reaction. As predicted, the conversion is increased with the increase in temperature. The reaction which follows pseudo first-order rate law, is a type of endothermic without occurring any other side-reaction. From Eq. (20), the apparent rate constant is obtained from the slope of the straight line by plotting $-\ln(1 - X)$ vs. time. In Fig. 3, the activated energy ($E_{a1} = 42.5 \text{ kcal mol}^{-1}$) is obtained from the slope of the Arrhenius plot of $\ln(k_{app,1})$ vs. $1/T$. The increase of

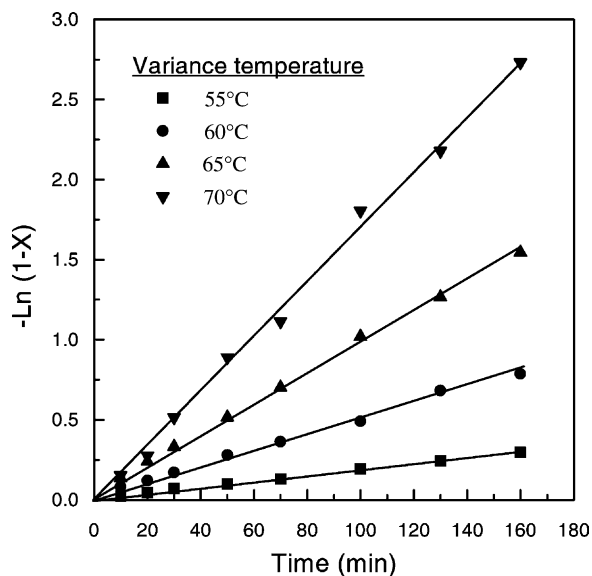


Fig. 2. Effect of the temperature on the conversion of bromoethane; 15 g of sodium hydroxide, 30 ml of water, 5.37 mmol of 4,4'-biphenol, 0.59 mmol of TBAHS, 4 mmol of bromoethane, 20 ml of chlorobenzene, 500 rpm.

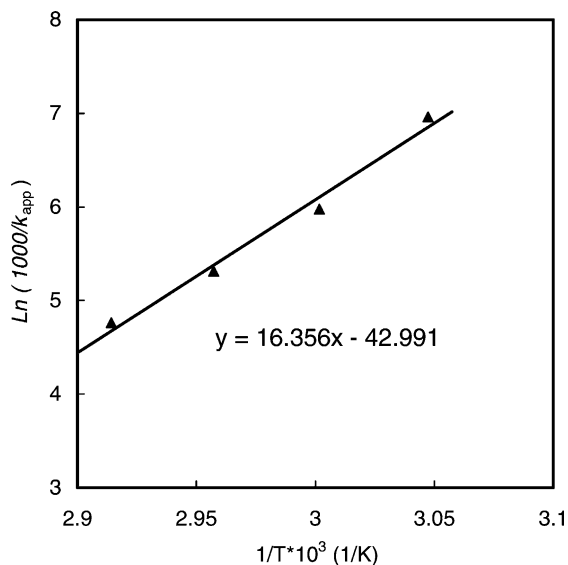


Fig. 3. Arrhenius plot of the apparent rate constant in the organic phase; 15 g of sodium hydroxide, 30 ml of water, 5.37 mmol of 4,4'-biphenol, 0.59 mmol of TBAHS, 4 mmol of bromoethane, 20 ml of chlorobenzene, 500 rpm.

temperature also enhances the solubility of aqueous phase reactant 4,4'-biphenol in the aqueous phase.

4.3. Effect of organic solvent

In this work, bromoethane reacts with $\text{QO}(\text{Ph})_2\text{OQ}$ in the two sequential steps producing second active catalyst and the desired product from the two sequential reactions in the organic phase. For this, the organic solvents, such as: chlorobenzene, toluene, *p*-xylene and dibutyl ether are employed to investigate their polarities on the synthesis of 4,4'-diethanoxy biphenyl. A plot of the conversion vs. time in various organic solvents is depicted in Fig. 4. The result indicates that the reaction follows a pseudo first-order law in using these organic solvents. The corresponding $k_{\text{app},1}$ values in various organic solvents are shown in Table 1. The reaction rate constant is increased with the increase in polarity of the organic solvent (or dielectric constant). Bromoethane, which possesses a dipole moment, forms a dipole–dipole bond with organic solvent in which the active catalyst $\text{QO}(\text{Ph})_2\text{OQ}$ is also affected. The higher the polarity of the organic solvent, the easier the ability to depart for bromide and Q^+ ion from ethyl and biphenoxide groups. Hence, it is

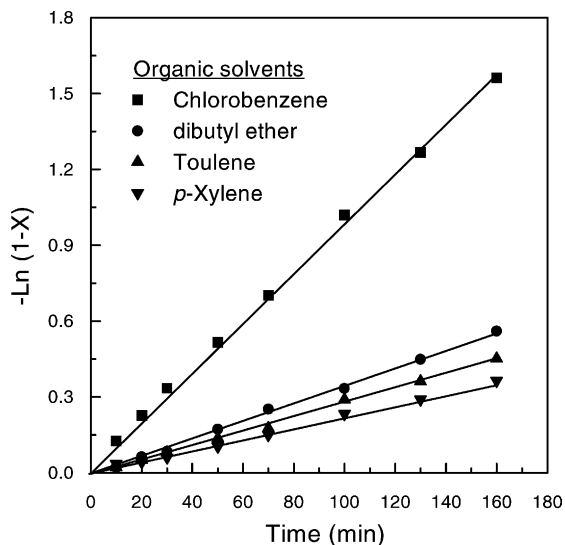


Fig. 4. Effect of the organic solvents on the conversion of bromoethane; 15 g of sodium hydroxide, 30 ml of water, 5.37 mmol of 4,4'-biphenol, 0.59 mmol of TBAHS, 4 mmol of bromoethane, 20 ml of organic solvent, 500 rpm, 55 °C.

Table 1

Effect of the organic solvents on the distribution coefficient of $\text{QO}(\text{Ph})_2\text{OQ}$ between organic and aqueous phases, intrinsic rate constant, percentage of active catalyst (Q , %), apparent rate constant; 15 g of sodium hydroxide, 30 ml of water, 5.37 mmol of 4,4'-biphenol, 0.59 mmol of TBAHS, 4 mmol of bromoethane, 30 ml of water, 20 ml of organic solvent, 500 rpm, 55 °C

Organic solvent	Dielectric constant, ϵ	$k_{\text{app},1} \times 10^{-3}$ (min^{-1})	$M_{\text{QO}(\text{Ph})_2\text{OQ}}$	Q (%) [*]	k_1' (min^{-1})	sk_1'' (min^{-1})
Chlorobenzene	5.71 (20 °C)	4.95	32.33	95.7	0.367	0.351
Dibutyl ether	3.06 (25 °C)	1.75	30.14	95.0	0.131	0.125
Toluene	2.39 (20 °C)	1.42	27.88	95.5	0.106	0.101
<i>p</i> -Xylene	2.26 (20 °C)	1.11	24.15	94.3	0.085	0.080

* Q (%) = $2 \times$ mole of $\text{QO}(\text{Ph})_2\text{OQ}$ /mole of QO . QO = Initial amount of catalyst.

favorable for $\text{O}(\text{Ph})_2\text{O}^{-2}$ and $\text{H}_5\text{C}_2\text{O}(\text{Ph})_2\text{O}^{-}$ to displace bromide ion in an organic solvent of high polarity (i.e. a low activated energy in the $\text{S}_{\text{N}}2$ nucleophilic substitution).

In principle, the concentration of the active catalyst $\text{QO}(\text{Ph})_2\text{OQ}$ can be measured by HPLC. It is found that about 95% of the catalyst is in a form of $\text{QO}(\text{Ph})_2\text{OQ}$. Most of $\text{QO}(\text{Ph})_2\text{OQ}$ distributed in the organic phase for all organic solvents. Therefore, the intrinsic rate constant, k_1' was calculated from the measured $k_{\text{app},1}$ value and $[\text{QO}(\text{Ph})_2\text{OQ}]_0$ shown in Eq. (18). In addition, the intrinsic rate constant k_1'' can also be calculated from the information of f , $M_{\text{QO}(\text{Ph})_2\text{OQ}}$, Q_0 and V_0 in Eq. (18). The results are given in Table 1. Both k_1' and k_1'' obtained from different approaches are very close. These results indicate that the proposed model is sufficient to describe the characteristics of the PTC reaction.

4.4. Effect of phase transfer catalysts

In general, there is no universal rule to guide in selecting an appropriate phase transfer catalyst except that determined from experiments. The reason is that different reactions need various catalysts to enhance the rate and to promote the yields. In this work, seven chemicals, such as: TBAC, TBAB, TBAHS, TBAI, tetraethylammonium bromide (TEAB), benzyltetraethylammonium bromide (BTEAB), and 4-(tributylammonium) propansulfate (a zwitterion, $(\text{C}_4\text{H}_9)_3\text{N}^+(\text{CH}_2)_3\text{SO}_3^-$; QSO_3) were employed to examine their reactivities. Table 2 depicts the apparent rate constants for these seven catalysts in which TBAI exhibits the highest reactivity. Comparing the results for TBAI, TBAB, TBAHS and TBAC, the order of the reactivities of the anions is: $\text{I}^- > \text{Br}^- > \text{HSO}_4^- >$

Cl^- . The order of the reactivities of the cations is: $\text{TBAB} > \text{TEAB}$. The result indicates that the reactivity of quaternary salt increases with the increase in total carbon number in the alkyl group of the cation. For this, the formation of active catalyst $\text{QO}(\text{Ph})_2\text{OQ}$ is more soluble in organic solvent to enhance the reaction. TEAB, which is more soluble in water, does not have high reactivity. TEAB is more reactive than BTEAB although the total number of carbon in the cation of BTEAB is larger than that of TEAB. The reason is that the benzyl group appears in the unsymmetric cation. The reaction system of the unsymmetric cation easily forms the emulsion solution which is a retardant state for the regeneration of catalysts and unfavorable for the attack of the nucleophilic reagent in the $\text{S}_{\text{N}}2$ reaction. The catalyst in other form of QSO_3 is a zwitterion compound. It will be anionic in base solution and cationic in acid solution, so the concentration of quaternary ammonium cation (Q^+) is very low in the alkaline solution. Therefore, the reaction rate of QSO_3 and $\text{NaO}(\text{Ph})_2\text{ONa}$ to produce the active catalyst $\text{QO}(\text{Ph})_2\text{OQ}$ is low.

Table 2

Effect of the catalyst on the apparent rate constant; 15 g of sodium hydroxide, 30 ml of water, 5.37 mmol of 4,4'-biphenol, 0.59 mmol of catalyst, 4 mmol of bromoethane, 30 ml of water, 20 ml of organic solvent, 500 rpm, 55 °C

Catalyst	$k_{\text{app},1} \times 10^{-3}$ (min^{-1})
TBAI	18.4
TBAB	5.59
TBAHS	4.95
TBAC	3.05
TEAB	2.10
BTEAB	0.95
QSO_3	0.30

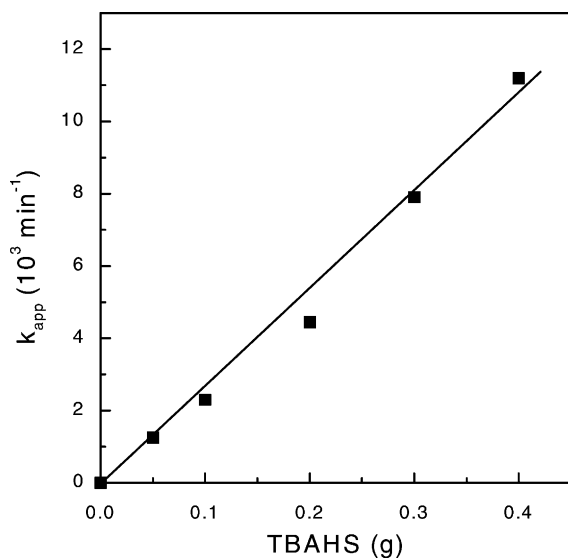


Fig. 5. Effect of the amount of TBAHS on the apparent rate constant in the organic phase; 15 g of sodium hydroxide, 30 ml of water, 5.37 mmol of 4,4'-biphenol, 4 mmol of bromoethane, 20 ml of chlorobenzene, 65 °C, 500 rpm.

4.5. Effect of the amount of TBAHS catalyst

Effect of the amount of TBAHS catalyst on the apparent rate constant is shown in Fig. 5. The reaction follows a pseudo first-order law using $\text{C}_2\text{H}_5\text{Br}$ as a limiting component. In the absence of catalyst, only 4.8% conversion of bromoethane is obtained after 160 min of reaction. Nevertheless, the conversion is increased to 98.5% after 160 min of reaction when 0.4 g of TBAHS catalyst is added. As shown in Fig. 5, the apparent rate constant increases linearly with the amount of TBAHS catalyst. Eq. (18) is simplified as: $k_{app,1} = (k_1/2V_o)Q_0$ for the partition coefficient $M_{\text{QO}(\text{Ph})_2\text{OQ}}$ which is larger than 1 in high pH value solution. This result indicates that the apparent rate constant was only determined by the amount of initial-addition of catalyst. The results were very consistent with Eq. (18).

4.6. Effect of the amount of water

In general, the concentration of NaOH, distribution of active catalyst between two phases and the organic–aqueous interfacial area are all affected by

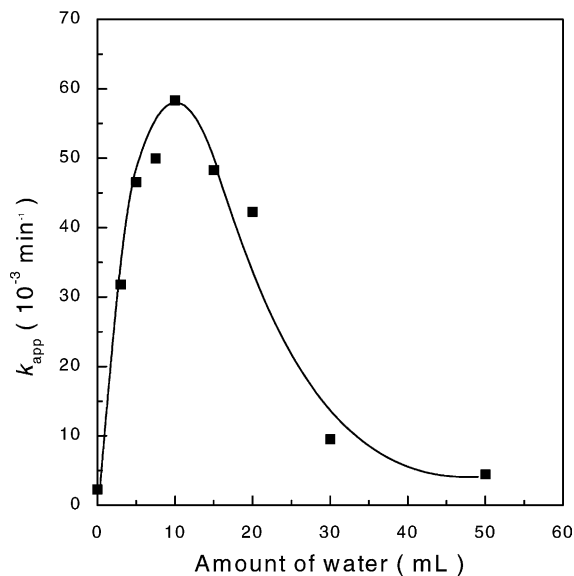


Fig. 6. Effect of the amount of water on the apparent rate constant in the organic phase; 15 g of sodium hydroxide, 5.37 mmol of 4,4'-biphenol, 0.59 mmol of TBAHS, 4 mmol of bromoethane, 20 ml of chlorobenzene, 65 °C, 500 rpm.

the amount of water. As shown in Fig. 6, the apparent rate constant is increased with the increase in the amount of water (0–10 ml) and then decreased with the increase in the amount of water. This result indicates that the largest value of $k_{app,1}$ is obtained using 10 ml of water. Four main points in affecting the rate due to the change of the amount of water are cited. First, the solvation of $\text{QO}(\text{Ph})_2\text{OQ}$ with water is increased by increasing the amount of water, which is unfavorable for the reaction. Second, the activity of $\text{QO}(\text{Ph})_2\text{OQ}$ decreased by increasing the amount of water, i.e., unfavorable to enhance the reaction. For this, the partition coefficient of $\text{QO}(\text{Ph})_2\text{OQ}$ ($M_{\text{QO}(\text{Ph})_2\text{OQ}} = [\text{QO}(\text{Ph})_2\text{OQ}]_o / [\text{QO}(\text{Ph})_2\text{OQ}]_a$) decreases with the increase in the amount of water. Third, the interface area is increased by increasing the amount of water. The reaction rate is increased with the increase of mass transfer area which is favorable for the reaction to proceed. Fourth, the solubility of 4,4'-disodium biphenoxide $\text{NaO}(\text{Ph})_2\text{ONa}$ is decreased by decreasing the amount of water. $\text{NaO}(\text{Ph})_2\text{ONa}$, which is dissociated into Na^+ and $\text{O}(\text{Ph})_2\text{O}^{-2}$, reacts with QBr to form the active catalyst. The solubility-product constant of $\text{NaO}(\text{Ph})_2\text{ONa}$

is 5.59 M^3 at 25°C . The concentration of $\text{O}(\text{Ph})_2\text{O}^{-2}$, which affects the concentration of $\text{QO}(\text{Ph})_2\text{OQ}$, is increased with the decrease in the alkalinity of the solution. Hence, the reaction is enhanced by increasing the amount of water. Therefore, there is an optimum value of the amount of water in this reaction.

4.7. Effect of the amount of sodium hydroxide

In principle, the concentration of NaOH affects the distribution of the active catalyst between two phases, and the solubility of 4,4'-biphenol in the aqueous phase. The active catalyst $\text{QO}(\text{Ph})_2\text{OQ}$ in the aqueous phase is solvated to form the complex compound $(\text{QO}(\text{Ph})_2\text{OQ})_m(\text{H}_2\text{O})_n$. The hydration number of $\text{QO}(\text{Ph})_2\text{OQ}$ is decreased by increasing the concentration of alkaline. Hence, the reaction rate is increased by increasing the amount of NaOH. Second, the solubility of 4,4'-biphenol in aqueous phase is low in the absence of NaOH. But as stated in 4.6, disodium salt would salt out upon using a large amount of NaOH. In this reaction condition, the effect of salting out due to the addition of disodium salt is not significant in using over 10 ml of water. Third, only active catalyst can be formed from the reaction of alcohol and the phase transfer catalyst in the presence of NaOH. The reason is that the biphenoxide is difficult to depart from the hydrogen by bromide ion of quaternary ammonium salt, i.e., the covalent bond of the biphenoxide and hydrogen is strong, not easy to be dissociated. As shown in Fig. 7, the conversion is only 23% after 160 min when the 5 g of NaOH is used and no reaction occurs in the absence of NaOH. The apparent rate constant is sensitive to the amount of NaOH ($k_{\text{app},1} = 8.4 \times 10^{-4} \text{ min}^{-1}$ at 5 g of NaOH, $k_{\text{app},1} = 11.2 \times 10^{-3} \text{ min}^{-1}$ at 20 g of NaOH). Therefore, the conversions are obviously affected by the amount of sodium hydroxide.

4.8. Effect of the volume of 25 M alkaline solution

In this work, the effect of the volume of alkaline solution (25 M) on the reaction is investigated. The reaction rate is decreased with decrease in the volume of NaOH solution. In the 25 M NaOH aqueous solution, disodium biphenoxide precipitate was observed in the reaction system. Hence, the concentrations of biphenoxide anion are the same in the NaOH

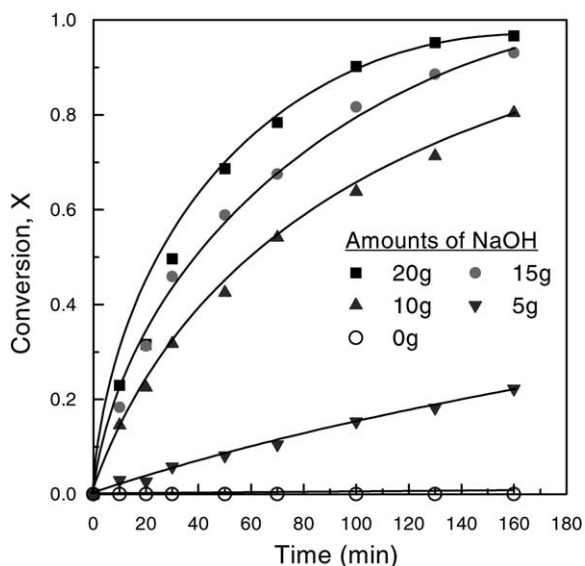


Fig. 7. Effect of the amount of NaOH on the conversion of bromoethane; 10 ml of water, 5.37 mmol of 4,4'-biphenol, 0.59 mmol of TBAHS, 4 mmol of bromoethane, 40 ml of chlorobenzene, 50°C , 500 rpm.

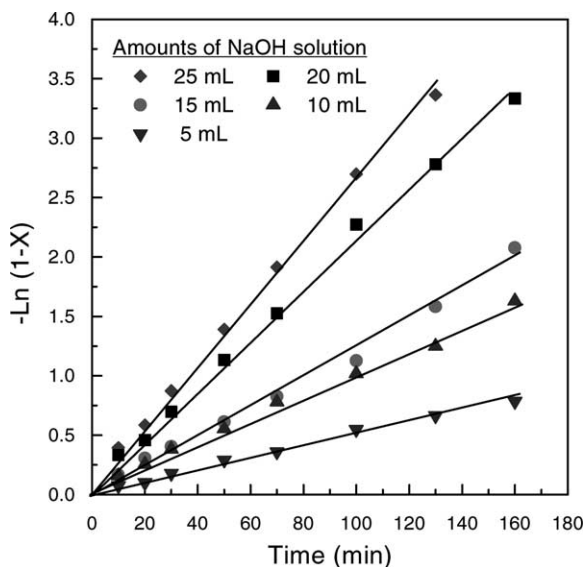


Fig. 8. Effect of the amount of NaOH solution (25 M) on the conversion of bromoethane; 5.37 mmol of 4,4'-biphenol, 0.59 mmol of TBAHS, 4 mmol of bromoethane, 40 ml of chlorobenzene, 50°C , 500 rpm.

solution. The interface contact area is increased by increasing the amount of NaOH solution. The conversion is increased with the increase of mass transfer area. As shown in Fig. 8, the conversion is only 30.2% after 70 min at 5 ml of solution, and the conversion is increased to 85.2% with the increase of 25 ml of solution.

5. Conclusion

In this work, 4,4'-dialkanoxy biphenyl was successfully synthesized by the phase transfer catalytic reaction which was carried out from the reaction of 4,4'-biphenol and bromoethane in an alkaline solution of NaOH/organic solvent two-phase medium. The kinetic model was constructed to satisfactorily account for the factors of the reaction. Two sequential reactions of the active catalyst and bromoethane in the organic phase for the S_N2 substitution were indicated. However, only the final di-tetrabutylammonium-substituted product was obtained. The second intrinsic rate constant (k_2) in the organic phase is much larger than the first intrinsic rate constant (k_1), so that the first S_N2 reaction is the rate determining step. The reaction is not influenced by the agitation speed larger than 250 rpm. Due to solvation effect, distribution of active catalyst, interface area and the solubility of 4,4'-biphenol, 10 ml of water is the optimum volume. A reasonable explanation was used satisfactorily the peculiar phenomena. In this work, the largest yield was obtained by using TBAI as the phase transfer catalyst. The reaction rate is increased with the increase in the amount of NaOH.

Acknowledgements

The authors would like to thank the National Science Council for financial support under the grant no. NSC-89-2214-E-194-017.

References

- [1] J. Jarrouse, The influences of quaternary ammonium chlorides on the reaction of labile hydrogen compounds and chlorine-substituted derivatives, CR Hebd. Seances Acad. Sci. Ser. C 232 (1951) 1424–1434.
- [2] E.V. Dehmlow, S.S. Dehmlow, Phase transfer catalysis, Monographs in Modern Chemistry, Vol. II, Verlag Chemie, Weinheim, 1983.
- [3] C.M. Starks, C.L. Liotta, M.E. Halpern, Phase transfer catalysis, Fundamentals, Applications and Industrial Perspectives, Chapman & Hall, New York, 1994.
- [4] C.M. Starks, R.M. Owens, Phase transfer catalysis. II. Kinetic details of cyanide displacement on 1-haloctanes, J. Am. Chem. Soc. 95 (1973) 3613–3617.
- [5] H.H. Freedman, Industrial applications of phase transfer catalysis: past, present and future, Pure Appl. Chem. 58 (6) (1986) 857–868.
- [6] P.J. Collings, M. Hird, Introduction to Liquid Crystals Chemistry and Physics, Taylor & Francis, New York, 1997, pp. 150–155.
- [7] S. Kobayashi, Catalysis in Precision Polymerization, Wiley, New York, 1997, pp. 143–157.
- [8] L.G. Wade Jr., Organic Chemistry, 3rd Edition, Prentice Hall, Englewood Cliffs, NJ, 1995, pp. 593–609.
- [9] C. Siswanto, T. Battal, O.E. Schuss, J.F. Rathamn, Synthesis of alkylphenyl ethers in aqueous surfactant solutions by micellar phase-transfer catalysis. 1. Single-phase system, Langmuir 13 (1997) 6047–6052.
- [10] M.-L. Wang, S.W. Chang, Synthesis of formaldehyde acetals by phase transfer catalysis, Bull. Chem. Soc. Jpn. 66 (8) (1993) 2149–2155.