Kinetic Study of Synthesizing Bisphenol A Diallyl Ether in a Phase-Transfer Catalytic Reaction

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In the synthesis of bisphenol A diallyl ether from bisphenol A and allyl bromide, the liquid–liquid mode of operation catalyzed by quaternary ammonium salts was carried out in an alkaline solution/organic solvent two-phase medium. The mono-substituted product was not detected during or after the reaction. In this work, a rational reaction mechanism is proposed and a kinetic model then established. The apparent rate constant of the organic-phase reaction was obtained from experimental data. The effects of the reaction conditions, including agitation speed, organic solvents, quaternary ammonium salts, inorganic salts, temperature, alkali compounds, amount of potassium hydroxide, and water on the conversion of allyl bromide, were investigated in detail. The presence of a small amount of tetrabutylammonium bromide (TBAB) in the chlorobenzene/water system produced a rate over several folds larger than that of the reaction system in the absence of phase-transfer catalyst. The presence of alkali compounds promoted the formation of alkoxide and enhanced the extractive efficiency due to the salting out effect. The present etherification via phase-transfer catalyst could operate at lower temperatures to avoid Claisen rearrangement, which usually occurs at higher temperatures. Rational reasons to account for the absence of mono-substituted product are explained satisfactorily. Peculiar phenomena in investigating the effects of the volume of organic solvent, amount of KOH, and the volume of water and alkali compounds on the apparent rate constants are also explained.

Phase-transfer catalysis (PTC)[1–3] is an effective technique for conducting heterogeneous reactions where the reagents are located in different continuous phases.[4] In order for phase-transfer catalysis to take place, the quaternary ammonium cation must effectively transport the reactant anion from the aqueous phase through the interfacial region into the organic phase[5] for an ion-pair extraction of a normal phase-transfer catalysis (NPTC). Undoubtedly, PTC offers many substantial advantages for the practical execution of numerous reactions.[6] Its wide application in organic synthesis is well deserved.[2] NPTC reactions generally include the Starks extraction mechanism and Makosza interfacial mechanism.[1–3,6] The model of Starks extraction mechanism argues that: (1) The main reaction takes place in the organic phase, (2) the desired anion is transferred to the organic phase, and (3) the catalyst is important for both the reaction step and the transfer step. The quaternary ammonium salt forms lipophilic ion pairs with the nucleophilic reagent (anion) entering the organic phase for further reactions. In principle, the reaction at high temperature and the use of protic and aprotic solvents can be avoided in phase-transfer catalytic reactions. Thus, the byproducts obtained from side reactions at higher temperatures and the impact to the environmental in using protic and aprotic solvents are prevented. The phase-transfer catalytic process consequently has lower safety risks and is environmentally friendlier.[7]

Bisphenol A diallyl ether (BPADAE) is a product of high economic-value, which is widely used for high-technology applications, including epoxidised adhesives for semiconductor chips, photoresists, tough impact resistant prepregs, mouldings with high breaking toughness for fibre reinforced structures, composites with high heat, water, and chemical resistance, and coatings with high heat, water, and chemical resistance.[8] It is also widely employed as a cross-linking agent in epoxy resin.[9,10]

The objective of this paper is to synthesize bisphenol A dially ether by a new path, i.e. phase-transfer catalysis. In the present work, bisphenol A diallyl ether was synthesized from the reaction of bisphenol A and allyl bromide catalyzed by quaternary ammonium salts used as PTC in an alkaline solution/organic solvent two-phase medium. Mono-substituted product was not observed during or after the reaction. The greatest advantage of using PTC to synthesize bisphenol A diallyl ether via PTC is that the reaction can be carried out at a lower temperature. Therefore, the Claisen rearrangement, which usually occurs at higher temperatures, can be avoided. From the experimental data, a rational reaction mechanism is proposed and pseudo-first-order rate kinetics are developed. The effects of the reaction conditions, such as agitation speed, organic solvents, quaternary ammonium salts, alkali compounds, amount of KOH, TBAB catalyst, volume of organic solvent, inorganic salts, and temperature, on the conversion of allyl bromide are investigated in detail. Peculiar phenomena in investigating the effects of the volume of organic solvents, the volume of water, and amount of KOH, and alkali compounds on the apparent rate constants are explained.

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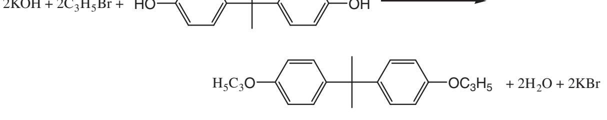
Experimental

Materials. The reactants: 4,4′-isopropylidenediphenol (bisphenol A) and allyl bromide; the solvents: benzene, chlorobenzene, cyclohexane, cyclohexanone, 1,4-dioxane, dibutyl ether, and toluene; the alkali compounds: potassium hydroxide and sodium hydroxide; the catalysts (QX): trioctylmethylammonium chloride (Aliquat 336), tetrabutylammonium bromide (TBAB), tetrabutylammonium chloride (TBAC), tetrabutylammonium hydrogensulfate (TBAHS), tetraethylammonium bromide (TEAB), tetraoctylammonium bromide (TOAB), and phenyltrimethylammonium bromide (PTMAB), and other reagents were all guaranteed grade (G. R.) chemicals.

Procedures. Synthesis of Bisphenol A Diallyl Ether and Its Separation: Measured quantities of bisphenol A (15 mmol), allyl bromide (300 mmol), cyclohexane (50 mL), TBAB catalyst (0.32 g, 1 mmol), water (20 mL), and potassium hydroxide (16.8 g) were charged in the reactor of a 250-mL three-neck Pyrex flask. The mixed solution was stirred continuously at an agitation speed of 600 rpm using a Yamato LR400C stirrer equipped with a PTFE stirring blade. At the same time, the reactor was submerged in a constant-temperature water bath, HAAKE refrigerating circulator F6-C40, in which the temperature was controlled to within ±0.1 °C at 30 °C. After 2.5 h of reaction, the two-phase solution was separated and the portion of the organic solution was washed five times with an alkaline solution to remove TBAB catalyst using a separatory funnel. Vacuum evaporation was carried out by using a Yamato RE-440 equipped with a BM-400 water bath. When the organic solvent (cyclohexane) was evaporated, the residual syrupy liquid was the product, bisphenol A diallyl ether (BPADAE). The product was identified by mass spectroscope (VG Quattro GC/MS/MS/DS) for molecular weight and NMR (^{1}H NMR and ^{13}C NMR) for functional groups, respectively.

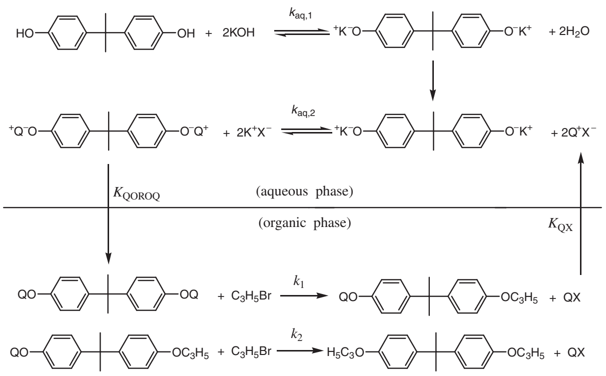
Kinetics of the Etherification: The reactor was a 150 mL three-neck Pyrex flask. Predetermined quantities of 4,4′-isopropylidenediphenol, allyl bromide, potassium hydroxide, naphthalene (as internal standard), organic solvent, water, and phase-transfer catalyst were introduced into the reactor. The reactor was kept in an isothermal water bath at a constant known temperature and mechanically agitated by an electric motor powered agitator. For a kinetic run, a sample (approximately 0.3 mL) was withdrawn from the mixed solution at a predetermined time. The withdrawn sample was then immediately added to 5 mL of cool methanol to quench the reaction. High performance liquid chromatography (HPLC) was carried out with a Shimadzu SPD-10AVP using Glass VP 5.0 analysis software with UV wavelength of 204 nm. An RP-18e (5 µm) column (Applied Merck Co.) was used to separate the components and to analyze the withdrawn sample experimentally.

Reaction Kinetics and Mechanism. A total reaction for this present system is



(1)

According to the experimental observation, mono-substituted product $Q^+O^-C_6H_4C(CH_3)_2C_6H_4OC_3H_5$ was not found. Only the di-substituted product (bisphenol A diallyl ether) $H_5C_3OC_6H_4C(CH_3)_2C_6H_4OC_3H_5$ was produced from the reaction solution. For this, a rational reaction mechanism is proposed as follows:



(2)

The mechanism was formulated on the basis of Starks' extraction model.[1,3] Thus, for this instance, the reactive anion was produced in base-initiated reactions by proton extraction from the substrate and then the formed active catalyst ion-pair $Q^+O^-C_6H_4C(CH_3)_2$-$C_6H_4O^-Q^+$, which is an organic soluble compound, was then transferred into the organic phase. During the reaction, the mono-substituted product $Q^+O^-C_6H_4C(CH_3)_2C_6H_4OC_3H_5$ was not detected. This phenomenon indicates that the value of the second intrinsic rate constant in the organic phase, k_2 is larger than that of the first intrinsic rate constant, k_1. Then, the mono-substituted product $Q^+O^-C_6H_4C(CH_3)_2C_6H_4OC_3H_5$ further reacted with allyl bromide to produce bisphenol A diallyl ether. Afterwards, Q^+X^- transferred from the organic phase to the aqueous phase for further regeneration. $[QOC_6H_4C(CH_3)_2C_6H_4OQ]_o$ and $[QX]_o$ were kept at constant values using a large excess of bisphenol A. From the experimental data, no other by-products were observed. In addition, independent experiment was carried out to demonstrate that bisphenol A would hardly dissolve in pure water or in the organic solvent. According to the proposed mechanism and the two-film theory, the material balances for the regenerated QX and the active catalyst, QOROQ, (i.e. $QOC_6H_4C(CH_3)_2C_6H_4OQ$), in the organic and aqueous phases are:

$$\frac{d[QOROQ]_O}{dt} = K_{QOROQ}A\left([^+Q^-ORO^-Q^+]_a - \frac{[QOROQ]_o}{M_{QOROQ}}\right) - k_1[C_3H_5Br]_o[QOROQ]_o, \tag{3}$$

$$\frac{d[^+Q^-ORO^-Q^+]_a}{dt} = k_{aq,2}[^+K^-ORO^-K^+]_a[Q^+X^-]_a^2 - K_{QOROQ}Af\left([^+Q^-ORO^-Q^+]_a - \frac{[QOROQ]_o}{M_{QOROQ}}\right), \tag{4}$$

$$\frac{d[QX]_o}{dt} = k_1[C_3H_5Br]_o[QOROQ]_o + k_2[C_3H_5Br]_o[QOROC_3H_5]_o - K_{QX}A([QX]_o - M_{QX}[Q^+X^-]_a), \tag{5}$$

$$\frac{d[Q^+X^-]_a}{dt} = K_{QX}Af([QX]_o - M_{QX}[Q^+X^-]_a) - 2k_{aq,2}[^+K^-ORO^-K^+]_a[Q^+X^-]_a^2, \tag{6}$$

$$Q_0 = V_o(2[QOROQ]_o + [QOROC_3H_5]_o + [QX]_o) + V_a(2[^+Q^-ORO^-Q^+]_a + [Q^+X^-]_a), \tag{7}$$

where f is the volume ratio of the organic solution (V_o) to the aqueous solution (V_a). R denotes the -$C_6H_4C(CH_3)_2C_6H_4$- group. The subscripts "o" and "a" denote the characteristics of the species in the organic and aqueous phases, respectively. k_1 and k_2 are the intrinsic rate constants of the two sequential reactions in the organic phase. $k_{aq,1}$ and $k_{aq,2}$ are the intrinsic rate constants of the two ionic reactions in the aqueous phase. A which is the interfacial area between two phases is defined as the interfacial area between the two phases/volume of organic solution, i.e. cm^2/cm^3. Q_0 is the total catalyst in the reaction solution. K_{QOROQ} and K_{QX} are the mass-transfer coefficients of QOROQ and QX between two phases, i.e. (cm/s). M_{QOROQ} and M_{QX} are the distribution coefficients of QOROQ and QX between two phases, respectively, i.e.

$$M_{\text{QOROQ}} = \frac{[\text{QOROQ}]_{\text{o,s}}}{[^{+}\text{Q}^{-}\text{ORO}^{-}\text{Q}^{+}]_{\text{a,s}}}, \tag{8}$$

$$M_{\text{QX}} = \frac{[\text{QX}]_{\text{o,s}}}{[\text{Q}^{+}\text{X}^{-}]_{\text{s,s}}}, \tag{9}$$

where the subscript "s" represents the equilibrium condition of the species at the interface.

On the basis of the experimental observation, the concentrations of QOROQ and QX in the organic and aqueous phases reached constant values at the beginning of the reaction.[11,12] Therefore, a pseudo-steady-state hypothesis (PSSH) is applied, i.e.

$$\frac{d[\text{QOROQ}]_{\text{o}}}{dt} = 0, \quad \frac{d[^{+}\text{Q}^{-}\text{ORO}^{-}\text{Q}^{+}]_{\text{a}}}{dt} = 0,$$
$$\frac{d[\text{QX}]_{\text{o}}}{dt} = 0, \quad \frac{d[\text{Q}^{+}\text{X}^{-}]_{\text{a}}}{dt} = 0. \tag{10}$$

Combining Eqs. 3–7 and 10, we obtain

$$\begin{aligned}\frac{Q_0}{V_{\text{o}}} &= [\text{QOROQ}]_{\text{o}}\left(2 + \frac{2}{fM_{\text{QOROQ}}}\frac{k_1[\text{C}_3\text{H}_5\text{Br}]_{\text{o}}}{K_{\text{QX}}A} + \frac{2k_1[\text{C}_3\text{H}_5\text{Br}]_{\text{o}}}{fK_{\text{QOROQ}}A}\right)\\ &\quad + [\text{QOROQ}]_{\text{o}}^{1/2}\left\{M_{\text{QX}}\left(\frac{fk_1[\text{C}_3\text{H}_5\text{Br}]_{\text{o}}}{k_{\text{aq},2}[^{+}\text{K}^{-}\text{ORO}^{-}\text{K}^{+}]_{\text{a}}}\right)^{1/2} + \left(\frac{k_1[\text{C}_3\text{H}_5\text{Br}]_{\text{o}}}{fk_{\text{aq},2}[^{+}\text{K}^{-}\text{ORO}^{-}\text{K}^{+}]_{\text{a}}}\right)^{1/2}\right\}.\end{aligned} \tag{11}$$

The following Damkohler numbers, Da_{QOROQ} and Da_{QX} are defined as,

$$Da_{\text{QOROQ}} = \frac{k_1[\text{C}_3\text{H}_5\text{Br}]_{\text{o}}}{K_{\text{QOROQ}}A}, \tag{12}$$

$$Da_{\text{QX}} = \frac{k_1[\text{C}_3\text{H}_5\text{Br}]_{\text{o}}}{K_{\text{QX}}A}. \tag{13}$$

R_{y} is defined as the ratio of the organic-phase reaction rate to the aqueous-phase reaction rate, i.e.

$$R_{\text{y}} = \frac{k_1[\text{C}_3\text{H}_5\text{Br}]_{\text{o}}}{k_{\text{aq},2}[^{+}\text{K}^{-}\text{ORO}^{-}\text{K}^{+}]_{\text{a}}}. \tag{14}$$

Introducing Eqs. 12–14 into Eq. 11 yields a dimensionless form,

$$\begin{aligned}\frac{Q_0}{V_{\text{o}}} &= [\text{QOROQ}]_{\text{o}}\left(2 + \frac{2}{fM_{\text{QOROQ}}} + \frac{2}{f}Da_{\text{QOROQ}} + Da_{\text{QX}}\right)\\ &\quad + [\text{QOROQ}]_{\text{o}}^{1/2}\left\{M_{\text{QX}}fR_{\text{y}}^{1/2} + \left(\frac{R_{\text{y}}}{f}\right)^{1/2}\right\}.\end{aligned} \tag{15}$$

Several independent experiments were carried out to measure the concentrations of QOROQ in the aqueous and organic phases. It was found that the concentration of QOROQ in the organic phase remained at a constant value after one minute of reaction. This result indicates that the values of $K_{\text{QOROQ}}A$ and $K_{\text{QX}}A$ are all larger than that of $k_1[\text{C}_3\text{H}_5\text{Br}]_{\text{o}}$. Furthermore, the rate of aqueous ion-exchange is more rapid than that of the organic phase. Thus, the value of the aqueous-phase rate constant $k_{\text{aq},2}$ is larger than that of the organic-phase rate constant k_1. For this, Eq. 15 is simplified to

$$[\text{QOROQ}]_{\text{o}} = \frac{Q_0}{2V_{\text{o}}}\frac{fM_{\text{QOROQ}}}{(1 + fM_{\text{QOROQ}})}. \tag{16}$$

Material balances for the compounds in the reaction solution are:

$$\begin{aligned}-\frac{d[\text{C}_3\text{H}_5\text{Br}]_{\text{o}}}{dt} &= k_1[\text{C}_3\text{H}_5\text{Br}]_{\text{o}}[\text{QOROQ}]_{\text{o}}\\ &\quad + k_2[\text{C}_3\text{H}_5\text{Br}]_{\text{o}}[\text{QOROC}_3\text{H}_5]_{\text{o}},\end{aligned} \tag{17}$$

$$\begin{aligned}\frac{d[\text{QOROC}_3\text{H}_5]_{\text{o}}}{dt} &= k_1[\text{C}_3\text{H}_5\text{Br}]_{\text{o}}[\text{QOROQ}]_{\text{o}}\\ &\quad - k_2[\text{C}_3\text{H}_5\text{Br}]_{\text{o}}[\text{QOROC}_3\text{H}_5]_{\text{o}},\end{aligned} \tag{18}$$

$$\frac{d[\text{H}_5\text{C}_3\text{OROC}_3\text{H}_5]_{\text{o}}}{dt} = k_2[\text{C}_3\text{H}_5\text{Br}]_{\text{o}}[\text{QOROC}_3\text{H}_5]_{\text{o}}. \tag{19}$$

The mono-substituted product QOROC_3H_5 was not observed during or after the reaction. Therefore, a pseudo-steady-state hypothesis (PSSH) is applied, i.e.

$$\frac{d[\text{QOROC}_3\text{H}_5]_{\text{o}}}{dt} = 0. \tag{20}$$

Thus, Eq. 18 becomes

$$[\text{QOROC}_3\text{H}_5]_{\text{o}} = \frac{k_1}{k_2}[\text{QOROQ}]_{\text{o}}. \tag{21}$$

Substituting Eq. 21 into Eq. 17, and applying Eq. 16, we obtain

$$-\frac{d[\text{C}_3\text{H}_5\text{Br}]_{\text{o}}}{dt} = 2k_{\text{app}}[\text{C}_3\text{H}_5\text{Br}]_{\text{o}}, \tag{22}$$

$$\begin{aligned}k_{\text{app}} &= k_1[\text{QOROQ}]_{\text{o}} = k_2[\text{QOROC}_3\text{H}_5]_{\text{o}}\\ &= \frac{k_1fM_{\text{QOROQ}}}{1 + fM_{\text{QOROQ}}}\frac{Q_0}{2V_{\text{o}}}.\end{aligned} \tag{23}$$

Integrating Eq. 22 yields

$$\frac{[\text{C}_3\text{H}_5\text{Br}]_{\text{o}}}{[\text{C}_3\text{H}_5\text{Br}]_{\text{o,i}}} = \exp(-2k_{\text{app}}t). \tag{24}$$

The subscript "i" represents the initial concentration of the species. Eq. 24 is rewritten as

$$-\ln(1 - X) = 2k_{\text{app}}t, \tag{25}$$

where X is defined as the conversion of $\text{C}_3\text{H}_5\text{Br}$, i.e.

$$X = 1 - \frac{[\text{C}_3\text{H}_5\text{Br}]_{\text{o}}}{[\text{C}_3\text{H}_5\text{Br}]_{\text{o,i}}}, \tag{26}$$

in which $[\text{C}_3\text{H}_5\text{Br}]_{\text{o,i}}$ denotes the initial concentration of allyl bromide in the organic phase. Thus, the value of k_{app} can be obtained from experimental data in conjunction with Eq. 25.

Results and Discussion

In the present work, bisphenol A diallyl ether was synthesized from the reaction of allyl bromide and bisphenol A catalyzed by phase-transfer catalysis in an alkaline aqueous solution/organic solvent two-phase medium. Two sequential substitution reactions in the organic phase were carried out. Only the final product bisphenol A diallyl ether was observed in the organic phase. The mono-substituted product $\text{QOC}_6\text{H}_4\text{C(CH}_3)_2\text{C}_6\text{H}_4\text{OC}_3\text{H}_5$ (QOROC_3H_5) in the organic phase was not obtained. This result indicates that the reactivity of QOROC_3H_5 is greater than that of QOROQ. Furthermore, this result indicates that two hydroxy groups of each bisphenol A molecule both react with quaternary ammonium salt and KOH to form QOROQ. In order to find out the optimum reaction con-

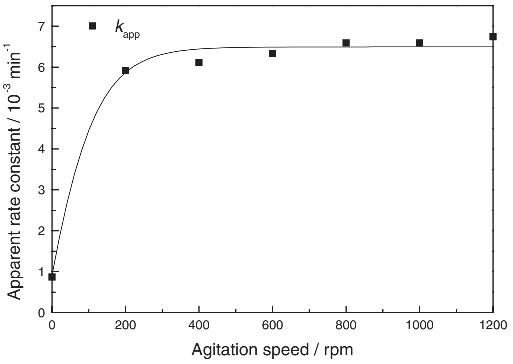


Fig. 1. Effect of the agitation speed on the apparent rate constant, k_{app}; 15 mmol of allyl bromide, 25 mmol of bisphenol A, 20 mL of chlorobenzene, 1 mmol of TBAB catalyst, 20 g of KOH, 40 mL of water, and 30 °C.

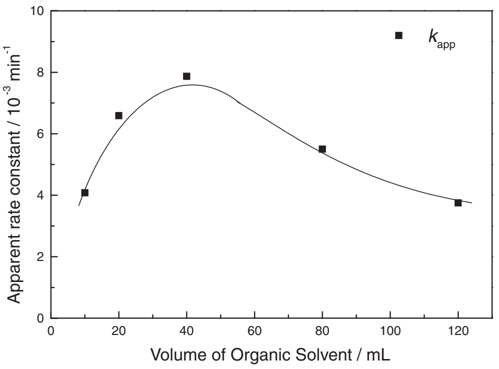


Fig. 2. Effect of the amount of organic solvent on the apparent rate constant, k_{app}; 15 mmol of allyl bromide, 25 mmol of bisphenol A, 1 mmol of TBAB catalyst, 20 g of KOH, 40 mL of water, 1000 rpm, and 30 °C.

ditions, agitation speed, amount of organic solvents, phase-transfer catalysts, potassium hydroxide, water, organic solvents, alkali compounds, quaternary ammonium salts, inorganic salts, and reaction temperature were all considered. The effects of the operating conditions are discussed and summarized below.

Effect of Agitation Speed. In the present study, experiments were carried out to examine the effects of agitation speed on the apparent rate constants. The values of the apparent rate constants k_{app} under various agitation speeds are given in Fig. 1. The agitation speed had no significant influence on the apparent rate constant in the range of 200–1200 rpm. For agitation speed less than 200 rpm, the conversion is highly affected by the agitation speeds in which the mass transfer and chemical reaction both play important role. The conversion of bisphenol A at 200–600 rpm was slightly lower than that in the range of 800–1200 rpm. Thus, the agitation speed was set at 1000 rpm to eliminate the mass-transfer resistance and to assess the effect of other variables on the reaction rate in the following experiments. The concentration of the active catalyst $[QOROQ]_o$ in the organic phase was constant. In other words, the rate of mass transfer is larger than that of reaction in the organic phase.

Effect of Volume of Organic Solvents. In this study, chlorobenzene was chosen as the organic solvent. The results are shown in Fig. 2. The optimal volume of organic solvents to obtain a maximum value of the apparent rate constant was observed. The apparent rate constant is first increased and then decreased with the increase in the volume of organic solvents. The phenomenon can be explained with the aid of Eqs. 16 and 23. In addition, the conditions for measuring the distribution coefficients of QOROQ between organic phase and aqueous phase are the same as those of the reaction conditions, i.e. bisphenol A, KOH, and QBr are all introduced to the measuring vessel. Under this circumstance, KOROK in a large quantity and QOROQ in a limited quantity are all produced in the aqueous phase. Then, the hydrophilic KOROK drives the hydrophobic QOROQ to the organic phase from the aqueous phase in the region of 10 to 40 mL of organic solvent. Thus, more QOROQ remains in the organic phase when the volume of organic phases is increased in the region of 10 to 40 mL. For this, the distribution coefficient of QOROQ is increased with an increase in the volume of organic solvent for 10–40 mL. For a further increase in the volume of organic solvent, the dilution effect becomes more important. The concentration of QOROQ in the organic solvent is then decreased with an increase in volume of organic solvent. Thus, the distribution coefficient of QOROQ is then decreased when the volume of organic solvent is larger than 40 mL. The main reason is that the volume of the organic phase affects the environment of the reaction, i.e., the concentration of the organic-phase reactant and the concentration of the internal standard. In addition, the capacity of the catalyst in the organic phase is also influenced by the volume of the organic phase. Therefore, the distribution coefficient of the active catalyst between two phases is affected by the volume of the organic phase. The distribution coefficients M_{QOROQ} between organic and aqueous phases (40 mL of water) are 0.60, 0.84, 7.57, 1.06, and 0.49, for 10, 20, 40, 80, and 120 mL of organic solvent, respectively. It is obvious that the concentration of the active catalyst $[QOROQ]_o$ in the organic phase is first increased when the volume of organic solvents rose up to 40 mL. A further increase in the volume of organic solvents reduced the concentration of QOROQ. Therefore, there was a maximum in the apparent rate constant at 40 mL of organic solvents. For this reason, Figure 2 exhibits an optimal value of organic solvents that maximizes the concentration of active catalytic species.

Effect of Quaternary Ammonium Salts. Quaternary ammonium salts are generally used as phase-transfer catalysts to promote reaction rate. In addition to TBAB, six other quaternary ammonium salts, such as TBAC, TBAHS, TEAB, TOAB, Aliquat 336, and PTMAB, were investigated to test their reactivities. The experimental results are listed in Table 1. The reactivity of the anion, $^{-}ORO^{-}$, depends on its degree of hydration and on the structure of its counter cation. Comparing TEAB, TBAB, and TOAB reveals that the more lipophilic the quaternary ammonium cation, the greater the effectiveness in transferring nucleophilic anion into the organic media is. In other words, the catalytic activities are mainly due to the solubilities of their ion-pairs $^{+}Q^{-}ORO^{-}Q^{+}$ in the organic phase, which in turn can be attributed to the nature and bulkiness of Q^{+} and the properties of the medium. As shown in Table 1, the reactivities of TBAB, TBAC, and TBAHS are not affected significantly by the anions, X^{-}, with the symmetric tetrabutyl-

Table 1. Effects of the Phase-Transfer Catalysts on the Apparent Rate Constant (k_{app})[a)]

Catalyst	$k_{app}/10^3$ min^{-1}
TBAB	6.59
TBAC	6.59
TBAHS	5.67
TEAB	3.22
TOAB	9.90
Aliquat 336	7.84
PTMAB	2.30

a) Reaction conditions: 15 mmol of allyl bromide, 25 mmol of bisphenol A, 3 mmol of internal standard (naphthalene), 20 mL of chlorobenzene, 20 g of KOH, 40 mL of water, 1000 rpm, and 30 °C.

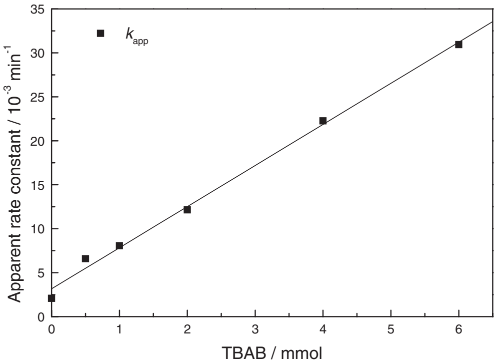


Fig. 3. Effect of the amount of TBAB catalyst on the apparent rate constant, k_{app}; 15 mmol of allyl bromide, 25 mmol of bisphenol A, 20 mL of chlorobenzene, 20 g of KOH, 40 mL of water, 1000 rpm, and 30 °C.

ammonium cation (Q^+). However, the sulfate ion of TBAHS catalyst is relatively weaker in basicity than those of Br^- and Cl^- of TBAB and TBAC catalysts. Therefore, the dissociation of HSO_4^- from TBAHS is more difficult than those of TBAB and TBAC catalysts. For this, the reactivity of TBAHS is less than those of TBAB and TBAC catalysts. Comparing PTMAB and TEAB shows that the symmetrical molecules possess high reactivity although the number of carbon atoms of PTMAB is greater than that of TEAB. It is because the phenyl group is much less lipophilic than the corresponding aliphatic straight chain containing the same number of carbon atoms and the steric hindrance of phenyltrimethylammonium cation. The activity of the lipophilic cation Q^+ is determined mainly by two factors: its extractability and the anion activation ability. Structural factors affect the formation of active catalyst cation–anion pairs between the organic phase and aqueous phase. Based on the above argument, the order of the reactivities of these quaternary ammonium salts are: TOAB > Aliquat 336 > TBAB > TBAC > TBAHS > TEAB > PTMAB.

Effect of the Amount of TBAB Catalyst. The effect of the amount of TBAB catalyst on the reaction was studied by conducting six experiments. As shown in Fig. 3, the apparent rate constant (k_{app}) is plotted against the TBAB catalyst amount ranging from 0 to 6 mmol. It is obvious that the apparent rate constant (k_{app}) increased linearly with the amount of TBAB catalyst. This result is in agreement with Eq. 23 in which the apparent rate constant is in proportion to the initial amount of catalyst added. In the absence of TBAB catalyst, 36% of the conversion of allyl bromide was obtained after 150 min. Nevertheless, 36% of the conversion was obtained only within 10 min of reaction when 6 mmol of TBAB catalyst was added to the solution. It shows that the phase-transfer catalyst is indeed capable of promoting the etherification effectively.

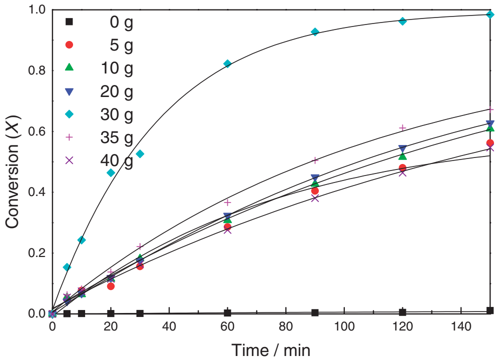


Fig. 4. Kinetics for studying the effect of the amount of potassium hydroxide on the conversion; 15 mmol of allyl bromide, 25 mmol of bisphenol A, 20 mL of chlorobenzene, 1 mmol of TBAB catalyst, 40 mL of water, 1000 rpm, and 30 °C.

Effect of the Amount of Potassium Hydroxide. The effect of the amount of potassium hydroxide on the reaction conversion of etherification was investigated and the results are shown in Fig. 4. No etherification was observed in the absence of potassium hydroxide (only 1% conversion after 150 min). However, the reaction was enhanced by adding KOH to the reaction solution. Nevertheless, the conversion of the reactant did not change significantly for the change in the amount of KOH from 5 to 20 g. The addition of a large excess of potassium hydroxide, 30 g, dramatically accelerated the reaction. From the conversion of allyl bromide monitored by high performance liquid chromatography (HPLC), it was confirmed that etherification proceeded smoothly to reach almost 100% conversion within 150 min. The reactivity of the anion, $^-ORO^-$, depended both on its degree of hydration and on its association with the quaternary ammonium cation. The degree of hydration was affected by the presence of KOH in the aqueous phase. The activity of the transferred anion was thus enhanced compared with its reactivity in the aqueous media as its degree of hydration was reduced.[13] It is interesting to note that the conversion decreased conspicuously after adding 40 g of potassium hydroxide. It is because the solution was saturated by the addition of 40 g of potassium hydroxide and 25 mmol of bisphenol A to 40 mL of water, leading to the salting out of bisphenol A as a white gel. Under this circumstance, the etherification system would be changing from a liquid–liquid PTC to a liquid–solid (bisphenol A) PTC. The change would decrease the reaction rate sharply. As shown in Fig. 5, the conversion of allyl bromide is first increased with an increase in the amount of KOH up to 30 g and then decreased with any further increase in the amount of KOH.

Effect of the Amount of Water. The effect of the volume of water on the apparent rate constant (k_{app}) was investigated.

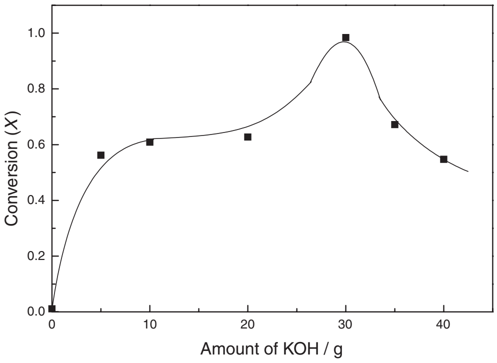


Fig. 5. Effect of the amount of potassium hydroxide on the conversion of allyl bromide; 15 mmol of allyl bromide, 25 mmol of bisphenol A, 20 mL of chlorobenzene, 1 mmol of TBAB catalyst, 40 mL of water, 1000 rpm, and 30 °C.

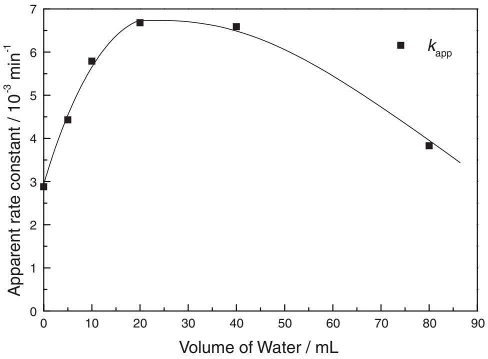


Fig. 6. Effect of the volume of water on the apparent rate constant, k_{app}; 15 mmol of allyl bromide, 25 mmol of bisphenol A, 20 mL of chlorobenzene, 1 mmol of TBAB catalyst, 20 g of KOH, 1000 rpm, and 30 °C.

As shown in Fig. 6, there is an optimal volume of water in this etherification. The apparent rate constant increased with an increase in the volume of water (0–20 mL) and then decreased with a further increase in the volume of water. A limited amount of water (0–20 mL) formed a local saturated water layer around the reacting species and consequently the reaction rate increased because of the increase in interface area by adding 0 to 20 mL of water. When an adequate amount of water was added, all of the reactants in the aqueous phase, bisphenol A and potassium hydroxide, dissolved. Therefore, all of the reagents facilitate the reaction in the optimum fraction between the aqueous phase and the organic phase. Further increasing the amount of water thus reduced both the alkaline concentration in the aqueous phase and the concentration of active catalyst in the organic phase, because a greater amount of active catalysts remained in the aqueous phase. Thus, the apparent rate constant (k_{app}) is decreased with an increase in the amount of water of more than 20 mL.

Table 2. Effects of the Organic Solvents on the Apparent Rate Constants (k_{app})$^{a)}$

Organic solvent	ε	E_T^N	$k_{app}/10^3$ min^{-1}
Dibutyl ether	2.8	0.07	3.57
Toluene	2.4	0.10	4.49
Benzene	2.3	0.11	4.13
Chlorobenzene	5.6	0.19	6.59
1,4-Dioxane	2.2	0.16	5.21
Cyclohexane	2.0	0.01	3.58
Cyclohexanone	18.3	0.28	4.93

a) Reaction conditions: 15 mmol of allyl bromide, 25 mmol of bisphenol A, 3 mmol of internal standard (naphthalene), 20 mL of organic solvent, 1 mmol of TBAB catalyst, 20 g of KOH, 40 mL of water, and 30 °C.

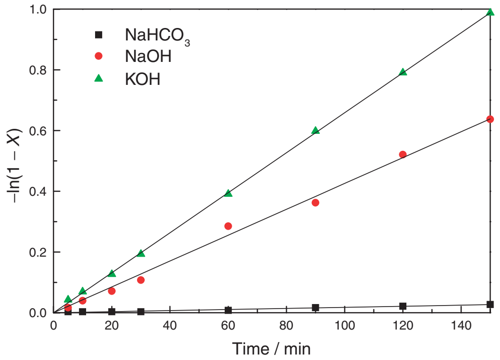


Fig. 7. Effect of the alkaline solution on the conversion of allyl bromide; 15 mmol of allyl bromide, 25 mmol of bisphenol A, 20 mL of chlorobenzene, 1 mmol of TBAB, 357 equi-mmol of alkaline compound, 40 mL of water, 1000 rpm, and 30 °C.

Effect of Organic Solvents. In the phase-transfer catalytic reaction, the solvent dramatically influences the reactive activity. Dibutyl ether, toluene, benzene, chlorobenzene, 1,4-dioxane, cyclohexane, and cyclohexanone were used to investigate the influence of organic solvents on reactivity. The results are shown in Table 2. The order of the reactivities for these organic solvents was: dibutyl ether ≒ cyclohexane < benzene < toluene < cyclohexanone < 1,4-dioxane < chlorobenzene. In this reaction system, organic solvents are used to dissolve the catalyst and reactive reagent. However, the active catalyst and the reacting molecules in the solution often become inactive because they are always surrounded by a number of solvent molecules. In general, the more polar the solvent, the more it can strip the bound water away from the catalyst. High solvation to the active catalyst and reacting molecules often has a negative effect on the acceleration of etherification. Furthermore, organic solvents also affect the distribution of the active catalyst between the two phases and the chemical environment of the reaction system. Therefore, the effect of organic solvents on the reaction is complicated. It is not simple to predict their effects simply by using only the dielectric constant or Dimroth–Reichardt parameter of organic solvents.

Effect of the Alkali Compounds. The effect of different alkali compounds, such as NaOH, KOH, and $NaHCO_3$, on the reaction rate was examined. As shown in Fig. 7, the etherification rate is enhanced owing to the increase in extractive efficiency of bisphenoxides by increasing the base concentration. In principle, the alkali compounds affect the distribution of the active catalyst between the two phases, and the solubility of bisphenol A in the aqueous phase. Both sodium hydroxide and potassium hydroxide exhibit strong basicity, and sodium hydrogencarbonate exhibits weaker basicity. As shown in Fig. 7, the reaction rate when using sodium hydroxide was much lower than when using potassium hydroxide. The reason is that the white gel (solid bisphenol A) was salted out when using NaOH during the reaction, i.e. the solution was oversaturated when using 40 mL of water to dissolve 357 equi-mmol of sodium hydroxide and 25 mmol of bisphenol A. Thus, for convenience, potassium hydroxide was used in all experimental runs of the present study. The diether compound could be obtained using a concentrated alkaline solution (NaOH and KOH). However, the stabilities of these catalysts decreased considerably in an aqueous–organic two-phase system with a strong alkaline aqueous solution. Other highly efficient phase-transfer catalysts, e.g. cryptands and crown ethers, are chemically stable in the presence of concentrated alkaline aqueous solution, but their relatively high costs and/or toxicity limit their usage.[14–18] On the other hand, quaternary ammonium salts are widely available and inexpensive. For this reason, quaternary ammonium salts are quite often the phase-transfer catalysts of choice, even in strongly alkaline aqueous solutions regardless of their low stability.[19]

Effect of the Inorganic Salts. In phase-transfer catalytic reactions, the inorganic salts added sometimes influence the conversion. To investigate the effect of inorganic salts on etherification, potassium bromide, potassium chloride, sodium bromide, and sodium chloride were added to the reaction system. In general, the hydration levels of all ions present in the system tend to decrease when the salt concentration in the aqueous phase is increased. The added salt ties up water molecules for the dehydrating effect on the ions present in the system.[13] Furthermore, the high-concentration inorganic salt in the aqueous phase salts out the quaternary onium salts into the organic phase and thereby alters the distribution coefficients of the phase-transfer catalysts. Thus, the inexpensive inorganic salts have the potential of promoting reaction rate when compared to the same reaction conditions without inorganic salts. Unfortunately, as shown in Fig. 8, adding inorganic salt did not increase the reaction rate. Instead a slight decrease in reaction rate was observed in this etherification system. It can be explained from the reaction mechanism that the presence of more inorganic salts does not favor the formation of the active catalyst, $^{+}Q^{-}ORO^{-}Q^{+}$, in the aqueous phase. Comparing the results for KCl, NaCl, KBr, and NaBr with the same anion gives the order of the conversion of allyl bromide as: KCl > NaCl and KBr > NaBr. The reason is that the presence of sodium cations causes their salting out as the white gel. From this viewpoint, the addition of sodium cations is more unfavorable than the addition of potassium cations. Moreover, comparing the results for KCl, KBr, NaCl, and NaBr with the same cation gives the order of the conversion of allyl bromide as: KBr > KCl and NaBr > NaCl. The reason is that hydrophilic complexes associate more strongly with a chloride ion among halide ions. In other words, the existence of bromide ions would make the aqueous phase more lipophilic than the existence of chloride ions which would make the aqueous phase more compatible with the organic solvents.

Effect of Temperature. Etherification was studied at different temperatures. The results are shown in Fig. 9. The conversion was found to increase substantially with increasing temperature. The reaction follows the pseudo-first-order rate law for all temperatures. At higher temperatures beyond 30 °C, allyl bromide was slightly evaporated and the kinetic data is unreliable. In addition, Claisen rearrangement is an intramolecular thermal rearrangement at higher temperature, as shown in Scheme 1. Plotting $\ln(k_{\mathrm{app}})$ against T^{-1} gives an apparent activation energy of 65.6 kJ mol^{-1} from the Arrhenius equation, as shown in Fig. 10. The apparent activation energy confirmed that etherification is kinetically controlled.

Conclusion

Preparation of bisphenol A diallyl ether from the reaction of biphenol A and allyl bromide using phase-transfer catalyst was achieved successfully at room temperature and effectively avoided the occurrence of Claisen rearrangement. The reaction rate is greatly enhanced by adding a small quantity of phase-transfer catalyst to the reaction system. The kinetic model was constructed and the mass transfer and phase equilibrium of the catalysts between the two phases were also constructed by the two-film theory. Under the appropriate conditions, the conversion reached as high as 100%. The reaction was found to be kinetically controlled. Chlorobenzene was the best organic solvent for the present system of the etherification reaction and tetraoctylammonium bromide (TOAB) was the best cata-

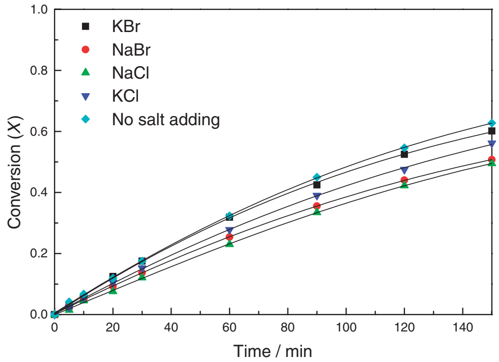


Fig. 8. Effect of salts added on the conversion of allyl bromide; 15 mmol of allyl bromide, 25 mmol of bisphenol A, 20 mL of chlorobenzene, 1 mmol of TBAB catalyst, 20 g of KOH, 40 mL of water, 10 equi-mmol of salt, 1000 rpm, and 30 °C.

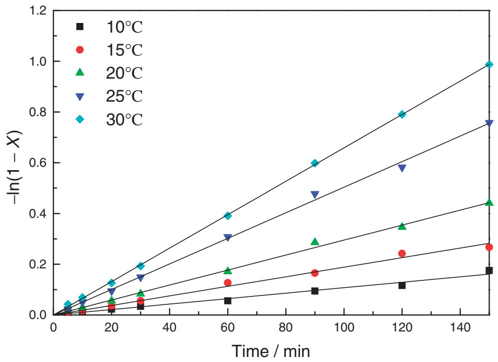
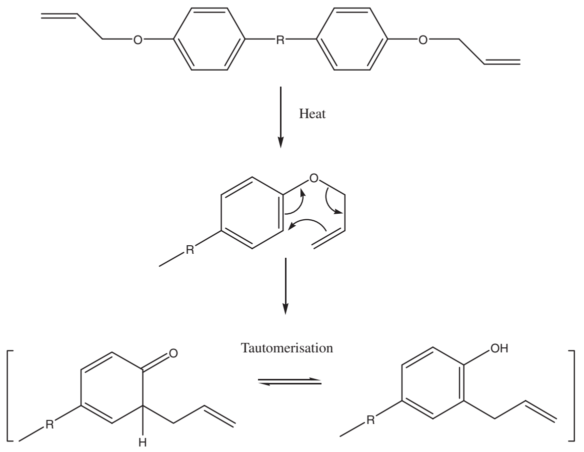


Fig. 9. Effect of the temperature on the conversion of allyl bromide; 15 mmol of allyl bromide, 25 mmol of bisphenol A, 20 mL of chlorobenzene, 1 mmol of TBAB catalyst, 20 g of KOH, 40 mL of water, and 1000 rpm.



Scheme 1. Claisen rearrangement for bisphenol A diallyl ether.

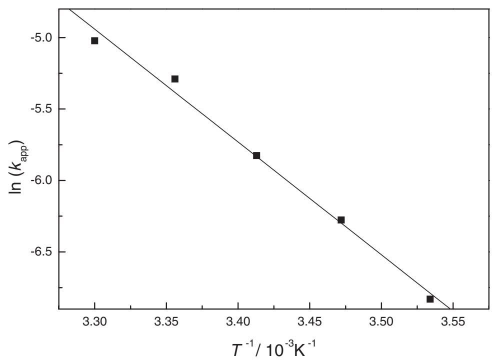


Fig. 10. Arrhenius plot for k_{app} vs $1/T$; 15 mmol of allyl bromide, 25 mmol of bisphenol A, 20 mL of chlorobenzene, 1 mmol of TBAB catalyst, 20 g of KOH, 40 mL of water, and 1000 rpm.

lyst. The anions in the ion pairs Q^+X^- do not affect catalyst efficiency. Potassium hydroxide is better than sodium hydroxide because sodium hydroxide salted out as a white gel in the reaction system. It was also found that the existence of sodium cations decreased the reaction rate when sodium hydroxide or sodium salts were added. The apparent activation energy obtained is 65.6 kJ mol^{-1}.

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