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REACTION MECHANISM OF PHASE-TRANSFER CATALYSIS INITIATED BY HYDROXIDE ION: EFFECT OF ALKALINITY

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ABSTRACT: The reaction of 2,4,6-tribromophenol (ArOH) and α-bromo-*o*-xylene (RBr) catalyzed by tetrabutylammonium bromide (QBr) was carried out in an alkaline solution of KOH/organic solvent two-phase medium. A peculiar phenomenon, in which the rate of a PTC/OH^- reaction does not change monotonously with the concentration of alkaline compound, is observed. This result comes from the fact that the concentration of the active intermediate ArOQ is affected by the concentration of alkaline compound added due to dissociation of ArOH and salting out effect. Not only the polarity of organic solvent, but also the Lewis base of the organic solvent affected by the concentration of alkaline compound influences the reaction rate. The dielectric constants and the Lewis base of organic solvents in affecting the solvation are used to explain how the reaction rate is influenced by the solvents. The concentration of tetrabutylammonium 2,4,6-tribromophenoxide (ArOQ) remains constant throughout the path of reaction. The resistance of mass transfer of ArOQ between the two phases is negligible compared to the slower rate of organic-phase reaction.

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Keywords: phase-transfer catalysis, hydroxide ion, solvation effect, polarity, Lewis base

INTRODUCTION

The slow rate and the low selectivity of reaction of two immiscible reactants in using cosolvents limit the industrial application. This deficiency was overcome by using a

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homogeneous solvent with the advent of phase-transfer catalysis (PTC)[1-5]. The main advantage of using PTC is that reactions can be carried out at a moderate temperature and pressure. The synthesis of ether or ester via PTC was carried out in an alkaline solution to obtain the desired product in high yields. Results from our previous experiments show that the reaction rate is proportional to the concentration of the organic-soluble active intermediate[6-9]. However, the concentration of the organic-soluble active intermediate does not change in proportion to the amount of alkaline compound added. The conversion of reactant (or the reaction rate) does not change monotonously with the increase in the amount of alkaline compound. The decrease of water molecules near the nucleophilic reagent caused by the hydration effect of the alkaline compound[6] cannot explain satisfactorily the same reaction rate obtained at low and high alkaline concentrations.

In this work, the reaction of 2,4,6-tribromophenol (ArOH) and benzyl halide (RBr) in an alkaline solution/organic solvent two-phase medium was carried out to study the effect of hydroxide ion concentration on the conversion of reactant. 2,4,6-Tribromophenoxide anion (ArO^-) which possesses weak alkalinity and unpaired electrons, is an excellent nucleophilic agent. It reacts easily with benzyl halide to produce 2,4,6-tribromophenyl benzyl ether. The dissociation of ArOH into ion, and the solubility of ArOH in aqueous phase are used to explain the peculiar phenomenon for the dependence of ArO^-Q^+ concentration on the concentration of alkaline compound. Thermodynamic functions determined from the reaction conditions in conjunction with the solvation effect of the solvent and reactants are used to explain the peculiar phenomenon of the reaction rate in various organic solvents. The dielectric constant and the Lewis base of the organic solvents are the two important factors affecting the solvation of organic solvents and reactants.

EXPERIMENTAL SECTION

Materials: Reactants used namely, 2,4,6-tribromophenol (ArOH), α-bromo-*o*-xylene (RBr), solvents (dichloromethane, 1,2-dichloroethane, 1,1,1-trichloroethane, carbon tetrachloride and chloroform) as well as other reagents were all guaranteed grade (G.R.) chemicals.

Procedures:

(A) Synthesis of active intermediate (tetrabutylammonium 2,4,6-tribromophenoxide, ArOQ) and ether product (2,4,6-tribromophenyl benzyl ether, ArOR)

Appropriate quantities of 2,4,6-tribromophenol (ArOH, 0.015 moles), potassium hydroxide (0.0357 moles) and tetrabutylammonium bromide (QBr, 0.0153 moles) were dissolved in deionized water (50 mL) and introduced into a 250-mL flask at constant temperature (40 ℃). A white precipitate of crystal form was obtained from the aqueous solution after several minutes of reaction. The solid product was filtrated and washed with pure water several times to remove potassium 2,4,6-tribromophenoxide (ArOK). After drying in a vacuum evaporator, a solid form of white powder (tetrabutylammonium 2,4,6-tribromophenoxide, ArOQ) was obtained.

In synthesis of the ether product (2,4,6-tribromophenyl benzyl ether, ArOR), similar procedure as that of synthesizing ArOQ was used. An appropriate quantity of α-bromo-*o*-xylene (RBr) in dichloromethane (50 mL) was put into the solution of tetrabutylammonium 2,4,6-tribromophenoxide (ArOQ) for reaction 3 hours. The organic solution was then washed by KOH solution to remove the residue of tetrabutylammonium bromide (QBr) after the separation of two phases. A solid precipitate was produced by drying in a vacuum evaporator. A high purity of product (ArOR) was obtained by further recrystallization.

(B) Two-phase phase transfer catalytic reaction

The reactor, controlled at a constant temperature, was a 150-mL three-necked Pyrex flask, fitted with agitator, thermometer, sample port and feed port. Known quantities of 2,4,6-tribromophenol (ArOH), and KOH were put in water and organic solvent to dissolve for 1 hour at an appropriate temperature and introduced into the reactor. In some experiments, the amount of KOH used exceeded the solubility limit of KOH in water. Measured quantities of α-bromo-*o*-xylene and internal standard (anthracene), which were also at the desired temperature, were then added to the reactor. To initiate the reaction, an amount of quaternary ammonium salt was added to the reactor. An aliquot sample (0.1 mL) was withdrawn from the solution and quenched in 4 mL dichloromethane at a chosen time. The sample for analyzing was withdrawn from the organic phase after the separation of two phases and then analyzed quantitatively by HPLC using the method of internal standards. For analysis on an HPLC (Shimadzu LC-9A, Japan), the conditions were: column RP-18 (5 μm), 12.5 cm; eluent, $CH_3CH/CH_3OH/H_2O=6/6/1$ (by volume) for product (ArOR) and organic reactants, $CH_3CN/CH_3OH/H_2O=2/2/1$ by volume for tetrabutylammonium 2,4,6-tribromophenoxide (ArOQ); flow rate 2.0 mL/min.

In addition to identifying the content quantitatively, the reactant and products were also examined by ^1H-NMR ($CDCl_3$, D-chloroform) and Mass spectroscopy to determine the molecular weight of the species. Satisfactory results were obtained when the sample compared with the standard species.

KINETICS OF THE TWO-PHASE REACTION

In this work, tetrabutylammonium 2,4,6-tribromophenoxide (ArO^-Q^+) was isolated from the reaction solution. The concentration of ArO^-Q^+ was measured during the course of reaction. Hence, the reaction of 2,4,6-tribromophenol and α-bromo-*o*-xylene in an alkaline solution of KOH/organic solvent two-phase medium is proposed as

$$\begin{array}{cccccccc}
\mathrm{ArOH} & + & \mathrm{KOH} & \leftrightarrow & \mathrm{ArO^-K^+} & + & \mathrm{H_2O} & \\
 & & & & \downarrow & & & \\
\mathrm{KBr} & + & \mathrm{ArO^-Q^+} & \leftarrow & \mathrm{ArO^-K^+} & + & \mathrm{Q^+Br^-} & \mathrm{(a)} \\
 & & \downarrow & & & & \uparrow & \\
\hline
\mathrm{RBr} & + & \mathrm{ArOQ} & \rightarrow & \mathrm{ArOR} & + & \mathrm{QBr} & \mathrm{(o)}
\end{array} \qquad (1)$$

In Equation (1), ArOH and RBr are the aqueous-phase reactant (2,4,6-tribromophenol) and organic-phase reactant (α-bromo-*o*-xylene), respectively. ArOK and ArOQ are the potassium 2,4,6-tribromophenoxide and tetrabutylammonium tribromophenoxide, respectively. The aqueous-phase concentration of tetrabutylammonium 2,4,6-tribromophenoxide, which was isolated from the aqueous solution, was measured during the course of reaction. The concentration of ArOQ in the organic phase reaches an equilibrium state within 10 seconds. Usually, it takes about 3 hours to complete the two-phase reaction in which the organic-phase reaction is a rate-determining step. Therefore, the resistance of mass transfer of ArOQ from aqueous to organic phase is negligible compared with the rate of reaction in the organic phase.

The rate of reaction in the organic phase is expressed as

$$\frac{dC_{RBr}^{org}}{dt} = -k_{\mathrm{int}} C_{ArOQ}^{org} C_{RBr}^{org} \qquad (2)$$

where C_{RBr}^{org} and C_{ArOQ}^{org} denote the concentration of α-bromo-*o*-xylene (RBr) and tetrabutylammonium 2,4,6-tribromophenoxide (ArOQ) in the organic phase, respectively. k_{int} is the intrinsic rate constant in the organic phase.

In this work, the concentration of ArOQ concentration in the organic phase remains constant throughout the path of reaction. Therefore, we obtain

$$\frac{dC_{RBr}^{org}}{dt} = -k_{app} C_{RBr}^{org} \qquad (3)$$

where k_{app} is the apparent rate constant and is defined as

$$k_{app} = k_{\mathrm{int}} C_{ArOQ}^{org} \qquad (4)$$

Equation (3) is integrated as

$$\ln(1 - X) = -k_{app} t \qquad (5)$$

where X is the conversion of RBr, i.e.

$$X = 1 - C_{RBr}^{org} / C_{RBr,0}^{org} \tag{6}$$

in which $C_{RBr,0}^{org}$ is the initial concentration of RBr in the organic phase. Plotting $-\ln(1-X)$ vs. t shows a straight line with a slope k_{app}.

RESULTS AND DISCUSSION

For the reaction of 2,4,6-tribromophenol and α-bromo-*o*-xylene in an alkaline solution/organic solvent two-phase medium under phase transfer catalysis, the mechanism of reaction can be expressed by Equation (1). In this study, the rate of reaction in the aqueous-phase and the rate of mass transfer of ArOQ and QBr are fast, compared to the rate of reaction in the organic phase. In this work, the concentration of ArOQ in the organic phase of the two phase reaction reaches a constant value within 10 seconds. This result confirms that the reaction in the organic phase is thus a rate-determining step.

(1) Organic-phase reaction

As stated, the active intermediate ArOQ (tetrabutylammonium 2,4,6-tribromophenoxide) can be synthesized and isolated from the reaction of 2,4,6-tribromophenol and tetrabutylammonium bromide (QBr) in an alkaline solution. Therefore, the intrinsic rate constant can be obtained from the organic-phase reaction of tetrabutylammonium 2,4,6-tribromophenoxide (ArOQ) and α-bromo-*o*-xylene (RBr). A large quantity of ArOH (or large ratio of $C_{ArOH,0}^{org} / C_{RBr,0}^{org}$) was used in the reaction. For this, the concentration of ArOQ in the organic phase is kept at a constant value because of the limiting amount of catalyst (QBr). An Arrhenius plot of $\ln(k_{int})$ vs. 1/T was employed to obtain the activation energy 67.96 kJ/mole. The intrinsic rate constant was expressed as

$$k_{int} = 2.28 \times 10^{10} \exp(-8173.7/T) \qquad (T: K) \tag{7}$$

In the PTC/OH$^-$ reaction system, it is important to understand the effect of the alkaline concentration on the reaction rate and the distribution of species between the organic and aqueous phases. Figure 1 shows the dependence of k_{app}-value on the amount of KOH. Figure 2 demonstrates the corresponding concentration of ArOQ in organic phase kept at a constant value for every reaction run (i.e., fixing the amount of KOH). Therefore, the reaction is described by the pseudo-first-order rate law. In Equation (4), the intrinsic rate constant is obtained from the value of k_{app} divided by

C_{ArOQ}^{org}. Thus, the intrinsic rate constants k_{int} are given in Figure 3. The values of k_{app}, k_{int} and C_{ArOQ}^{org} all exhibit a peculiar phenomenon.

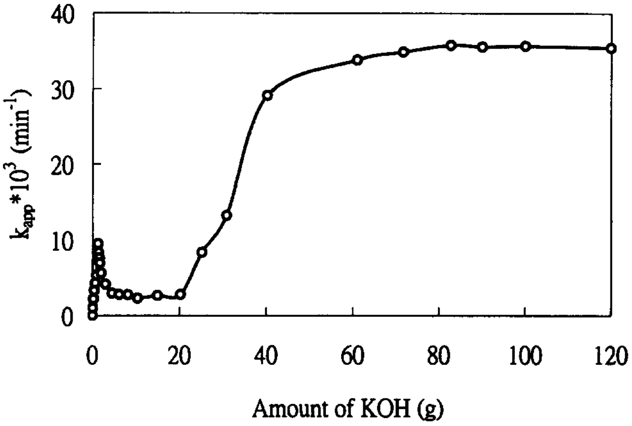

Figure 1 Relation between apparent rate constant (k_{app}) and the amount of KOH in the two-phase reaction; 8 g of 2,4,6-tribromophenol (ArOH), 0.01 mol of α-bromo-*o*-xylene (RBr), 1 g of TBAB (QBr) catalyst, 25 mL of water, 100 mL of dichloromethane, 293 K, 700 rpm

In previous studies[1-5], many researchers recognized that a high reaction rate obtained from a large amount of alkaline compound is due to the action of hydration. Water molecules were repelled by alkaline compounds from the surroundings of the aqueous reactant (or nucleophilic reagent). The naked aqueous-phase reactant (nucleophile) is thus formed to facilitate the reaction. In principle, the hydration number of the aqueous-phase reactant (nucleophile) is zero when a solution of 25 M KOH concentration (corresponding to 35 g of KOH/25 mL of H_2O) is applied. The reaction rate is only affected by the hydration of alkaline compound, the conversion (or the reaction rate) will not further be influenced by the amount of alkaline compound larger than 25 M. However, the k_{app}-value still increases beyond 25 M of KOH from our experimental observation. It is obvious that two points are inconsistent with the experimental observation. First, the same reaction rates are obtained at two different alkaline concentrations. As stated, if only the effect of hydration on reaction is considered, the reaction rate should increase monotonously with the increase in the alkaline concentration. Second, the aqueous-phase reactant (or nucleophile) will no longer be surrounded by water molecules if the alkaline concentration is larger than 25 M (equivalent to 35 g of KOH/25 mL of H_2O), while the reaction rate should approach a constant value. However, as shown in Figure 3, the intrinsic rate constant still increases with the increase in the amount of KOH larger than 35 g of KOH/25 mL of H_2O (25 M). This result indicates that though the effect of hydration is important, it is not the only factor affecting the reaction rate. Therefore, it is interesting to study the effect of alkaline concentration on the conversion.

(2) Effect of the alkaline concentration on the distribution of 2,4,6-tribromophenol

Tribromophenol (ArOH) does not dissolve in pure water but dissolves only in organic solvent (e.g., CH_2Cl_2). The solubility of 2,4,6-tribromophenol (ArOH) in water is highly dependent on the content of alkali within the aqueous solution. The content of 2,4,6-tribromophenol in organic solvent and in aqueous solution vs. the amount of KOH are given in Figures 4 and 5, respectively. As shown in Figure 4, about 98% of ArOH (2,4,6-tribromophenol) in the form of free molecules stays in aqueous solution of higher KOH concentration. In Figures 4 and 5, the amount of 2,4,6-tribromophenol, which dissolves in the alkaline solution, increases greatly up to 5 g of KOH/25 mL of H_2O. Further increase in the amount of KOH leads to a sharp decrease in the amount of ArOH in the alkaline solution. Under this situation, most ArOH reacts with KOH to produce ArOK. Few ArOH in the free molecules exist in the aqueous phase. ArOK precipitates from the solution.

In principle, 2,4,6-tribromophenol (ArOH) is a weak acid with pKa=8.15. The degree of dissociating 2,4,6-tribromophenol into ion in pure water is low. However,

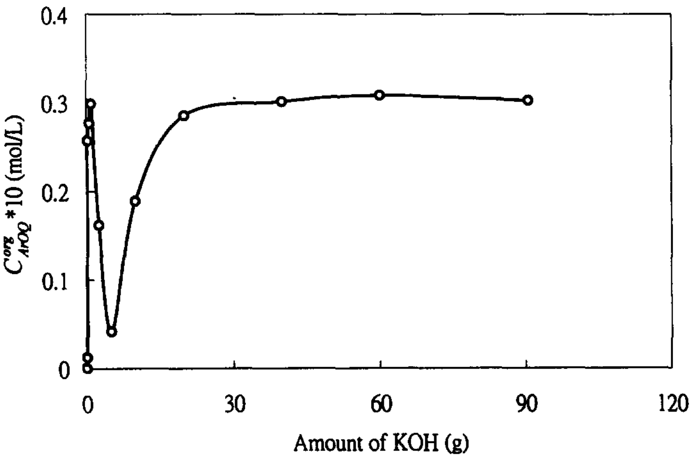

Figure 2 The dependence of the concentration of ArOQ on the amount of KOH in the two-phase reaction (same reaction conditions as given in Figure 1)

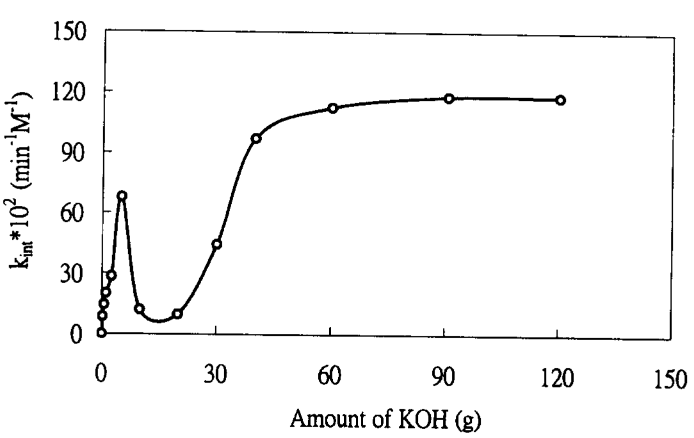

Figure 3 The dependence of the intrinsic rate constant (k_{int}) on the amount of KOH in the two-phase reaction (same reaction conditions as given in Figure 1)

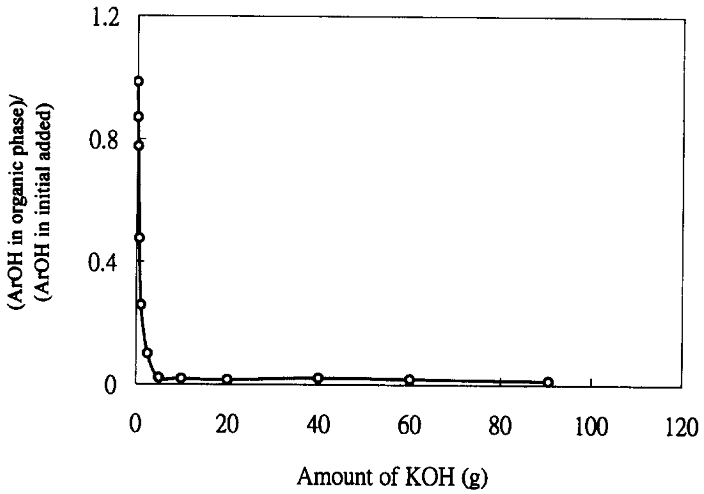

Figure 4 Relation between the concentration of ArOH in the organic- phase and the amount of KOH; 8 g of 2,4,6-tribromophenol (ArOH), 1 g of QBr (TBAB) catalyst, 25 mL of water, 100 mL of dichloromethane, 293 K, 700 rpm

ArO^- appears in the aqueous phase with alkaline added because of the neutralization of ArOH and KOH to produce ArO^-, i.e.

$$Ka = \frac{[H^+]_a[ArO^-]_a}{[ArOH]_a} = \frac{Kw[ArO^-]_a}{[OH^-]_a[ArOH]_a} \tag{8}$$

where Ka and Kw are the acid ionization constant and autoprotolysis constant, respectively. As shown in Equation (8), a greater amount of ArOH transfers to the aqueous phase and dissociates into ion to form ArO^- when $[OH^-]$ is increased. Thus, as shown in Figures 4 and 5, the amount of ArOH dissolving in water is increased with the increase in the amount of KOH up to 5 g. However, the solubility of the content in the aqueous phase is decreased by adding a large amount of alkaline compound. Thus, ArO^- combines with K^+ to form ArOK and precipitates from the solution because of salting out effects when a large amount of ArO^- accumulates in the aqueous solution (with a greater amount of alkaline compound added). Thus, as shown in Figures 4 and 5, the amount of ArOH in free molecule form is decreased with the increase in the amount of KOH larger than 5 g. This result indicates that most of ArOH reacts with QBr in KOH solution to form ArOQ in the aqueous phase. Then, ArOQ in the aqueous solution transfers further to the organic phase in preparation for reaction with the organic-phase reactants. It is, thus, obvious that the concentration of ArOQ in the aqueous phase or in the organic phase is not monotonously increased with the increase of the amount of alkaline compound. Therefore, the rate of reaction, which is dependent on the concentration of ArOQ, is not monotonously with the increase of the amount of alkaline compound.

In this work, the apparent rate constant (k_{app}) at low alkaline concentration is proportional to the amount of catalyst. However, k_{app} is not a linear function of the amount of catalyst at high alkaline concentration. This deviation is mainly due to the activity of the catalyst. As shown in Figure 6, the activity of QBr is decreased with the increase in its concentration. Similar property of tetrabutylammonium 2,4,6-tribromophenoxide (ArOQ) is also obtained.

In general, the activity of the alkaline compound is decreased with the increase in the concentration of ionized compound. Therefore, as expected, the reaction rate is decreased with the increase in the concentration of the reactant species within the range of 1 g KOH to 20 g KOH.

In this work, the effect of organic solvents on the conversion of α-bromo-*o*-xylene is studied. The order of the reactivities of the organic solvents used are:

(a) Low alkaline concentration

Chloroform > Dichloromethane > 1,2-Dichloroethane > Carbon tetrachloride > 1,1,1-Trichloroethane

(b) High alkaline concentration

Chloroform > Dichloromethane > 1,2-Dichloroethane

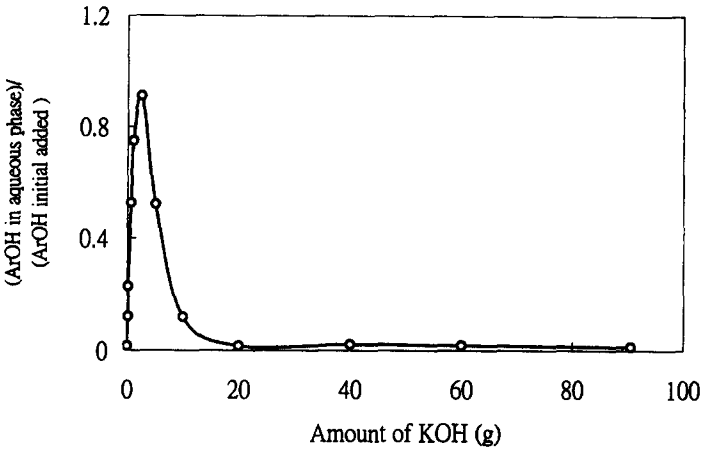

Figure 5 Relation between the concentration of ArOH in the aqueous- phase and the amount of KOH; 8 g of 2,4,6-tribromophenol (ArOH), 1 g of TBAB (QBr) catalyst, 25 mL of water, 100 mL of dichloromethane, 293 K, 700 rpm

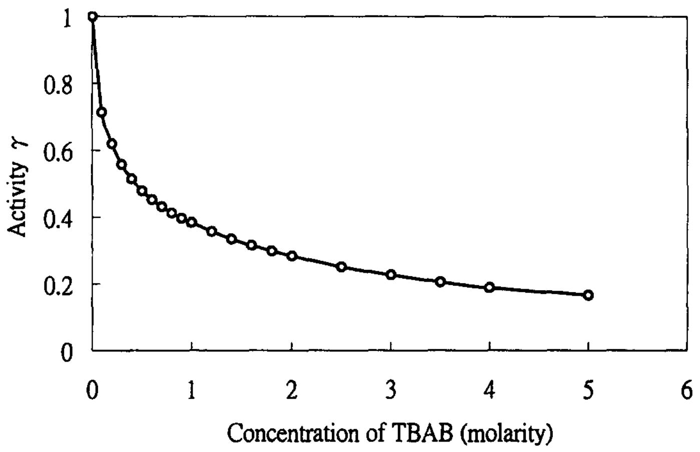

Figure 6 Activity of tetrabutylammonium bromide catalyst vs. its concentration

The order of dielectric constants of these organic solvents are:
1,2-Dichloroethane > Dichloromethane > 1,1,1-Trichloroethane > Chloroform > Carbon tetrachloride

It is obvious that there is no correlation between the reactivity and the dielectric constants of the organic solvents. Thus, it is important to investigate the thermodynamic functions in studying the effect of organic solvents in addition to understanding the kinetics. For an irreversible reaction, the thermodynamic properties of a reaction system can be realized by employing the transition state theory.

According to the Arrhenius classical theory for a reaction to take place, the energy input to a reaction system should overcome the barrier of the activation energy. For a reaction system, the equilibrium constant ($K^{\neq}$) is related to the Gibbs energy ($\Delta G^{\neq}$), enthalpy ($\Delta H^{\neq}$) and entropy of activation ($\Delta S^{\neq}$),

$$\Delta G^{\neq} = -RT\ln(K^{\neq}) \qquad (9)$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \qquad (10)$$

In general, $\Delta S^{\neq}$ denotes the interaction between the activated complex and organic solvent. A positive value of $\Delta S^{\neq}$ reflects that the interaction between the reactants and solvent is stronger than that of the activated complex and solvent. Thus, the reaction rate is slow[10]. However, a negative value of $\Delta S^{\neq}$ indicates that the interaction between the activated complex and the solvent is stronger than that of the reactants and solvent. Thus, the reaction rate is fast with the rate constant (k_{int}) obtained from experiments. The Gibbs free energy $\Delta G^{\neq}$ is calculated from quasi-thermodynamic equilibrium constant $K^{\neq}$. Meanwhile, by plotting $\Delta G^{\neq}$ vs. T, the enthalpy $\Delta H^{\neq}$ and entropy $\Delta S^{\neq}$ can also be determined from the slope of the intercept of the straight line.

The calculated activation energy (Ea), enthalpy ($\Delta H^{\neq}$) and entropy ($\Delta S^{\neq}$) are given in Tables 1 and 2. The order of $\Delta S^{\neq}$ values (J/mol/K) are:

Chloroform (-72.75) < Dichloromethane (-66.87) < Carbon tetrachloride (-61.65) < 1,2-Dichloroethane (-61.61) < 1,1,1-Trichloroethane (-3.20)

These results are consistent with the effect of the organic solvents on the rate of reaction. As shown in Tables 1 and 2, a large deviation of $\Delta S^{\neq}$-value is exhibited in using various organic solvents. A large difference in the Lewis acid (or Lewis base) of the organic solvent causes the reforming of the activated complex which is surrounded by the organic solvent molecules. This results in the difference in interaction between various organic solvents and reactants. For the case of 1,1,1-

trichloroethane, the effect of solvophobic[11,12] is significant when the organic solvent molecules are repelled by the activated complex. Thus, the interaction for the organic solvent and activated complex is less than that for the organic solvent and reactants. Hence, the reaction rate is slow. Chloroform when used as organic solvent, tends to solvate with the activated complex. The organic solvent surrounding the activated complex, is more compact than that near the reactants. Thus, the activated complex tends to solvate with the organic solvent to enhance the reaction rate. The reason for a slow reaction rate in using carbon tetrachloride is that the value of $\Delta H^{\neq}$ is too large.

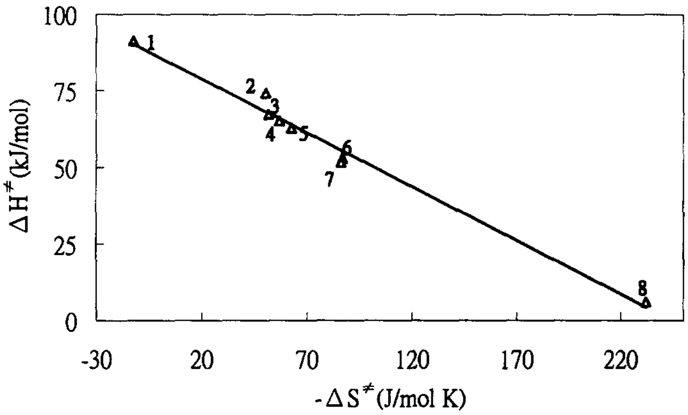

Figure 7 Isokinetic behavior for the effect of organic solvents;
1: 1,1,1-Trichloroethane (1 g KOH) 2: Carbon tetrachloride (1 g KOH)
2: 1,2-Dichloroethane (1 g KOH) 4: Dichloromethane (1 g KOH)
5: Chloroform (1 g KOH) 6: 1,2-dichloroethane (90 g KOH)
7: dichloromethane (90 g KOH) 8: Chloroform (90 g KOH)

Table 1 Effect of organic solvents on the Arrhenius activation functions at low alkalinity, less than 10 g of KOH

Organic solvent	Ea (kJ/mol)	$\Delta H^{\neq}$ (kJ/mol)	$\Delta S^{\neq}$(J/mol/K)
1,2-Dichloroethane	69.67	67.33	-61.61
Dichloromethane	67.16	65.10	-66.87
1,1,1-Trichloroethane	94.17	90.59	-3.20 (≅ 0)
Chloroform	66.74	62.73	-72.75
Carbon tetrachloride	78.34	74.47	-61.65

Table 2 Effect of organic solvents on the thermodynamic functions at high alkalinity, large than 30 g of KOH

Organic solvents	Ea (kJ/mol)	$\Delta H^{\neq}$ (kJ/mol)	$\Delta S^{\neq}$ (J/mol/K)
1,2-Dichloroethane	56.69	53.01	-96.76
Dichloromethane	54.18	51.28	-97.52
Chloroform	2.26	6.12	-242.28

A plot $\Delta H^{\neq}$ vs. $\Delta S^{\neq}$ is given in Figure 7 in which the experimental data are located on a straight line. This result indicates that the reactions in various solvents are isokinetic[11]. Hence, the effect of organic solvent on the interaction with the activated complex is due to the change in the organic solvent. The alkaline compound interacts with the organic solvent. That is, the Lewis base of the organic solvent is increased with the addition of alkaline compound. In the same organic solvent, both $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are increased with the concentration of alkaline compound. The arrangement of the organic solvent molecules near the activated complex at high alkaline concentration is more compact than that at low alkaline concentration. The properties of the organic solvent are changed with the addition of alkaline compound, i.e. the Lewis base becomes stronger from which it is favorable for the existence of carbonium. Thus, the reaction rate is greatly enhanced. In other words, the intrinsic properties of the organic solvent are changed owing to to the change in alkaline concentration.

As shown in Tables 1 and 2, a large deviation of $\Delta S^{\neq}$ comes between these organic solvents. It is understandable that the most important factor affecting the reaction comes directly from the reforming of the organic solvent molecules which surround the activated complex. This reforming results in the deviation for these organic solvents in the solvation of the activated complex and the organic solvent.

CONCLUSION

In this work, a wide spectrum of the concentration of alkaline compound (KOH) was employed to investigate its effect on the conversion of α-bromo-*o*-xylene. A peculiar phenomenon in which the conversion of α-bromo-*o*-xylene does not monotonously change with the amount of KOH was found. The conversion first increases, then decreases, increase again and further remains constant with the amount of KOH. This result was explained by the fact that the concentration of ArOQ in the aquoeus phase or in the organic phase highly depends on the dissociation of ArOH and the salt out effect. The solvation of the organic solvent and the reactant, and the Lewis base of the organic solvent, which are influenced by the properties of the organic solvents offer a satisfactory explanation of this peculiar phenomenon. The thermodynamic functions for the reaction system in various organic solvents were estimated. According to the thermodynamic properties, the conversions were satisfactorily explained by the estimated values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$.

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