

# Kinetics of Synthesizing 2,4,6-Tribromophenyl Benzyl Ether in a Triphase Catalysis

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## SYNOPSIS

The reaction of benzyl bromide with 2,4,6-tribromophenol in an organic solvent/aqueous alkaline solution of KOH to synthesize 2,4,6-tribromophenyl benzyl ether by triphase catalysis was investigated. The macroporous and microporous polymer pellets that served to support the catalyst were prepared by reacting styrene monomers, chloromethylstyrene monomers, and divinylbenzene in a suspension polymerization. Tributylamine was then immobilized on the surface of the polymer pellet to form the three-phase phase-transfer catalysts. The effects of the rate of agitation, degree of cross-linking of the polymer, solvents, inorganic salts, and temperature on the conversion of benzyl bromide and the reaction rate in the three-phase catalytic reaction were investigated in detail. We recommend that a macroporous polymer pellet with a small degree of cross-linking be used to react in a highly polar solvent to obtain high conversion of benzyl bromide and a rapid reaction. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Since Jarrouse and Hebd<sup>1</sup> carried out experiments to promote the rates of reaction between two immiscible reactants by adding a small amount of quaternary ammonium salt, phase transfer catalysis (PTC) has been extensively discussed.<sup>2-4</sup> It is considered to be an effective tool in organic synthesis of specialty chemicals.<sup>5-7</sup> A generally accepted mechanism is that the catalyst will transfer between the two phases. The onium salts mask and thereby make metal ions soluble. The anions of the reacting salts transfer into the organic medium in the form of ion pairs. The greatest advantages of PTC are that expensive anhydrous or aprotic solvents are no longer required and that reaction rates are increased, with a low reaction temperature and high selectivity.

Although there are several advantages in use of PTC to synthesize specialty chemicals, the separation of the catalyst from the final product is difficult. For this, Regen and co-workers<sup>8-11</sup> first used a solid-phase catalyst, from which the tertiary amine was

immobilized on a polymer support, in the reaction between an organic reactant and an aqueous reactant. Thus, the insoluble polymer-supported phase-transfer catalyst was readily separated from the reaction mixtures simply by filtration or centrifugation. The most common method used for triphase catalysis is nucleophilic displacement.<sup>9,10,12-14</sup> The triphase catalysis possesses high potential in industrial-scale applications for the synthesis of organic chemicals from two immiscible reactants. Nevertheless, the structure of polymer support, synthesized from the emulsion polymerization of styrene and chloromethylstyrene monomers, will highly affect the reaction rate of the triphase catalysis. The effects of the internal molecular structure, which plays an important role in the imbibed composition, on the reaction rate have been seldom discussed. Therefore, the main purpose of the present study was to investigate the three-phase catalytic reaction rates, which are influenced by the bromide density within the catalyst, the inorganic salt, the degree of cross-linking, and the organic solvents.

In general, triphase catalysis is useful for those reactions that occur in two-phase phase-transfer catalytic reactions. We investigated the kinetics of synthesis of 2,4,6-tribromophenyl benzyl ether in a

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liquid (organic)–solid (catalyst)–liquid (aqueous) three-phase batch reactor. The specific reaction was between 2,4,6-tribromophenol and benzyl bromide in an aqueous alkaline solution of KOH/organic solvent with triphase catalysis. The factors affecting the rate of overall reaction, including rate of agitation, particle size, solvent, concentration of potassium hydroxide, amount of catalyst, and temperature, were examined to determine the optimal operating conditions. A pseudo-first-order rate law for the  $S_N2$  displacement reaction is proposed to describe our kinetic data. We investigated the effects of the intraparticle diffusion and intrinsic reactivity on the observed reaction rate.

## EXPERIMENTAL

### Materials

2,4,6-Tribromophenol [(C<sub>6</sub>H<sub>2</sub>)Br<sub>3</sub>OH], benzyl bromide (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Br), tributylamine [(C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>N], and other reagents were all guaranteed-grade (G.R.) chemicals.

### Procedures

#### *Preparation of Poly(styrene-co-chloromethylenestyrene), 2% Divinylbenzene Cross-linked, Macroporous and Microporous*

The reactor was a Pyrex flask (500 mL) having four necks to serve the purposes of agitating the solution, inserting the thermometer, inserting the reflux condenser, and feeding the feed. The reactor was immersed in a constant temperature water bath in which the temperature (90°C) was controlled within  $\pm 0.1^\circ\text{C}$ .

To start a polymerization experiment to prepare the macroporous polymer pellets,<sup>11–14</sup> known quantities of boric acid (1.0 g), sodium hydroxide (25%, 4 mL), gelatin (1.2 g), calcium carbonate (3.2 g), and water (500 mL) were prepared and introduced into the reactor, which was thermostated at the desired temperature (87°C). The solution was agitated at 400 rpm for 30 min, and the reactor was purged with inert nitrogen gas. Known quantities of styrene monomers (28.68 g), chloromethylstyrene monomers (12.02 g), divinylbenzene (DVB, 8.53 g, purity 60%), and 4-methyl-2-pentanol (15 mL) were then added to the reactor. Benzoyl peroxide (BPO, 0.4 g) served as initiator of the polymerization reaction. After 5 h of reaction, the polymer particles produced were then washed with a sodium hydroxide solution (1%), hydrochloric acid (1 M), and sodium hydrox-

ide solution (1%) in sequence five times. Then, 4-methyl-2-pentanol was stripped out by steam in a distillation chamber. In addition, 4-methyl-2-pentanol was further extracted with acetone in a Soxhlet extractor. The final products were dried in a vacuum oven.

In principle, the procedure and conditions for preparing the microporous polymer pellets were exactly the same as those for preparing the macroporous polymer pellet, except that 4-methyl-2-pentanol was not added in the polymerization. Therefore, it was not necessary to strip 4-methyl-2-pentanol by steam or to extract it further with acetone.

#### *Immobilizing Tributylamine on the Polymer Support*

A flask (250 mL), which contained the polymer support (5.0 g), dimethylformamide (30 mL), and tributylamine (10 g), was set in a vibrating oven at 60°C for 6 days. The polymer was filtered and washed with methanol and dried under vacuum at 60°C. The content of the chloride ion was determined by the Volhard method.

#### *Kinetics of the Triphase Catalytic Reactions*

The reactor used was the same as that used in preparing the polymer-supported pellet. The reactor was submerged in a constant-temperature water bath in which the temperature was controlled within  $\pm 0.1^\circ\text{C}$ . To start a kinetic run, measured quantities of the immobilized catalyst on the polymer support, organic solvent (chlorobenzene) (50 mL), and diphenyl ether (internal standard) were added to the reactor, which was thermostated at the desired temperature for 30 min to ensure full swelling of the catalyst pellet. Known quantities of potassium hydroxide and 2,4,6-tribromophenol were prepared and dissolved in the water. The solution was then introduced into the reactor. The mixture was stirred mechanically at 400 rpm for 30 min. After the agitation was increased to the desired value, benzyl bromide was added to the reactor to start the reaction at zero time. During the reaction, an aliquot sample (0.5 mL) was withdrawn from the solution at a chosen time. The sample was immediately added to 3 mL of hydrochloric acid to quench the reaction and then analyzed for the contents in the organic phase quantitatively by HPLC using the internal standard method. The HPLC instrument (Waters Model 440) has a variable-wavelength detector (254 nm was used) with RP-18 (5  $\mu\text{m}$ , Merck Co., Germany).

The eluent was CH<sub>3</sub>OH/CH<sub>3</sub>CN/H<sub>2</sub>O = 4/1/1, with a flow rate 1.1 mL/min.

## REACTION KINETICS

The addition of a small catalytic quantity of the immobilized catalyst pellet greatly enhanced the reaction rate. Both organic and aqueous phases were found within the catalyst pellet in a triphase catalytic reaction.<sup>15</sup> Thus, the substitution reaction in the organic phase, the ion-exchange reaction in the aqueous phase, and the mass transfer of reactant in the bulk phase or within the particle should all be considered in such a rapidly reacting system with triphase catalysis. The resistance of particle diffusion can be neglected only when the particle size of the triphase catalyst is smaller than 20 μm.<sup>12</sup> The particle size of our triphase catalyst was about 200–300 μm. Therefore, the reaction system of the triphase catalysis in this study was affected by diffusion for both the organic-phase and aqueous-phase reactions. According to the experimental data, the characteristics of the reaction are described by a pseudo-first-order rate law.

The reaction of benzyl bromide (RBr) and 2,4,6-tribromophenol (ArOH) in an alkaline solution of KOH/chlorobenzene solvent was catalyzed by immobilizing tributylamine on the polymer support. 2,4,6-Tribromophenol (ArOH) first reacted with potassium hydroxide in the presence of the immobilized catalyst to form Resin-OAr. Then Resin-OAr reacted with benzyl bromide (RBr) to form the desired product. In general, the reaction system is controlled by film diffusion when a linear relation is obtained in the plot of the apparent rate coefficient ( $k_{app}$ ) vs. the reciprocal of particle size ( $r$ ). The value of  $k_{app}$  is almost a linear function of the reciprocal of the particle size of an mi2 polymer-supported catalyst pellet.<sup>16</sup> Therefore, the reaction system is controlled by film diffusion for this mi2 (see Table I) polymer-supported catalyst pellet.

For the ion-exchange step in the aqueous phase, the intrinsic ion-exchange rate is large. Therefore, the rate-determining step in the aqueous phase is probably film diffusion in the bulk solution and particle diffusion within the catalyst pellet. Even though the molecular structure of an mi2 polymer-supported pellet (small degree of cross-linking) is generally not compact, the resistance of particle diffusion still cannot be neglected. The reaction system is then controlled by film diffusion in the aqueous phase and particle diffusion within the catalyst pellet.

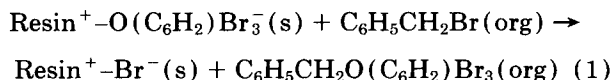
In a triphase reaction,<sup>12–15</sup> a general acceptable

**Table I Effect of the Structure of the Polymer Pellet on the Molar Equivalence of Activity of Catalysts**

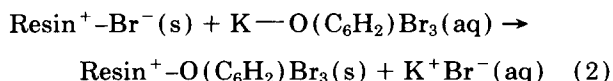
Polymer-supported Pellet	Molar Equivalence of Activity of Catalyst
mi2, RS20%	0.830
mi6, RS20%	0.708
mi10, RS20%	0.750
ma2, RS20%	0.702
ma10, RS20%	0.626
mi2, RS10%	0.544
mi2, RS20%	0.830
mi2, RS30%	1.045
mi2, RS49%	1.358
mi2, RS60%	1.589

mi2 denotes a microporous polymer pellet with 2% degree of cross-linking. ma10 denotes a macroporous polymer pellet with 10% degree of cross-linking. RS20 denotes 20% of ring substitution of the polymerization.

mechanism is to divide the overall kinetics into two steps by virtue of the presence of two practically immiscible liquid phases: a chemical conversion step in which the active catalyst sites (resin with 2,4,6-tribromophenoxide ion, or Resin<sup>+</sup>-O(C<sub>6</sub>H<sub>2</sub>)Br<sub>3</sub><sup>-</sup>, Resin<sup>+</sup>-OAr<sup>-</sup>) react with the benzyl bromide in organic solvents, i.e.:



and the ion-exchange step in which the attached catalyst sites are in contact with the aqueous phase, i.e.:



The total quantity of the catalytically active sites are  $S$ ; thus,

$$S = [\text{Resin}^+ - \text{O}(\text{C}_6\text{H}_2)\text{Br}_3^- (\text{s})] + [\text{Resin}^+ - \text{Br}^- (\text{s})] \quad (3)$$

An acceptable reaction mechanism for the triphase catalysis was proposed by Tomoi et al.<sup>13</sup> Both reactants in the organic and aqueous phases diffuse through the pores to the catalytically active sites of the particles. Reaction occurs at the catalytically active sites to generate the desired products, after which the products diffuse to the bulk solution. Ac-

ording to the experimental data, the reaction obeyed the pseudo-first-order rate law with respect to the organic reactant when an excess of 2,4,6-tribromophenol was used, i.e.:

$$\frac{d[\text{RBr}]_o}{dt} = -k_{\text{app}}[\text{RBr}]_o \quad (4)$$

in which the subscript "0" represents the concentration of benzyl bromide (RBr) in the organic phase. The apparent rate coefficient ( $k_{\text{app}}$ ) is given as

$$k_{\text{app}} = k[\text{Resin-OAr}] \quad (5)$$

In eq. (5),  $k$  is the intrinsic rate constant of the reaction of aqueous reactant with Resin-OAr. Equation (4) is solved with the initial condition to give the conversion of benzyl bromide,  $X$ , i.e.:

$$\ln(1 - X) = -k_{\text{app}}t \quad (6)$$

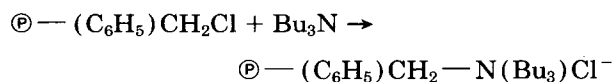
with  $X$  defined as

$$X = 1 - [\text{RBr}]_o / [\text{RBr}]_o^0 \quad (7)$$

The superscript "0" denotes the concentration of benzyl bromide (RBr) in the organic phase at the initial condition. The value of  $k_{\text{app}}$  was obtained by plotting  $\ln(1 - X)$  vs. time for the conversion of benzyl bromide obtained from the experimental data.

## RESULTS AND DISCUSSION

We determined the chlorides contained in the catalyst pellet, which was obtained by means of suspension polymerization, by elemental analysis. This analysis confirms that the catalytic activity of the polymer support results directly from immobilized tributylamine. In this way, portions of the chlorides in the polymer-supported pellet will be ionized according to the following equation:



The ionized chlorides then possess the required catalytic activity. We conducted several blank experiments by using a polymer-supported pellet without immobilization of tributylamine. The chlorides in the polymer-supported pellets possessed no catalytic activity. Only those ionized chlorides pres-

ent in the polymer-supported pellet by immobilizing tributylamine possessed catalytic activity.

We used the measured concentration of chlorides in the catalyst pellets to express the activity of the polymer-supported catalyst. The equivalent of the polymer-supported catalyst was defined in terms of the molar equivalence (meq). The Volhard method was employed to carry out this measurement. The results showing equivalent activity of the polymer-supported catalyst vs. various experimental conditions are given in Table I.

Photographs of the macroporous pellet by scanning electron microscopy (SEM) appear in Figure 1 in which many sizes of macropores (average size: 10–20  $\mu\text{m}$ ) are obtained. To identify the structure within the pellet, we sliced the pellet with an ultramicrotome and then photographed the slice by SEM. Figure 1(b) shows that there are many pores within the pellet. The average pore size and the total surface area for the corresponding microporous pellets and macroporous pellets are shown in Table II. It is seen that the macroporous pellets have a larger pore size than that of the microporous pellets.

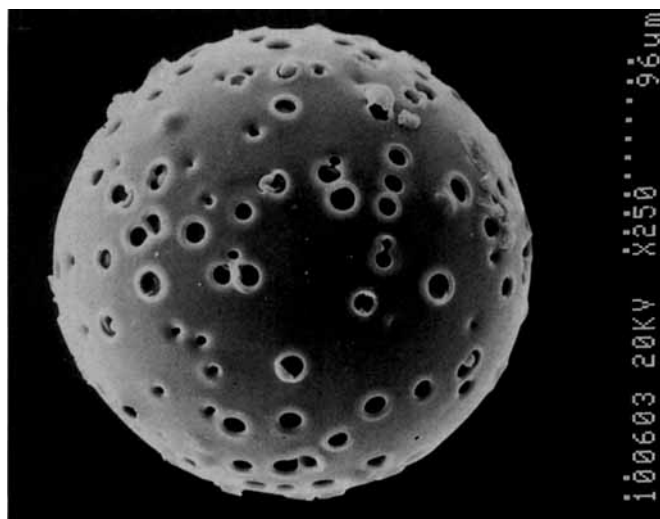
The operating conditions that affect the conversion are summarized as follows:

### Effect of Speed of Stirring on Conversion

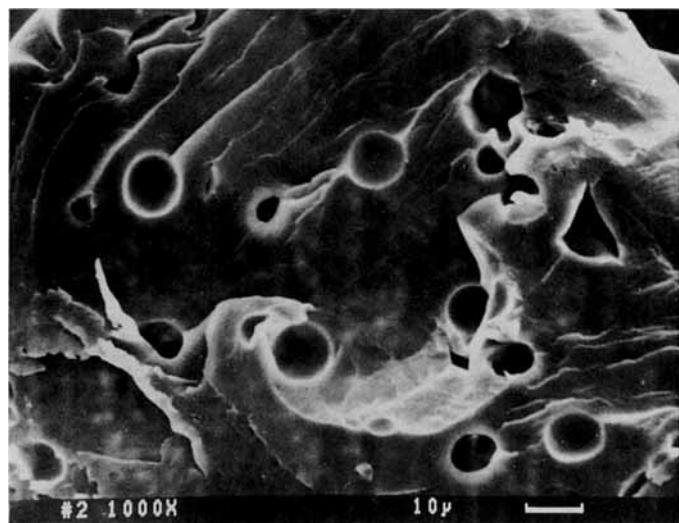
The tributylamine catalyst pellets with 0.932 meq/g equivalent activity, which were immobilized on the mi2 40–80 mesh polystyrene polymers, were employed to study the effects of the rate of agitation on the conversion of benzyl bromide in the organic phase. The results are presented in Figures 2 and 3. The mixing effect by agitation was fully developed when the stirring speed exceeded 400 rpm. For stirring speeds greater than 400 rpm, the resistances to mass transfer of the bulk solution (film diffusion) and within the catalyst pellet were constant. In succeeding experiments, the agitation speeds were all kept at 600 rpm.

### Effects of the Amount of Polymer-supported Catalysts

A polymer-supported catalyst with 0.932 meq/g equivalent activity (mi2, 40–80 mesh) was employed to study the effect of the amount of polymer-supported catalyst on the conversion of benzyl bromide. The results (Fig. 4) indicate that the rate of reaction is increased with increasing amount of the polymer-supported catalyst. A plot of the  $k_{\text{app}}$  value vs. the amount of polymer-supported catalyst (Fig. 5) shows that  $k_{\text{app}}$  exhibits a linear relation with the amount of the polymer-supported catalyst. The



(a) Single particle (ma10, 40-80 mesh)



(b) internal characteristics  
(ma10, 40-80 mesh)

**Figure 1** The surface characteristics of the macroporous polymer particle photographed by SEM: (a) single particle (ma2, 40-80 mesh), magnification  $\times 250$ ; (b) the internal characteristics of the macroporous polymer particle photographed by SEM (ma2, 40-80 mesh), magnification  $\times 1000$ .

straight line passes through the origin, which indicates that the reaction fails without addition of the triphase catalyst.

#### Effects of Degree of Cross-linking of the Polymer

The degree of cross-linking is preset before a polymerization reaction. The pore size and degree of

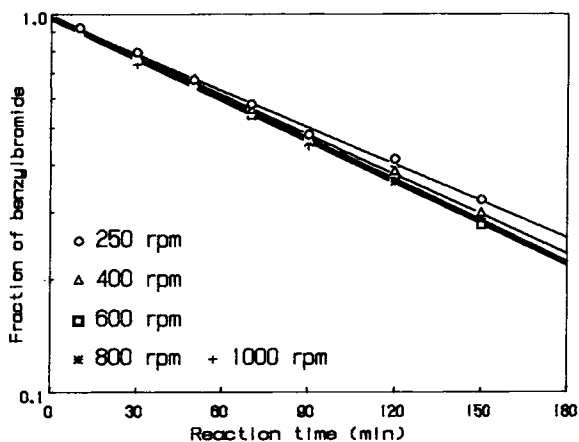
swelling of the polymer-supported pellet by the solvent depend strongly on the degree of cross-linking of the polymer support. For extensive cross-linking, the molecular structure of the polymer is compact. Use of extensive swelling for a slightly cross-linked polymer in an organic solvent is advantageous. The results for the effects of cross-linking (macropores, 0.932 meq/g, 40-80 mesh) on conversion of benzyl

**Table II** Characteristic Properties of the Polymer-supported Pellet

	Size of Polymer-supported Pellet (Mesh)			
	20-40	40-80	80-120	120-200
<b>Microporous pellet (degree of cross-linking: 6%, ring substitution: 10%)</b>				
Average pore diameter (nm)	36.4	35.0	28.3	16.1
Total pore area (m <sup>2</sup> /g)	78.2	112.0	165.0	293.0
Porosity ( $\epsilon$ )	0.418	0.517	0.551	0.561
<b>Macroporous pellet (degree of cross-linking: 10%, ring substitution: 20%)</b>				
Average pore diameter (nm)	64.3	52.7	51.0	28.8
Total pore area (m <sup>2</sup> /g)	45.67	64.38	70.82	130.44
Porosity ( $\epsilon$ )	0.431	0.463	0.495	0.496

bromide in a chlorobenzene solvent are depicted in Figure 6 and show that a little polymer cross-linking enhances the reaction rates.

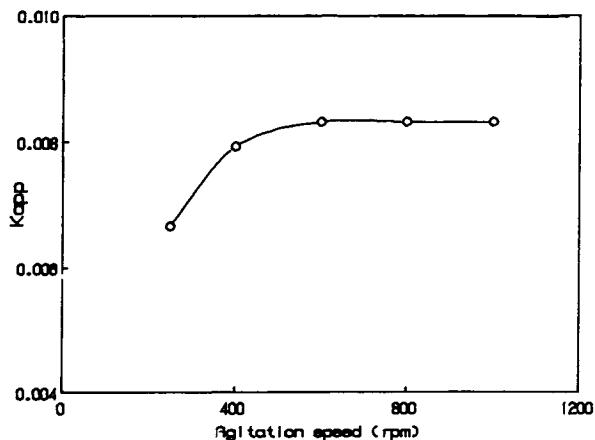
Cross-linking signifies the covalent bonds between two or more linear polymeric chains. Extensive cross-linking implies that the molecular structure of the polymer is compact and is therefore not readily swollen by the solvent. Because of the small amount of swelling with extensive cross-linking, it is difficult to immobilize tributylamine on the internal portions of the polymer-supported pellet. Therefore, a small equivalent activity of the catalyst was obtained when using a polymer with extensive cross-linking. This effect is seen from the data shown in Table I.



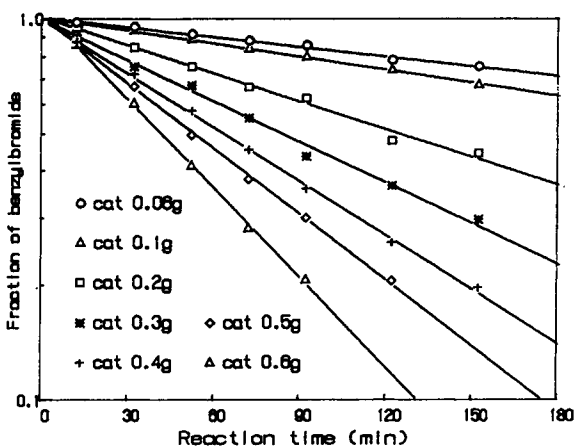
**Figure 2** Effect of the agitation speed on the conversion of benzyl bromide; 4 g of 2,4,6-tribromophenol, 0.9 g of KOH, 0.6 mL of benzyl bromide, 50 mL of water, 50 mL of chlorobenzene, and catalyst (mi2, 0.932 meq/g, 40-80 mesh), 40°C.

### Effects of the Inorganic Salt (KBr) on the Rate of Reaction

The effects of added KBr on the conversion may be positive or negative in a phase-transfer catalytic reaction. First, extra KBr decreases the water content within the polymer pellet; therefore, the concentration (or content) of Resin-OAr is increased; a small concentration of Resin-OAr is favorable for the organic-phase reaction. Second, the anion of the inorganic salt, which is added to the reaction solution, becomes hydrated by water molecules. Therefore, the hydration number of Resin-OAr is obviously decreased. For such a case, the reaction rate is enhanced due to decreasing hydration. Third, the anion of the inorganic salt competes with Resin-OAr for location of catalytically active sites. Therefore, the addition of KBr to the reaction system is unfavorable for the reaction.

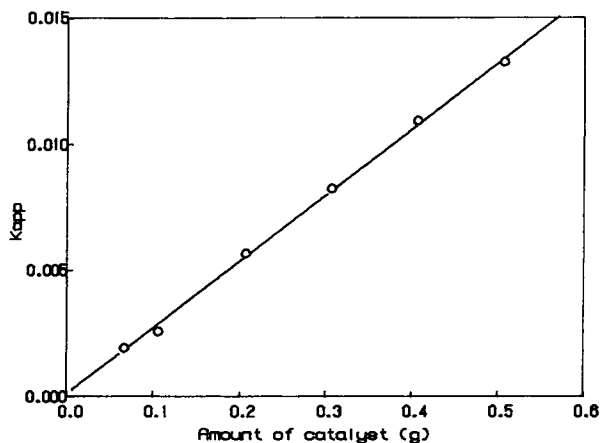


**Figure 3** Effect of the agitation speed on  $k_{app}$  value; same reaction conditions as given in Figure 2.

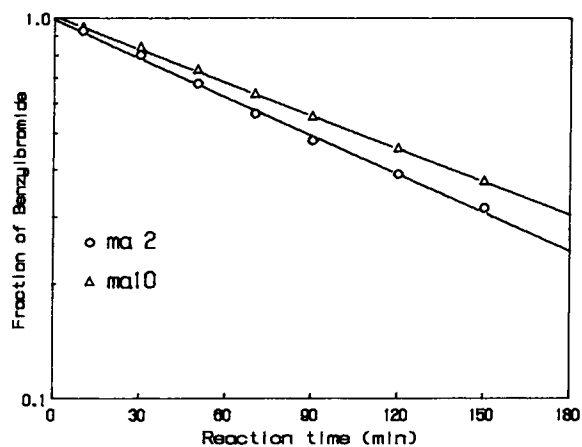


**Figure 4** Effect of the amount of catalyst on the conversion of benzyl bromide; 4 g of 2,4,6-tribromophenol, 0.9 g of KOH, 0.6 mL of benzyl bromide, 50 mL of water, 50 mL of chlorobenzene, and catalyst (mi2, 0.932 meq/g, 40–80 mesh), 40°C.

Figures 7 and 8 show the effects of the addition of KBr on the reaction in chlorobenzene. The addition of KBr decreased the reaction rate. The competition for the catalytically active sites dominated the reaction due to added KBr. However, as shown in Figure 9, the addition of KBr to the reaction system with hexane as solvent exhibited a contrasting behavior. The apparent rate coefficient ( $k_{app}$ ) at first increased with increasing addition of KBr to the reaction system, but with further increased KBr to the reaction solution, the apparent rate coefficient ( $k_{app}$ ) decreased. The reason is probably that increasing Resin-OAr concentration (or content) and the hydration effect dominated the reaction where added KBr was less than 2 g. However, the com-



**Figure 5** Effect of the amount of catalyst on the  $k_{app}$  value; same reaction conditions as given in Figure 4.

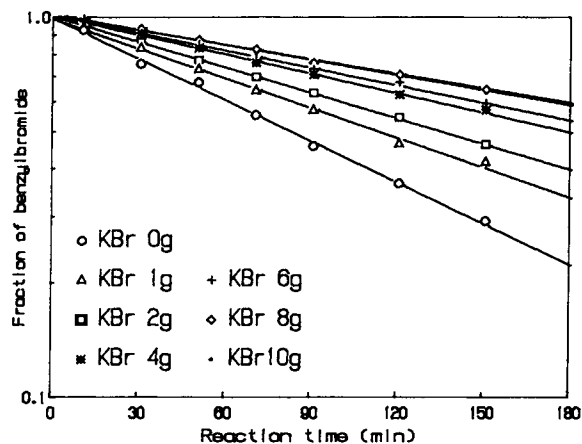


**Figure 6** Effect of the degree of cross-linking of the macroporous polymer pellet on the conversion of benzyl bromide; 4 g of 2,4,6-tribromophenol, 0.9 g of KOH, 0.6 mL of benzyl bromide, 50 mL of water, 50 mL of chlorobenzene, and catalyst (ma2, ma10, 0.932 meq/g, 40–80 mesh), 40°C.

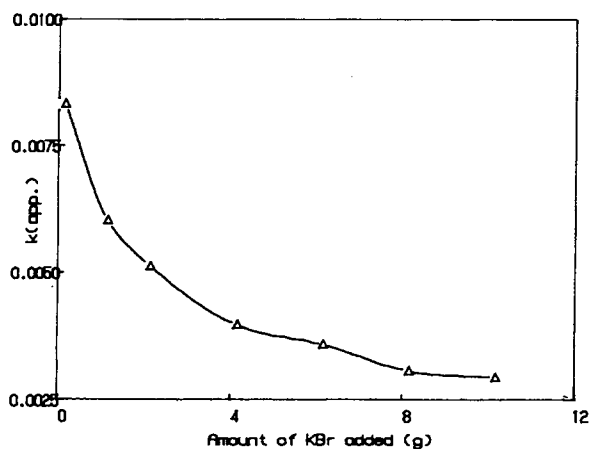
petition for the catalytically active sites dominated the reaction when KBr added to the reaction system exceeded 2 g.

### Effects of Temperature

We tested the effects of temperature on the conversion of benzyl bromide in triphase catalysis in the solvents 1,2-dichloroethane, chlorobenzene, and toluene. Typical results of conversion vs. time at various temperatures in chlorobenzene, 1,2-dichloroethane, and toluene are depicted in Figures 10–



**Figure 7** Effect of the amount of KBr added on the conversion of benzyl bromide; 4 g of 2,4,6-tribromophenol, 0.9 g of KOH, 0.6 mL of benzyl bromide, 50 mL of water, 50 mL of chlorobenzene, and catalyst (mi2, 0.932 meq/g, 40–80 mesh), 40°C.

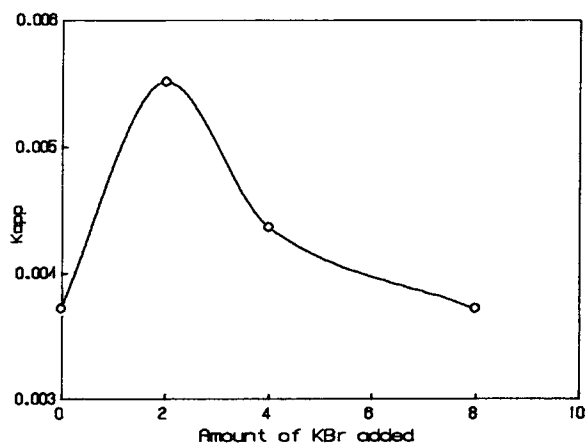


**Figure 8** Effect of the amount of KBr added on the  $k_{app}$  value using chlorobenzene as the organic solvent; same reaction conditions as given in Figure 7.

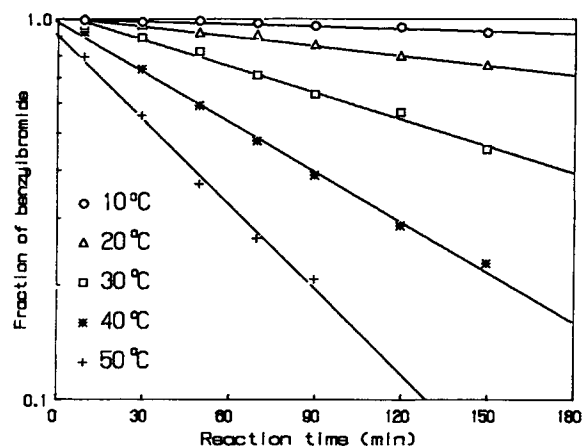
12, respectively. The greater the reaction temperature, the larger was the conversion of benzyl bromide. The apparent rate coefficient ( $k_{app}$ ) increased with increasing temperature. An Arrhenius plot is shown in Figure 13 for the various solvents; the order of the apparent rate coefficients is 1,2-dichloroethane > chlorobenzene > toluene. The activation energies obtained are 57.9 kJ/mol for 1,2-dichloroethane, 66.0 kJ/mol for chlorobenzene, and 72.8 kJ/mol for toluene.

### Effects of the Solvents

The polarity of the organic solvent affects the rate of reaction in a two-phase catalytic reaction. The

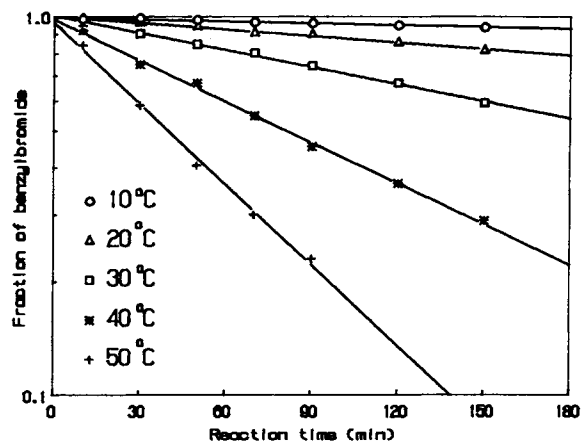


**Figure 9** Effect of the amount of KBr added on the  $k_{app}$  value using hexane as the organic solvent; 4 g of 2,4,6-tribromophenol, 0.9 g of KOH, 0.6 mL of benzyl bromide, 50 mL of water, 50 mL of hexane, and catalyst (mi2, 0.932 meq/g, 40–80 mesh), 40°C.



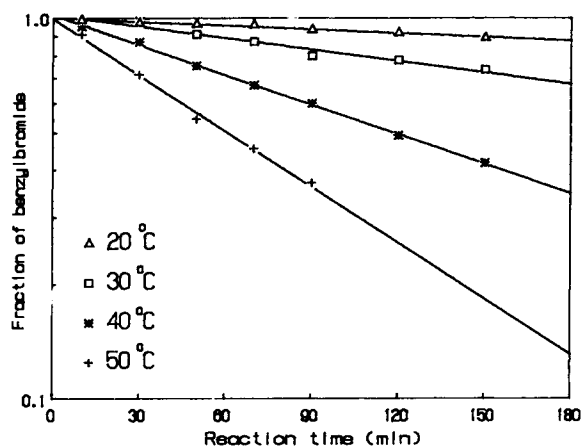
**Figure 10** Effect of temperature on the conversion of benzyl bromide using chlorobenzene as the organic solvent; 4 g of 2,4,6-tribromophenol, 0.9 g of KOH, 0.6 mL of benzyl bromide, 50 mL of water, 50 mL of chlorobenzene, and catalyst (mi2, 0.932 meq/g, 40–80 mesh).

rate of reaction increases with enhanced polarity of the solvent. For triphase catalysis, the polarity of the solvent also significantly influences the rate of reaction. The degree of swelling (Fig. 6) is obviously affected by the polarity of the solvent. The organic solvent that contains the organic reactant also interacts with the polymer pellet due to its lipophilicity. We used 1,2-dichloroethane, chlorobenzene, and toluene as organic solvents in the triphase catalysis. The order of the rate coefficients (Figs. 13 and 14) is 1,2-dichloroethane > chlorobenzene > toluene. This result is consistent with the order



**Figure 11** Effect of temperature on the conversion of benzyl bromide using 1,2-dichloroethane as the organic solvent; 4 g of 2,4,6-tribromophenol, 0.9 g of KOH, 0.6 mL of benzyl bromide, 50 mL of water, 50 mL of 1,2-dichloroethane, and catalyst (mi2, 0.932 meq/g, 40–80 mesh).



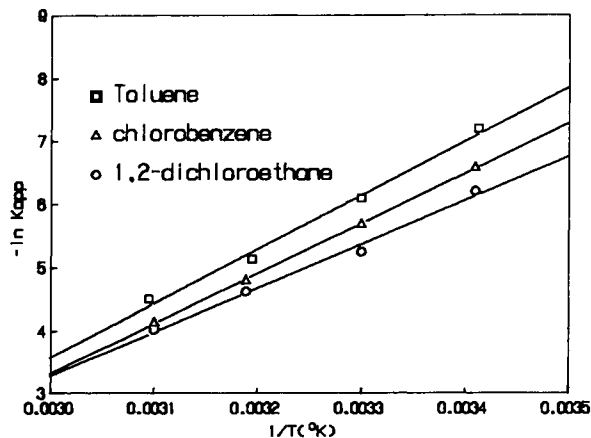


**Figure 12** Effect of temperature on the conversion of benzyl bromide using toluene as the organic solvent; 4 g of 2,4,6-tribromophenol, 0.9 g of KOH, 0.6 mL of benzyl bromide, 50 mL of water 50 mL of toluene, and catalyst (mi2, 0.932 meq/g, 40–80 mesh).

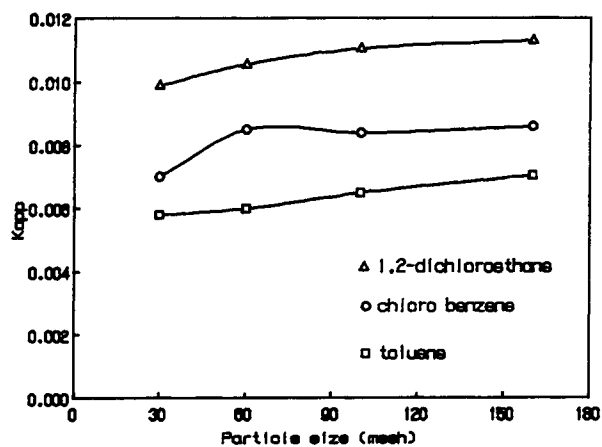
of the polarity of the solvent, i.e., the reaction is favorable for a highly polar solvent.

#### Other Polymer Support (Long-chain Polymer and Dowex-1 Resin)

In addition to the synthesized polymer pellet as the supported material for the triphase catalyst, we investigated the characteristics of polymers of two other kinds: a long-chain polymer, synthesized from the reaction of 1,6-dibromohexane and styrene monomer, and Dowex-1 resin, a commercial product. These polymers were immobilized with tributylamine using the same procedure described above. The experimental results appear in Figure 15. The reactivities of both the long-chain polymer and Dowex-



**Figure 13** An Arrhenius plot for the triphase catalysis; same reaction conditions as given in Figures 10–12.

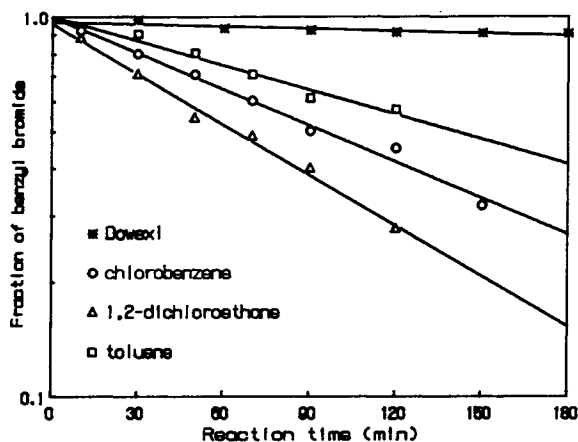


**Figure 14** Effect of the solvent on the  $k_{app}$  value; 4 g of 2,4,6-tribromophenol, 0.9 g of KOH, 0.6 mL of benzyl bromide, 50 mL of water, 50 mL of organic solvent, and catalyst (mi2, 0.932 meq/g, 40–80 mesh), 40°C.

1 resin are small. The reason is that the long-chain polymer is highly lipophilic, whereas Dowex-1 resin is highly hydrophilic. Both polymer pellets are unsuitable as polymer-support materials in triphase catalysis.

#### CONCLUSION

The experimental results indicated that the rate of reaction depended strongly on the rate of agitation of the stirrer below 400 rpm. Using a smaller catalyst particle led to an increased reaction rate. A polar solvent, such as 1,2-dichloroethane, enhanced the



**Figure 15** Effect of the long-chain polymer support and Dowex-1 on the conversion of benzyl bromide, 4 g of 2,4,6-tribromophenol, 0.9 g of KOH, 0.6 mL of benzyl bromide, 50 mL of water, 50 mL of chlorobenzene, and catalyst (0.932 meq/g, 40–80 mesh), 40°C.

reaction rate. Utilizing a greater concentration of catalyst linearly increased the reaction rate. The behavior of the apparent rate coefficient  $k_{app}$  in various solvents due to added KBr was presented; this peculiar phenomenon in the various solvents was explained by the effect of hydration, the concentration of Resin-OAr, and the competition of catalytically active sites between bromide ions and the 2,4,6-tribromophenoxide ions. According to the experimental data, a long-chain polymer pellet that is highly lipophilic, and a Dowex-1 resin (a commercial polymer pellet product) that is highly hydrophilic were unsuitable for polymer-support pellets of the triphase catalyst.

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