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Process Development Aspects of Production of Dibenzyl Ether

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Abstract:

To develop an economically viable process for the synthesis of dibenzyl ether, the reaction of benzyl chloride with aqueous sodium hydroxide in the presence of phase-transfer catalysts has been investigated. The effects of agitation speed, catalyst type and concentration, reaction temperature, mole ratio of reactants, concentration of aqueous sodium hydroxide on the conversion of benzyl chloride, and yield of dibenzyl ether have been evaluated. Tributylamine is found to be a suitable catalyst. The reaction is favored by high molar ratio of sodium hydroxide to benzyl chloride. Conversion of benzyl chloride to benzyl alcohol is found to be the rate-controlling step at high sodium hydroxide concentration. Deprotonation of benzyl alcohol at the interphase by aqueous sodium hydroxide is a key step in the formation of dibenzyl ether. The yield of dibenzyl ether is dependent on the concentration of sodium hydroxide in the aqueous phase, the yield being almost 100% at high concentrations of sodium hydroxide. The successful recycle of excess NaOH in the aqueous phase in subsequent batches, without affecting the progress of the reaction, has been demonstrated.

1. Introduction

Dibenzyl ether is used as a plasticizer in the surface coating industry, for special purposes in rubber and textile industries, and as a solvent for artificial musk and other odourants. There are many routes for the synthesis of dibenzyl ether. The most conventional amongst them is Wiliamson's synthesis, the reaction of benzyl chloride with sodium benzylate ($NaOCH_2Ph$). The other routes can be broadly classified into five categories, viz.: (1) from benzyl chloride and an alkali using a phase-transfer catalyst (PTC),[1−4] (2) by dehydration of benzyl alcohol,[5] (3) by the reaction of benzyl chloride with benzyl alcohol,[6,7] (4) by reduction of benzaldehyde,[8,9] and (5) via electrochemical methods.[10] Routes 2 and 3 need benzyl alcohol. It may be noted that in the commercial process for benzyl alcohol from benzyl chloride about 20% excess (over stoichiometric requirement) of soda ash or caustic soda is used, generating a corresponding excess of inorganic salts. In addition to this, benzyl alcohol has reasonable solubility in the aqueous phase and hence dissolved benzyl alcohol is recovered either by salting out or by extraction and this adds one more step in the benzyl alcohol manufacture.[11] Route 1 indicates that dibenzyl ether can be made in a single-pot reaction directly from benzyl chloride. The literature indicates use of trialkylamines as catalysts for synthesizing dibenzyl ether from benzyl chloride and aqueous sodium hydroxide.[4] Therefore, it was decided to study the reaction of benzyl chloride with aqueous sodium hydroxide in the presence of phase-transfer catalysts, with the aim that the system can be further modified for the synthesis of substituted dibenzyl ethers from substituted benzyl chlorides. The effects of stirring speed, different catalysts, temperature, the mole ratio of reactants, the concentration of aqueous phase, the catalyst and cocatalyst concentration on the conversion of benzyl chloride, and yield of dibenzyl ether were investigated in the present work.

1.1. Mechanism and Factors Governing Progress of Reaction. The following mechanism gives the formation of dibenzyl ether from benzyl chloride when a trialkylamine (NR_3) is used as a phase-transfer catalyst. Let us represent $(C_6H_5)CH_2-$ by Bn, and BnN^+R_3 by Q^+:

$$\underset{\text{benzyl chloride}}{\text{BnCl}} + R_3N \rightleftharpoons \underset{\text{quaternary ammonium chloride}}{[Q^+Cl^-]} \qquad \text{(organic phase)} \quad (1)$$

In the first step, quaternerisation of the tertiary amine takes place in the organic phase. This quaternary ammonium salt actually acts as the phase-transfer catalyst.

$$[Q^+Cl^-]_{org} + OH^-_{aq} \rightleftharpoons [Q^+OH^-]_{org} + Cl^-_{aq} \qquad \text{(both phases)} \quad (2)$$

In the second step, extraction of OH^- ions into the organic phase takes place.

$$[Q^+OH^-]_{org} + \text{BnCl} \rightarrow \underset{\text{benzyl alcohol}}{\text{BnOH}} + [Q^+Cl^-]_{org} \qquad \text{(organic phase)} \quad (3)$$

In the third step, benzyl alcohol is formed by the reaction of extracted OH^- with benzyl chloride. There are two possible ways by which the benzyl alcohol formed can react:

$$\text{BnOH}_{org} + [Q^+OH^-]_{org} \rightleftharpoons [Q^+OBn^-]_{org} + H_2O \qquad (4a)$$

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Benzyl alcohol can react with extracted OH^- to give $[Q^+OBn^-]$ in the organic phase. Benzyl alcohol can also produce $[Q^+OBn^-]$ in the organic phase by an interfacial mechanism, which comprises the following two steps:[12,13]

$$BnOH_{org} + Na^+_{aq} + OH^-_{aq} \rightleftharpoons Na^+_{\text{anchored to interface}} + OBn^-_{\text{anchored to interface}} + H_2O \quad (4b\text{-}1)$$

Benzyl alcohol gets deprotonated at the phase boundary. The anion OBn^- remains anchored at the interphase but in the organic phase, and similarly Na^+ gets anchored to the interphase but in the aqueous phase, a sort of bilayer arrangement in the absence of a phase-transfer catalyst.

$$OBn^-_{\text{anchored to interface}} + [Q^+Cl^-]_{org} \rightleftharpoons [Q^+OBn^-]_{org} + Cl^-_{aq} \quad \text{(both phases)} \quad (4b\text{-}2)$$

The anchored anion is carried to the interior of the organic phase-by the phase transfer catalyst.

$$[Q^+OBn^-] + BnCl \rightarrow [Q^+Cl^-] + \underset{\text{dibenzyl ether}}{BnOBn} \quad \text{(organic phase)} \quad (5)$$

OBn^-, which is carried to the organic phase, reacts with benzyl chloride irreversibly to give dibenzyl ether.

The following factors affect the progress of the reaction.

(1) Nature of anion to be extracted: It is difficult to extract OH^- ion into the organic phase because of its low polarizibility. OBn^- is much more lipophilic compared to OH^- and is, therefore, extracted very easily into the organic phase.[14]

(2) Effect of change in NaOH concentration: This has a two-fold effect on the overall reaction, as explained below.

(a) As the concentration of NaOH decreases, more OH^- is transferred to the organic phase in the form of $[Q^+OH^-]\cdot nH_2O$. Landini et al. reported a 45 times increase in the $K^{sel}_{OH/Cl}$ value when the NaOH concentration was changed from 50% to 15% (w/w).[15] The $K^{sel}_{Cl/OH}$ value reported by de la Zerda et al. is 950, and that of $K^{sel}_{BnO/OH}$ is 1900.[16]

(b) As the concentration of NaOH increases, fewer water molecules are transferred per OH^- ion (as $[Q^+OH^-]\cdot nH_2O$). Hydroxyl ions, which are less hydrated, are more reactive, and hence as the concentration of NaOH increases the reactivity of transferred OH^- increases.[15,17]

(3) Degradation of the catalyst: There are two possible reactions by which the catalyst is degraded. A catalyst such as $[BnN^+Et_3OH^-]$ may undergo the following reactions:

$$[BnN^+Et_3OH^-] \rightleftharpoons BnOH + Et_3N \quad (6)$$

$$[BnN^+Et_3OH^-] \rightarrow BnNEt_2 + H_2C{=}CH_2 + H_2O \quad \text{(Hoffman elimination)} \quad (7)$$

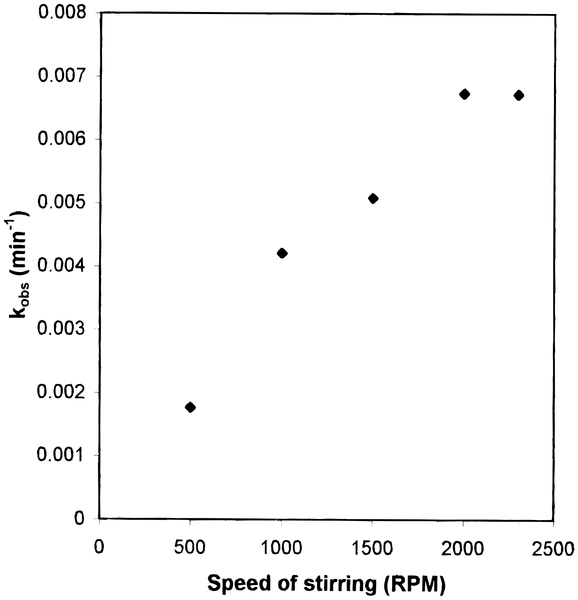

Figure 1. **Effect of speed of stirring. Moles of benzyl chloride = 0.3. Moles of tributylamine = 0.003. NaOH solution = 11.5 M, 160 mL. Temperature = 80 °C.**

It has been reported that degradation of benzyltriethylammonium chloride in the presence of strong alkali (50% NaOH) produces benzyldiethylamine (80%), triethylamine (6%), and dibenzyl ether (3%).[18] This eliminates the possibility of reaction 6 being the major route for the degradation of catalyst, and the catalyst is lost mainly due to the Hoffman elimination reaction. As the concentration of NaOH increases, the rate of decomposition of the catalyst increases.[17]

1.2. Kinetics. When transfer of anions to the organic phase follows the extraction mechanism, we observe a first-order dependence of the rate of reaction on both the substrate concentration and the catalyst concentration.[13,14,19] In such cases, a plot of $-\ln(1 - x)$ versus time is a straight line, where x is the fractional conversion of the substrate, defined as

$$x = \frac{\text{moles of the substrate consumed}}{\text{moles of the substrate charged}}$$

The slope of the line gives the observed pseudo-first-order rate constant, k_{obs}. Also, a plot ln k_{obs} versus ln C_0 is a straight line, where C_0 is the initial concentration of the catalyst.

2. Experimental Section

2.1. Method. All the experiments were carried out in a batch manner. A borosillicate glass reactor of 400-mL capacity, provided with a stirrer and baffles, was used. A constant-temperature bath was used for maintaining the desired temperature.

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A predetermined quantity of aqueous sodium hydroxide was added to the reactor. The temperature of the bath was raised to the predetermined value and maintained there. The measured quantity of benzyl chloride preheated to the required temperature was then added, followed immediately by a known quantity of the catalyst, and the run was started. Very small quantities of samples were withdrawn at predetermined time intervals, and the organic phase was analyzed by gas chromatography for the conversion of BnCl and the yield of dibenzyl ether. The effect of impeller speed was also investigated.

2.2. Analysis. The organic phase was analyzed by gas chromatography using a 2-m 10% OV-17 column. Nitrogen was the carrier, and detector was FID. Other parameters were as follows:

injection temperature	350 °C
detector temperature	325 °C
nitrogen flow rate	30 mL/min
temperature programming	110 °C for 5 min, 110 °C → 275 °C at 30 °C/min, 275 °C maintained for 2 min

3. Results and Discussion

The terms conversion and yield have been defined as follows:

$$\% \text{ conversion of BnCl} = \frac{\text{moles of BnCl consumed}}{\text{moles of BnCl charged}} \times 100$$

$$\% \text{ yield of DBE} = \frac{\text{moles of BnCl consumed for the formation of DBE}}{\text{moles of BnCl consumed}} \times 100$$

The effects of the following variables on the conversion of BnCl and the yield of dibenzyl ether were studied: (1) stirring speed, (2) catalyst, (3) catalyst and cocatalyst loading, (4) temperature, (5) concentration of aqueous sodium hydroxide, and (6) volume of the aqueous phase.

3.1. Effect of Change in the Stirring Speed. A phase-transfer-catalysed reaction is said to be mass-transfer rate-limited when the rate of anion transfer across the interface is slower than the rate of intrinsic reaction. The phase-transfer-catalysed reaction is said to be intrinsic reaction rate-limited when the rate of anion transfer across the interface is fast but the rate of intrinsic reaction is slow. At the low stirring speed, the requirement for sufficiently rapid mass transfer of the anions is not met, and mass-transfer rate-limited kinetics is observed. As we increase the speed of stirring, the rate of mass transfer across the interface increases and becomes faster than the intrinsic reaction rate. Thus, at higher stirring speed, the reaction goes from being mass-transfer rate-limited to intrinsic reaction rate-limited.

When dibenzyl ether is synthesised by treating benzyl chloride with aqueous alkali in the presence of tertiary amine as catalyst, the kinetics of the overall reaction can be described by a first-order model based on the concentration of benzyl chloride in the organic phase after an induction period.[4] We have also found a first-order dependence of the reaction on the benzyl chloride concentration in the organic phase. To study the effect of the speed of stirring, experiments were performed at 80 °C using tri-*n*-butylamine as a catalyst. Here, 160 mL of 11.5 M sodium hydroxide and 0.3 mol of benzyl chloride were taken. The molar catalyst loading was 1% of the organic phase. Figure 1 shows the effect of impeller speed on k_{obs}. It can be seen that the value of k_{obs} does not increase beyond 2000 rpm, and the reaction becomes intrinsic reaction rate controlled.

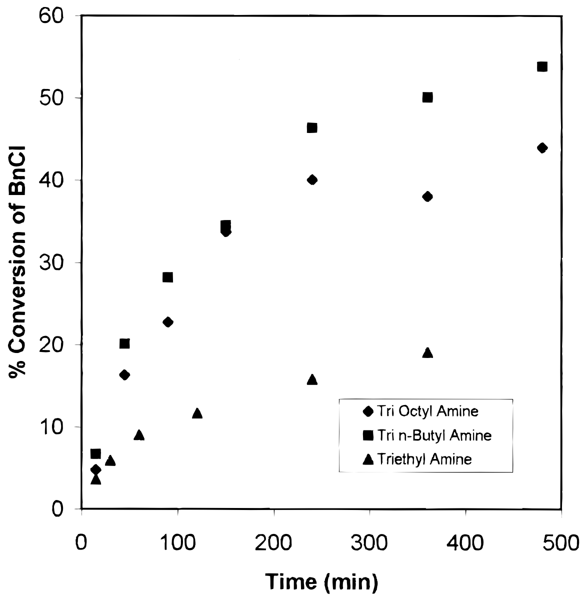

Figure 2. **Effect of different catalysts on the conversion of BnCl. Moles of benzyl chloride = 0.3. Moles of PTC = 0.00075. NaOH solution = 11.5 M, 160 mL. Temperature = 80 °C. Speed of stirring = 2500 rpm.**

Once the progress of the reaction is controlled by the intrinsic reaction, the rate of mass transfer is considerably higher than the intrinsic reaction rate. At very high agitation speeds (i.e., intrinsic reaction-controlled conditions), we have observed that the rate of consumption of benzyl chloride is higher with Bu_3N^+Bn than that obtained with Et_3N^+Bn (Figure 2). Further, since the progress is intrinsic reaction controlled, the mass-transfer rate is higher than the intrinsic reaction rate (with Bu_3N^+Bn), which obviously means that at the same speed of agitation the mass-transfer rate would be considerably higher than the intrinsic reaction rate with Et_3N^+Bn, and hence no mass-transfer limitation would exist in this case. All the subsequent experiments were performed at 2500 rpm.

3.2. Effect of Catalyst. Experiments were carried out at 80 °C with different catalysts. The catalysts used were triethylamine, tri-*n*-butylamine, and trioctylamine. Molar loading of all the catalysts was 0.25% of organic phase. Again, 0.3 mol of benzyl chloride and 160 mL of 11.5 M sodium hydroxide were used. The results are shown in Figure 2.

As can be seen from the figure, tri-*n*-butylamine and trioctylamine have comparable catalytic activities in the initial period, and both in turn are more active than triethylamine. However, tri-*n*-butylamine gives higher conversion in the later period of the reaction as compared to trioctylamine. It has been demonstrated that, as the lipophilic nature of the quat increases, extractability of OH^- into the organic phase increases.[20] Therefore, the $[Q^+OH^-]$ concentration in the organic phase is expected to be higher for tri-

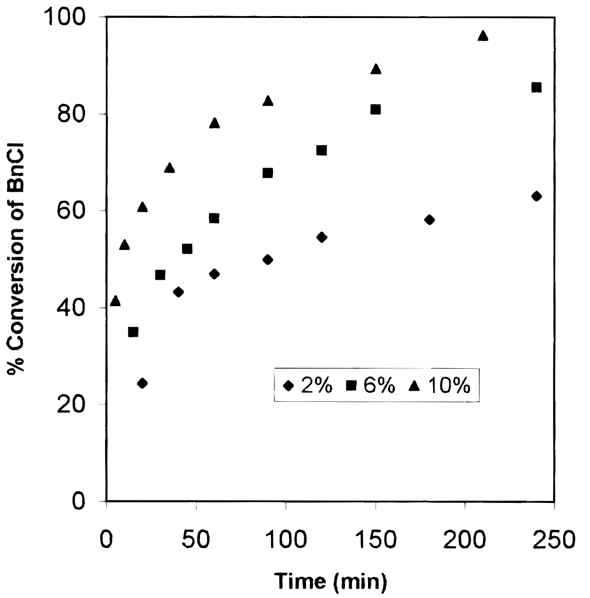

Figure 3. **Effect of catalyst concentration on the conversion of BnCl. Moles of benzyl chloride = 0.3. PTC = triethylamine. Moles of NaOH = 0.4. NaOH solution = 11.5 M. Temperature = 80 °C. Speed of stirring = 2500 rpm.**

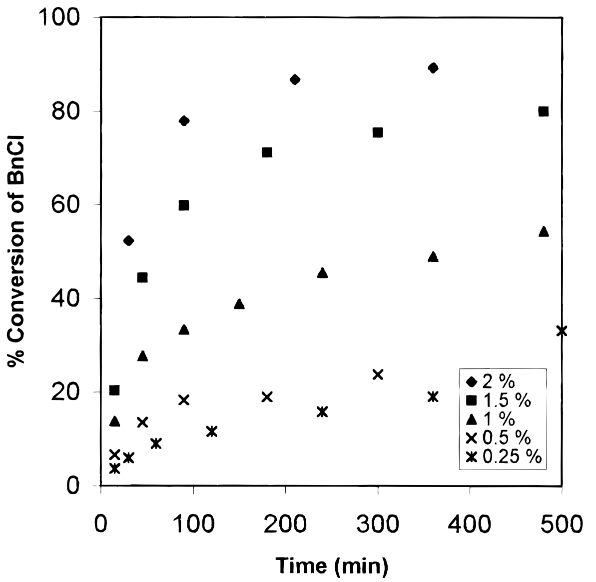

Figure 4. **Effect of the catalyst concentration on the conversion of BnCl. Moles of benzyl chloride = 0.3. PTC = triethylamine. NaOH solution = 11.5 M, 160 mL. Temperature = 80 °C. Speed of stirring = 2500 rpm.**

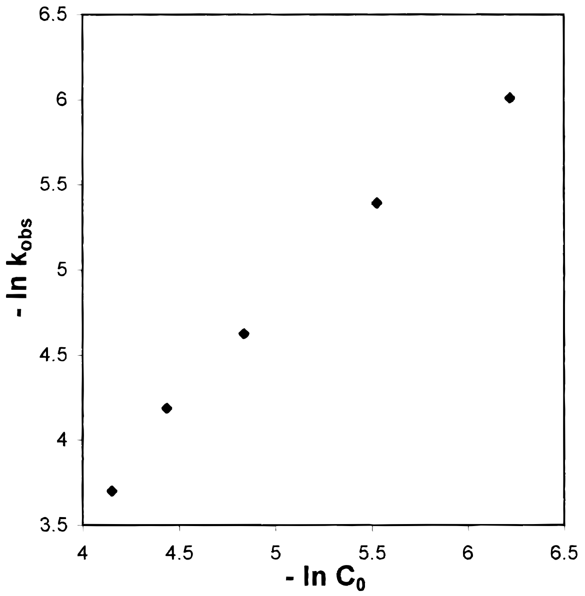

Figure 5. **Effect of the catalyst concentration. Moles of benzyl chloride = 0.3. PTC = triethylamine. NaOH solution = 11.5 M, 160 mL. Temperature = 80 °C. Speed of stirring = 2500 rpm.**

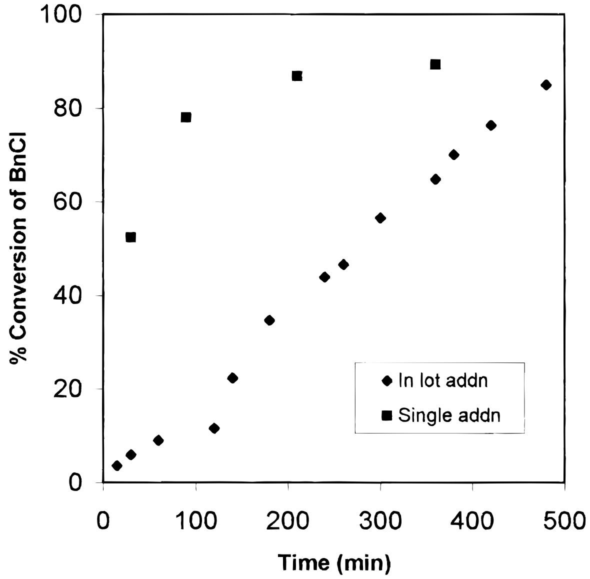

Figure 6. **Effect of the stepwise addition of the catalyst on the conversion of BnCl. Moles of benzyl chloride = 0.3. PTC = triethylamine. Single addition = 0.006 mol of triethylamine. In-lot addition = 0.0015 mol of triethylamine at 0, 120, 240, and 360 min. NaOH solution = 11.5 M, 160 mL. Temperature = 80 °C. Speed of stirring = 2500 rpm.**

n-butylamine and trioctylamine than that for triethylamine. As the $[Q^+OH^-]$ concentration in the organic phase increases, benzyl chloride is consumed (reaction 3) at a faster rate, and the rate of overall reaction increases. Similar results have been reported for the synthesis of dibenzyl ether.[4] The effect of increasing hydrophobicity of the quaternary ion seems to level off after tri-*n*-butylamine. In all the above experiments, the yield of dibenzyl ether was almost 100% throughout the reaction. This indicates that the intrinsic reaction 3, involving $[Q^+OH^-]$ leading to the formation of benzyl alcohol, is influenced by the type of the catalyst used and hence is likely to be the rate-determining step. Results presented in the subsequent sections have been used to justify the same.

3.3. Effect of Catalyst and Cocatalyst Loading. The effect of the catalyst loading was investigated for two different mole ratios of reactants. Figure 3 shows the effect of the catalyst loading for a benzyl chloride-to-sodium hydroxide mole ratio of 3:4, and Figure 4 shows that for the mole ratio of 3:18.3.

As can be seen from both figures, the conversion of BnCl increases as the catalyst loading increases. For the data in Figure 4, we determined the pseudo-first-order rate constant corresponding to different catalyst concentrations. Only the

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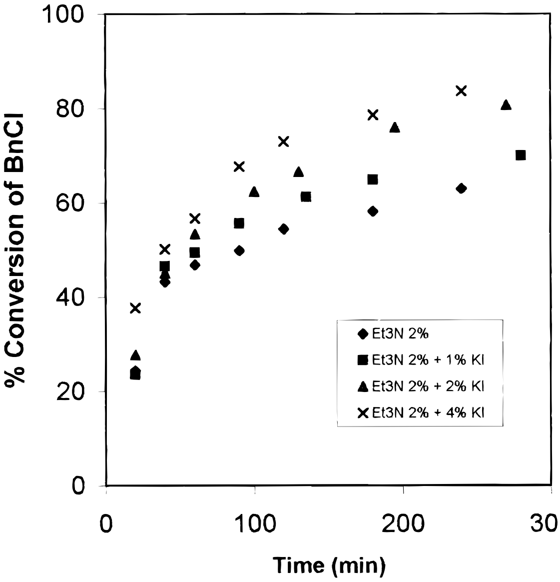

Figure 7. **Effect of cocatalyst concentration on the conversion of BnCl. Moles of benzyl chloride = 0.3. PTC = triethylamine, 0.006 mol. Cocatalyst = potassium iodide. Moles of NaOH = 0.4. NaOH solution = 11.5 M. Temperature = 80 °C. Speed of stirring = 2500 rpm.**

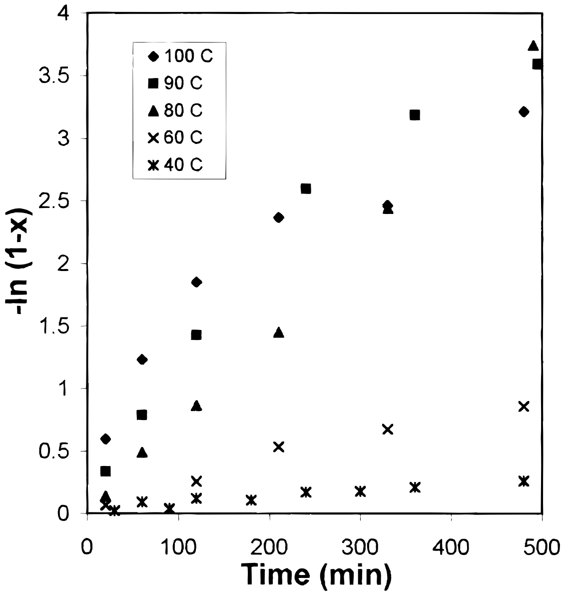

Figure 8. **Kinetics plot—first-order dependence. Moles of benzyl chloride = 0.3. Moles of tributylamine = 0.003. NaOH solution = 11.5 M, 160 mL. Speed of stirring = 2500 rpm.**

initial data points were considered, as the value of k_{obs} drops with time due to catalyst degradation at higher temperatures. A plot of ln k_{obs} vs ln C_0 was made (Figure 5). This gave a straight line whose slope was unity. This type of trend is characteristic of an extraction mechanism.[19] This indicates that the OH^- ions are extracted into the organic phase.

We also attempted in-lot addition of catalyst at different intervals. Figure 6 shows the comparison of addition of 2% triethylamine in a single stage and addition of 0.5% triethylamine in four steps of 2 h. It can be seen from Figure 6 that the latter strategy reduces neither the batch time nor the catalyst requirement.

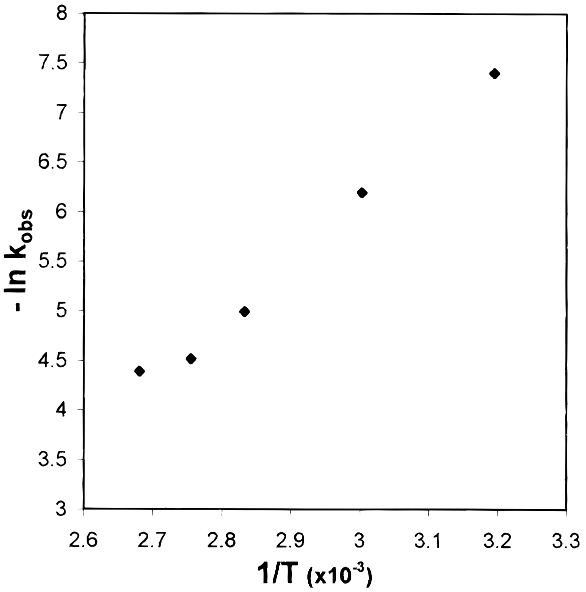

Figure 9. **Arrhenius plot. Moles of benzyl chloride = 0.3. Moles of tributylamine = 0.003. NaOH solution = 11.5 M, 160 mL. Speed of stirring = 2500 rpm.**

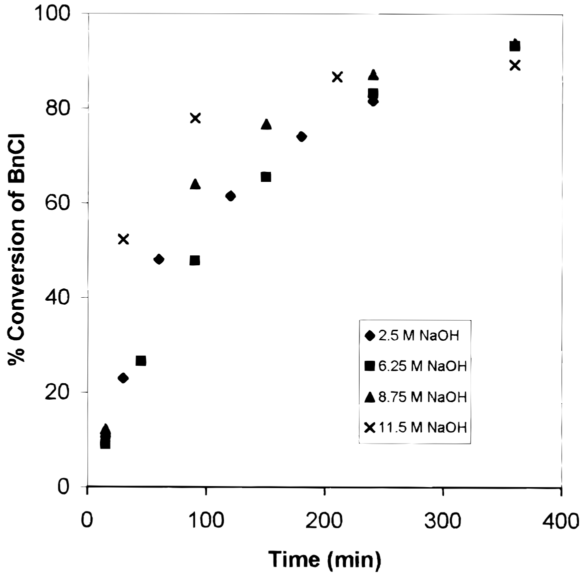

Figure 10. **Effect of change in NaOH concentration at constant aqueous phase volume on the conversion of BnCl. Moles of benzyl chloride = 0.3. Moles of triethylamine = 0.006. NaOH solution = 160 mL. Temperature = 80 °C. Speed of stirring = 2500 rpm.**

Potassium iodide acts as a cocatalyst for many phase-transfer catalysis reactions. Figure 7 shows the effect of potassium iodide concentration on the progress of the reaction when the benzyl chloride-to-NaOH mole ratio is 3:4. Increasing the concentration of potassium iodide increases the rate of the reaction. Because of the large ionic radius and greater polarizability of the I^- ion, it is a good nucleophile as well as a good leaving group. When KI is used along with triethylamine, the rate of benzyl chloride consumption increases with an increase in the concentration of KI. I^- gets transferred to the organic phase through PTC and forms benzyl iodide, which is more reactive than benzyl chloride and hence increases the rate of formation of benzyl

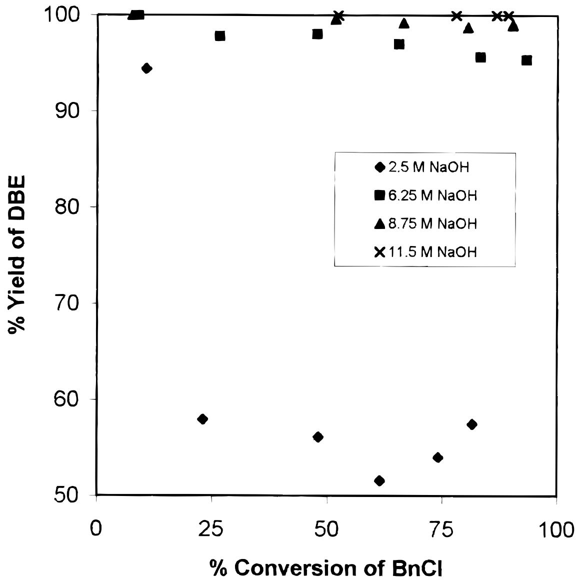

Figure 11. **Effect of change in NaOH concentration at constant aqueous phase volume on the yield of dibenzyl ether (DBE). Moles of benzyl chloride = 0.3. Moles of triethylamine = 0.006. NaOH solution = 160 mL. Temperature = 80 °C. Speed of stirring = 2500 rpm.**

alcohol together with that of the overall reaction. Similar results have been reported by Hwu et al.[4] for the synthesis of dibenzyl ether from benzyl chloride. This also supports the earlier observation in section 3.2 that the intrinsic reaction (reaction 3) is the rate-influencing step. From Figures 3 and 7, it is seen that, though the addition of KI increases the rate of conversion of benzyl chloride, increasing the catalyst concentration is a better proposition, as the cost of KI is considerably higher than that of triethylamine. Hence, further studies were carried out in the absence of KI.

3.4. Effect of Temperature. Figure 8 shows the effect of temperature for the case of tri-*n*-butylamine as a catalyst. The experiments were carried out using 160 mL of 11.5 M aqueous sodium hydroxide solution, 0.3 mol of benzyl chloride, and 0.003 mol of tri-*n*-butylamine as catalyst. Figure 8 also shows the pseudo-first-order kinetics of the reaction under consideration. We notice that at higher temperature the value of k_{obs} drops gradually. It can also be seen from Figure 8 that the rate of reaction does not increase appreciably when temperature changes from 90 to 100 °C. This may be because of the higher rate of degradation of catalyst due to Hoffman elimination. The Arrhenius plot was made (Figure 9). The energy of activation was found to be 13.14 kcal/gmol. This high value also confirms the absence of mass-transfer resistance, and the progress of the reaction is governed by the intrinsic reaction. In all the above experiments, the yield of dibenzyl ether is almost 100% throughout the reaction.

3.5. Effect of Concentration of Aqueous Sodium Hydroxide. The effect of concentration of aqueous phase was studied in two ways: (1) by changing sodium hydroxide concentration at a constant volume of the aqueous phase and (2) by changing aqueous sodium hydroxide concentration at a constant mole ratio of reactants. The experiments were conducted at 80 °C with 2% triethylamine as a catalyst.

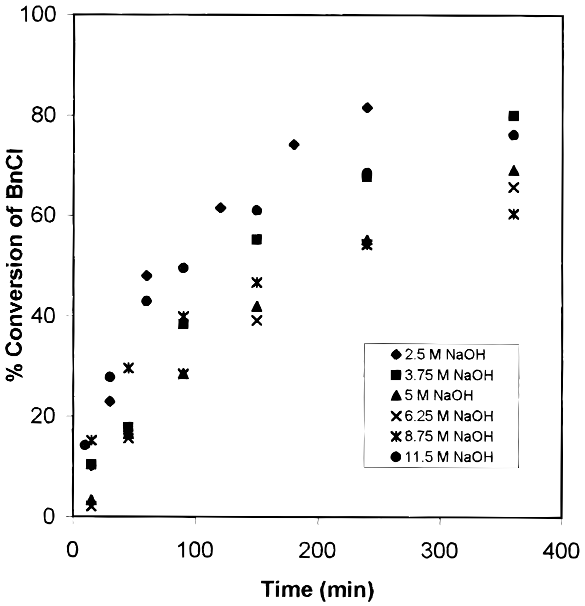

Figure 12. **Effect of change in the concentration of NaOH, keeping the mole ratio constant, on the conversion of BnCl. Moles of benzyl chloride = 0.3. Moles of triethylamine = 0.006. Moles of NaOH = 0.4. Temperature = 80 °C. Speed of stirring = 2500 rpm.**

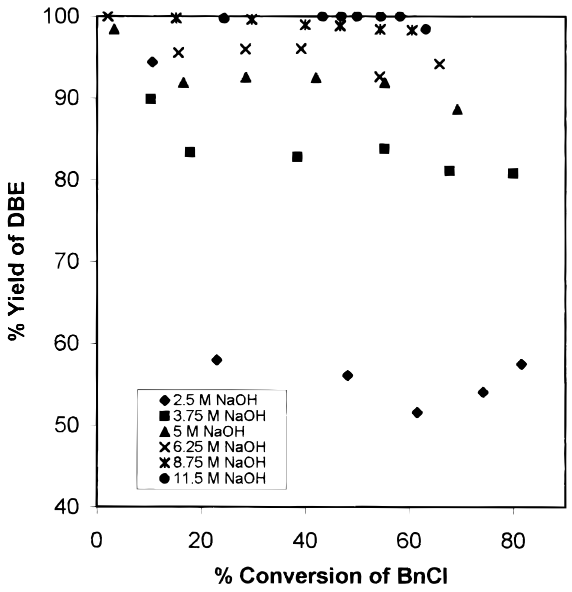

Figure 13. **Effect of change in the concentration of NaOH, keeping the mole ratio constant, on the yield of dibenzyl ether (DBE). Moles of benzyl chloride = 0.3. Moles of triethylamine = 0.006. Moles of NaOH = 0.4. Temperature = 80 °C. Speed of stirring = 2500 rpm.**

3.5.1. Effect of NaOH Concentration, Keeping Volume of Aqueous Phase Constant. When the concentration of aqueous sodium hydroxide is increased, keeping the volume constant, the mole ratio of benzyl chloride to sodium hydroxide increases with increasing concentration. The effects of changes in the concentration of aqueous NaOH on the conversion of BnCl and the yield of dibenzyl ether are shown in Figures 10 and 11, respectively.

3.5.2. Effect of NaOH Concentration, Keeping Mole Ratio of Reactants Constant. The initial concentration of

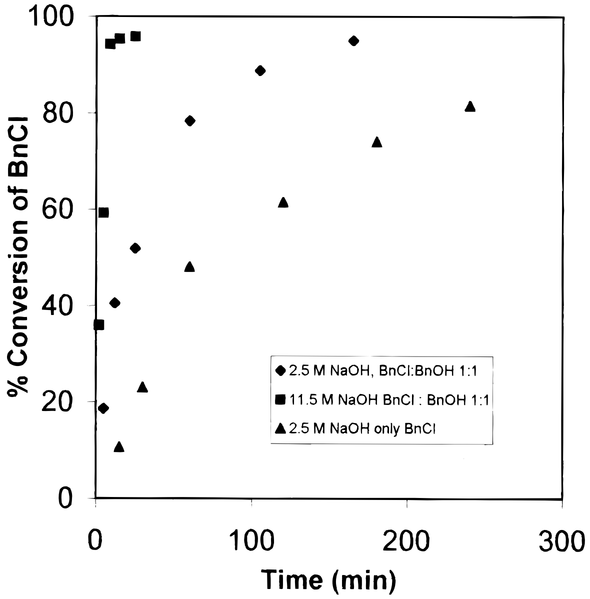

Figure 14. **Effect of NaOH concentration on the progress of the reaction between benzyl chloride and benzyl alcohol.**

aqueous phase was varied, keeping the mole ratio of benzyl chloride to sodium hydroxide constant, viz. 3:4. It may be noted that, with an increase in sodium hydroxide concentration, the volume of the aqueous phase decreases, and vice versa. The effect of NaOH concentration on the conversion of BnCl and the yield of dibenzyl ether is shown in Figures 12 and 13, respectively.

From Figures 11 and 13, it is clear that the yield of dibenzyl ether is a function of NaOH concentration. Changes in the catalyst, the temperature, and the catalyst and cocatalyst concentrations had practically no effect on the yield of dibenzyl ether. With increasing concentration of NaOH, deprotonation of benzyl alcohol increases (reaction 4b-1). Further, more [Q^+OBn^-] is formed in the organic phase (reaction 4b-2), which reacts with benzyl chloride (reaction 5) to give dibenzyl ether, thereby improving its yield.

To determine the rate-limiting step in the said mechanism, we performed the following experiments.

(A) A mixture of 0.15 mol of benzyl chloride and 0.15 mol of benzyl alcohol was reacted with 160 mL of 11.5 M NaOH at 80 °C in the presence of 0.006 mol of triethylamine at 2500 rpm.

(B) Another mixture of 0.15 mol of benzyl chloride and 0.15 mol of benzyl alcohol was reacted with 160 mL of 2.5 M NaOH at 80 °C in the presence of 0.006 mol of triethylamine at 2500 rpm.

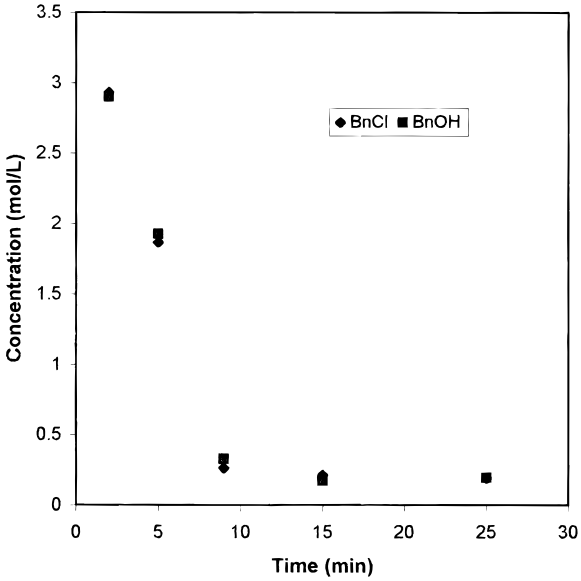

Figure 15. **Progress of the reaction between benzyl chloride and benzyl alcohol (experiment A). Moles of benzyl chloride = 0.15. Moles of benzyl alcohol = 0.15. Moles of triethylamine = 0.006. NaOH solution = 11.5 M, 160 mL. Temperature = 80 °C. Speed of stirring = 2500 rpm.**

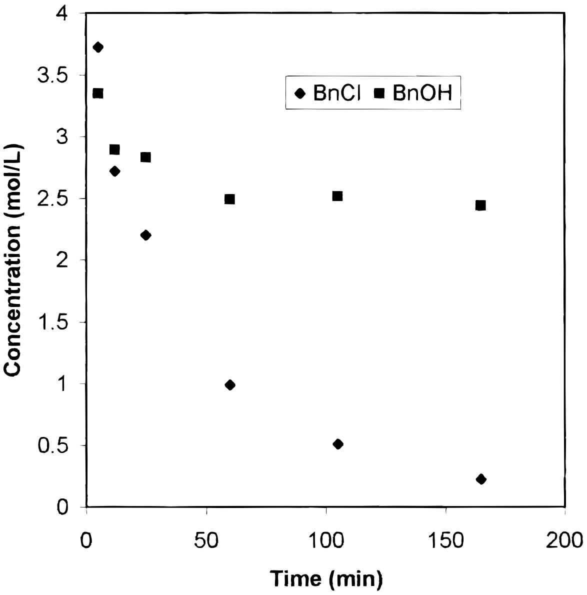

Figure 16. **Progress of the reaction between benzyl chloride and benzyl alcohol (experiment B). Moles of benzyl chloride = 0.15. Moles of benzyl alcohol = 0.15. Moles of triethylamine = 0.006. NaOH solution = 2.5 M, 160 mL. Temperature = 80 °C. Speed of stirring = 2500 rpm.**

Figure 14 shows the conversion profile for both experiments. The figure also shows the results of the experiment in which only 0.3 mol of benzyl chloride is used, the other conditions being same as those of experiment B. In the first case, when the concentration of NaOH is 11.5 M, 95% conversion of BnCl takes place in less than 10 min. When the concentrations of benzyl chloride and benzyl alcohol are plotted against time (Figure 15) for experiment A, we observe that both are consumed at the same rate. This shows that, in the presence of the catalyst and highly concentrated NaOH, benzyl chloride and benzyl alcohol react rather rapidly. From a similar plot (Figure 16) for experiment B, we observe that though concentration of benzyl chloride decreases, the concentration of benzyl alcohol does not decrease correspondingly but reaches a limiting value. In experiment B, benzyl alcohol gets deprotonated to a lesser extent due to the lower NaOH concentration. Therefore, the formation of dibenzyl ether takes place at a slower rate. Benzyl chloride is consumed by two reactions, first for the formation of benzyl alcohol (reaction 3) and then for the formation of dibenzyl ether (reaction 5). When the rate of consumption

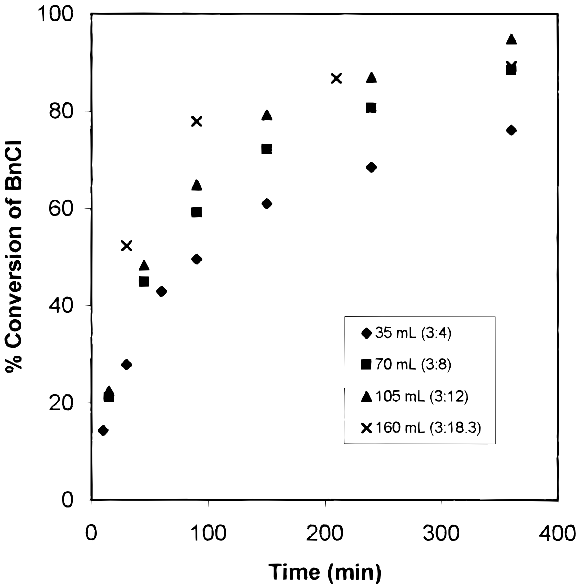

Figure 17. **Effect of the change in the volume of aqueous phase on the conversion of BnCl. Moles of benzyl chloride = 0.3. Moles of triethylamine = 0.006. NaOH solution = 11.5 M. Temperature = 80 °C. Speed of stirring = 2500 rpm.**

of benzyl alcohol for the formation of dibenzyl ether equals the rate of formation of benzyl alcohol from benzyl chloride, the concentration of benzyl alcohol remains constant, and the concentration of benzyl chloride decreases. It is very clear from the discussion that, at high NaOH concentration, conversion of benzyl chloride to benzyl alcohol is the rate-limiting step.

3.5.3. Effect of Volume of the Aqueous Phase. Here, 0.3 mol of benzyl chloride was treated with different volumes of 11.5 M NaOH solutions in the presence of 0.006 mol of triethylamine at 80 °C and 2500 rpm. The volume of aqueous phase was increased from 35 to 160 mL. Figure 17 shows the effect of the aqueous phase volume on the conversion of BnCl. As the volume of aqueous phase increases, the organic phase gets completely dispersed in the aqueous phase. Here, the aqueous phase is the continuous phase, and more area is made available for mass transfer. As we go on increasing the aqueous phase volume, the interfacial area increases until complete dispersion of the organic phase has occurred and further increases in the aqueous phase volume will not increase the interfacial area for mass transfer to take place. This levels off the effect of the aqueous phase volume. This is confirmed by the results in Figure 17. There is a noticeable increase in the rate of reaction when the volume of aqueous phase increases from 35 to 70 mL but no appreciable change when the aqueous phase volume is further increased to 160 mL.

We can broadly divide the mechanism in two steps, viz.: (1) formation of benzyl alcohol and (2) reaction of benzyl alcohol with benzyl chloride to give dibenzyl ether. Benzyl chloride is consumed in the first step for the formation of benzyl alcohol according to reaction 3 and in the second step for the formation of dibenzyl ether by reaction 5. Therefore, plots of conversion of benzyl chloride versus time as shown in Figures 10 and 12 do not give much information regarding both steps. The relative rates of both steps decide the overall conversion profiles as given in Figures 10 and 12. The information regarding the first step for each experiment cannot be obtained directly from Figures 10 and 12. Therefore, we separately plotted conversion to benzyl alcohol versus time for experiments in Figures 10 and 12. The results are presented in Figures 18 and 19. Conversion to benzyl alcohol was calculated by using the following formula:

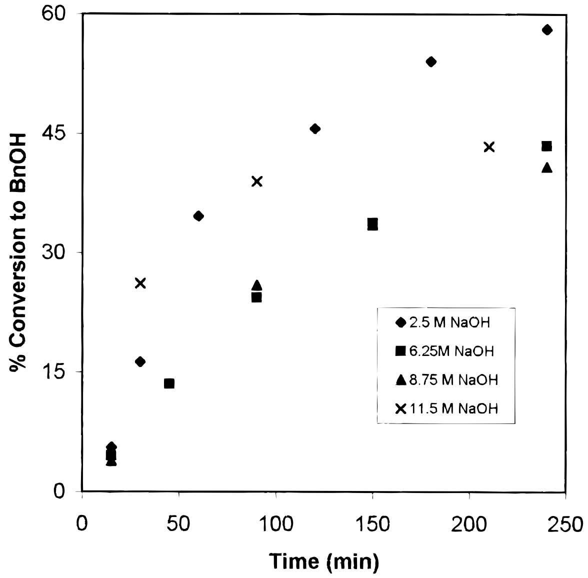

Figure 18. **Effect of the change in NaOH concentration at constant aqueous phase volume on the conversion to BnOH. Moles of benzyl chloride = 0.3. Moles of triethylamine = 0.006. NaOH solution = 160 mL. Temperature = 80 °C. Speed of stirring = 2500 rpm.**

$$\text{\% conversion to BnOH} = \frac{\text{moles of BnOH observed} + \text{moles of dibenzyl ether formed}}{\text{moles of BnCl taken initially}} \times 100$$

Conversion to benzyl alcohol refers to the consumption of benzyl chloride by reaction 3 alone.

As can be seen from Figure 18, the conversion to benzyl alcohol is dependent on the aqueous phase concentration. In 2.5 M NaOH solution, the amount of OH^- extracted to the organic phase is higher, but it is highly hydrated and less reactive.[15,17] As the concentration of aqueous phase increases, the amount of OH^- extracted decreases, but the extracted OH^- is more reactive.[15,17] The reactivity of OH^- in our set of experiments is maximum when 11.5 M NaOH is used. In the case of 11.5 M NaOH, the amount of OH^- extracted to the organic phase is much less than that in 2.5 M NaOH. But because of the high reactivity of extracted OH^-, the conversion to BnOH is the same initially for 2.5 and 11.5 M NaOH. Also, we observe that the rate of conversion to BnOH drops significantly after some time in the case of 11.5 M NaOH. This is because of degradation of catalyst due to the higher concentration of NaOH. For 2.5 M NaOH, the degradation of catalyst is minimal because the concentration of aqueous phase decreases sharply with the progress of the reaction.

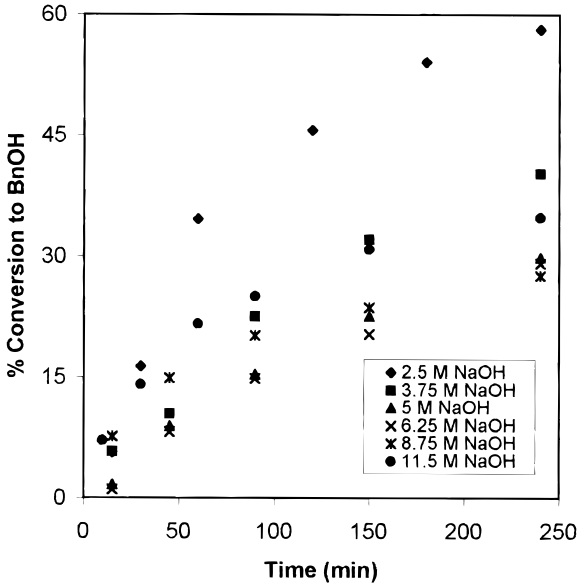

Figure 19. **Effect of change in the concentration of NaOH, keeping the mole ratio constant, on the conversion to BnOH. Moles of benzyl chloride = 0.3. Moles of triethylamine = 0.006. Moles of NaOH = 0.4. Temperature = 80 °C. Speed of stirring = 2500 rpm.**

When the concentration of aqueous phase is changed, keeping the benzyl chloride-to-sodium hydroxide molar ratio constant, the volume of aqueous phase changes. In all the experiments presented in Figure 19, the benzyl chloride-to-sodium hydroxide molar ratio is 3:4. Therefore, there is a rather sharp change in the aqueous phase concentration with progress of reaction. We can clearly conclude that 11.5 M NaOH solution in this set of experiments (BnCl:NaOH = 3:4) cannot behave exactly in a manner similar to that in the previous case, where the molar ratio of BnCl to NaOH was 3:18.3. With BnCl:NaOH at 3:18.3, the concentration of NaOH in the aqueous phase does not change substantially because of the large stoichiometric excess of NaOH used. As the initial concentration of aqueous phase increases, the deviation in the behavior of the aqueous phase from the prior case increases. In the present set of experiments, as we move from 2.5 to 11.5 M NaOH, the volume of aqueous phase decreases. When the initial volume of aqueous phase decreases from 160 to 80 mL, the amount of OH^- extracted decreases as the concentration of aqueous phase increases. As the concentration of aqueous phase remains relatively low, there is practically no change in the level of hydration of the extracted OH^-. The net result is that the rate of conversion to BnOH decreases. For an aqueous phase volume of 64 (initial concentration 6.25 M)−34.78 mL (initial concentration 11.5 M), the effect of change in volume of the aqueous phase becomes dominant. We therefore notice that, as the initial concentration of aqueous phase increases from 2.5 to 6.25 M, the rate of the first step decreases. But as the concentration of aqueous phase increases further, the dehydrating effect of NaOH becomes dominant and more than compensates for low OH^- extraction. We therefore see a minimum at around 6.25 M NaOH solution, and then the rate of conversion to BnOH increases. In this set of experiments, the aqueous phase concentration decreases considerably with the progress of the reaction, and hence there is no deactivation of catalyst for concentrated NaOH solutions.

3.6. Discussions: Mechanism and the Rate Determining Step (RDS). Rabinovitz et al.[19] have given the criteria for determining whether the anions are transferred to the organic phase by the extraction mechanism or by the interfacial mechanism. Accordingly, the following observations in the present study support that the OH^- is transferred by the extraction mechanism into the organic phase:

(a) In the initial period of the reaction, the rate of consumption of benzyl chloride shows a first-order dependence on the concentration of catalyst triethylamine (Figure 5) and benzyl chloride (Figure 8).

(b) The rate also increases with increasing hydrophobisity of the catalyst (i.e., from triethyl- to tri-*n*-butylamine).

To understand the formation of $[Q^+OBn^-]$, consider reactions 4a, 4b-1, and 4b-2. For deprotonation by reaction 4a, formation of $[Q^+OBn^-]$ depends on the activity as well as the concentration of $[Q^+OH^-]$. It has been reported that with an increase in NaOH concentration the extractability of OH^- decreases while its activity (decided by hydration state) increases.[15] Thus, the concentration and activity of $[Q^+OH^-]$ in organic phase are affected in opposite directions by NaOH concentration. It may be pointed out that the rate of formation of benzyl alcohol, which depends on the concentration and activity of $[Q^+OH^-]$, first decreases and then increases with an increase in the concentration of NaOH (Figures 18 and 19). Thus, a monotonic increase in the formation of $[Q^+OBn^-]$ according to reaction 4a may not occur with an increase in the concentration of NaOH. However, formation of $[Q^+OBn^-]$ will increase continuously with an increase in the NaOH concentration according to reaction 4b-1 followed by 4b-2. The increase in concentration of $[Q^+OBn^-]$ leads to an increased rate of etherification according to reaction 5. The observed data (Figures 11, 13−16) support this proposed mechanistic step of interfacial deprotonation of benzyl alcohol.

The following points may be noted regarding the rate-determining step (RDS):

(1) The initial rate of consumption of benzyl chloride is directly proportional to benzyl chloride concentration (first-order dependence). This indicates that reaction 1 or 3 or 5 is the RDS.

(2) For quaternisation (reaction 1) to be the RDS, the rates of reactions with 11.5 and 2.5 M NaOH should have been the same. However, results in Figure 14 show that sodium hydroxide concentration has a pronounced effect on the rate of overall reaction.

(3) At very high concentrations of NaOH, the yield of dibenzyl ether is almost 100% throughout the reaction. This indicates that the etherification reaction (reaction 5) is very fast, particularly at high NaOH concentration.

(4) When conversion of benzyl chloride to BnOH is plotted against time (Figures 18 and 19), the trends observed match well with the trends observed when conversion of BnCl for the overall reaction is plotted against time (Figures

10 and 12). This is also an indirect proof of benzyl alcohol formation being the RDS.

(5) At low NaOH concentration, there is an appreciable amount of benzyl alcohol in the reaction mixture. Under these circumstances, it is possible that the rates of reactions 3 and 5 are comparable. This fact can be confirmed from results presented in Figures 14 and 16. Further, Figure 15 shows that at high NaOH concentration, concentrations of benzyl chloride and benzyl alcohol are equal at any time during the reaction. Further, we do not see any excess benzyl alcohol formation, indicating that the rate of etherification is very fast compared to the rate of benzyl alcohol formation. With the concentration of NaOH equal to 2.5 M, benzyl alcohol concentration reaches a limiting value while benzyl chloride concentration decreases with time (Figure 16). This limiting value indicates that the rate of formation of benzyl alcohol equals the rate of consumption of benzyl alcohol, which in turn equals the rate of formation of dibenzyl ether.

For the conditions under which the effect of stirring speed, catalyst, catalyst and cocatalyst loading, temperature are studied, the rate-determining step, therefore, is given by reaction 3.

Thus, the mechanism based on the results reported here consists of extraction of OH^- into the organic phase. This extracted OH^- reacts with benzyl chloride to give benzyl alcohol by reaction 3. This intrinsic nucleophillic substitution reaction is the rate-determining step at higher sodium hydroxide concentrations. The benzyl alcohol formed undergoes interfacial deprotonation. The OBn^- anion formed at the interface is carried to the bulk organic phase by the PTC, where it reacts with benzyl chloride to give dibenzyl ether.

3.7. Recycle of Aqueous Phase. For the higher yields of dibenzyl ether together with high conversion of benzyl chloride, high concentration and large excess of sodium hydroxide are necessary. In such cases, after benzyl chloride is consumed completely, there is still a considerable amount of sodium hydroxide present in the aqueous phase, which if recycled reduces the cost of production of dibenzyl ether considerably. The results of such recycle experiments are shown in Figure 20. In the first experiment, 0.3 mol of benzyl chloride was treated with 160 mL of sodium hydroxide solution of 11.5 M concentration, and 0.003 mol of tri-*n*-butylamine was used as a catalyst at 90 °C and 2500 rpm. After 8 h, the reaction was stopped, the reaction mixture was cooled to room temperature, and both phases were separated. The amount of NaOH consumed was calculated and added to the separated aqueous phase, and the volume was made to 160 mL by adding distilled water. With this aqueous phase, the first recycling experiment was performed. This aqueous phase was reacted with 0.3 mol of benzyl chloride and 0.003 mol of tri-*n*-butylamine at 90 °C and 2500 rpm. After 8 h, the experiment was stopped, and as in the previous case, both phases were separated. The aqueous phase now contained a considerable amount of sodium chloride crystals. The clear aqueous phase was carefully decanted and analysed for sodium hydroxide with standard oxalic acid solution. After the sodium hydroxide concentration was determined accurately, makeup NaOH and distilled water was added to make 11.5 M NaOH and 160 mL of aqueous phase volume. With this aqueous phase, the second recycling experiment was performed. Figure 20 shows the results of five such experiments. The only difference in the aqueous phase of the first experiment and all recycling experiments is that in the first experiment the concentration of sodium chloride in the aqueous phase increases with the progress of the reaction, and in all the other recycling experiments the aqueous phase remains saturated with sodium chloride throughout the reaction. Conversion of BnCl versus time curves of all the experiments are practically identical. We can, therefore, conclude that concentration of sodium chloride in the aqueous phase does not affect the rate of the reaction. Identical conversion profiles also indicate that the PTC is not recycled with the aqueous phase. It is either present in the organic phase or is degraded by the end of the reaction. The net consumption of NaOH in all the experiments was around 8% more than the stoichiometric requirements. The alkali was lost mainly in the separation of sodium chloride formed in the aqueous phase.

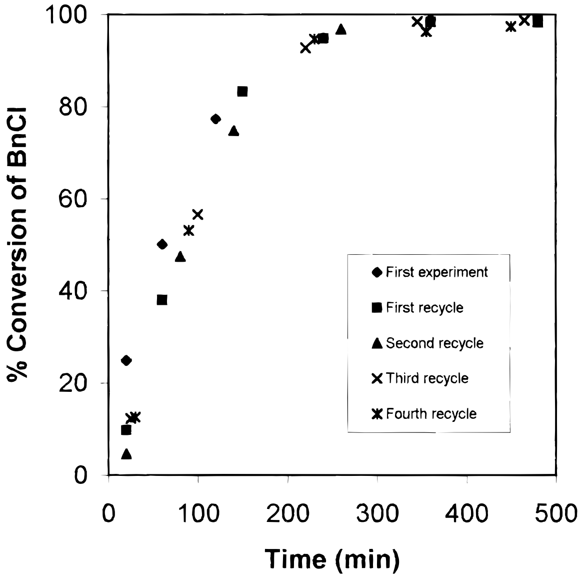

Figure 20. **Effect of recycling of the aqueous phase on the progress of the reaction. Moles of benzyl chloride = 0.3. Moles of tributylamine = 0.003. NaOH solution = 11.5 M, 160 mL. Temperature = 90 °C. Speed of stirring = 2500 rpm.**

We have thus demonstrated a single-pot conversion of benzyl chloride to dibenzyl ether with following features: (1) almost quantitative conversion of benzyl chloride and (2) almost 100% yield of dibenzyl ether throughout the batch.

4. Conclusions

(1) Dibenzyl ether can be prepared by using trialkylamines as phase-transfer catalysts in high yields (~100%) at high sodium hydroxide concentration (>8.75 M).

(2) At low concentration of sodium hydroxide, the yield of dibenzyl ether is low.

(3) Conversion of benzyl chloride to benzyl alcohol by action of [Q^+OH^-] in the organic phase is the rate-determining step at high concentrations of sodium hydroxide.

(4) [Q^+OBn^-] is formed in the organic phase by interfacial deprotonation of benzyl alcohol.

(5) Though high excess of sodium hydroxide is used, unreacted sodium hydroxide can be recycled together with makeup sodium hydroxide without affecting the conversion of benzyl chloride and the yield of dibenzyl ether.

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