Reaction of benzyl chloride with ammonium sulfide under liquid–liquid phase transfer catalysis: Reaction mechanism and kinetics

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Abstract

The reaction between benzyl chloride and aqueous ammonium sulfide was carried out in an organic solvent – toluene, using tetrabutylammonium bromide (TBAB) as phase transfer catalyst (PTC). Two products, namely dibenzyl sulfide (DBS) and benzyl mercaptan (BM), were identified in the reaction mixture. The selectivity of DBS was maximised by changing various parameters such as NH_3/H_2S mole ratio, stirring speed, catalyst loading, concentration of benzyl chloride, volume of aqueous phase, and temperature. The highest selectivity of DBS obtained was about 90% after 445 min of reaction with excess benzyl chloride at 60 °C. Complete conversion of benzyl chloride could be achieved at the cost of very low selectivity of DBS and very high selectivity of BM. The apparent activation energy for the kinetically controlled reaction was found to be 12.3 kcal/mol. From the detailed study of the effects of various parameters on the reaction, a suitable mechanism was established which could explain the course of the reaction.
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1. Introduction

With gradual decline of light and easy-to-process crude oils, refineries throughout the world are forced to process heavy crudes containing high amount of sulfur and nitrogen. In addition, refiners are forced to hydrotreat such crude to bring down the sulfur and nitrogen levels to those prescribed by environmental protection agencies. During hydrotreatment of heavy and sour crude, large quantities of hydrogen sulfide and ammonia are produced. The stream containing these gases are first scrubbed with water to remove ammonia and then sent through amine treating unit to remove hydrogen sulfide, which is further processed in the Claus unit to produce elemental sulfur [1,2]. This elemental sulfur is mainly used for sulfuric acid production and to some extent in the rubber industry. Due to very high production rate compared to the consumption rate, refineries processing sour crude are facing severe problem in disposing

elemental sulfur produced in the sulfur recovery units (SRUs). Therefore, any process, which could convert hydrogen sulfide to value-added products, will be very much helpful to the refining industry in alleviating the sulfur disposal problem. The present work was undertaken to synthesize value-added chemicals such as dibenzyl sulfide (DBS) and benzyl mercaptan (BM) by using components of hydrotreater off gas, i.e., ammonia, and hydrogen sulfide.

The DBS finds many applications as additives for extreme pressure lubricants, anti-wear additives for motor oils, stabilisers for photographic emulsions, in refining and recovery of precious metals, and in different anticorrosive formulations [3]. BM is useful as a raw material for the synthesis of herbicides in the thiocarbamate family [4]. It is mainly used for the synthesis of herbicides like esprocarb, prosulfocarb, tiocarbazil, etc. The present work deals with the synthesis of DBS and BM under liquid–liquid phase transfer catalysis (PTC) conditions.

Sodium sulfide is well known for the preparation of DBS. Pradhan and Sharma [3] synthesized DBS and bis (4-chloro benzyl) sulfide from the respective chlorides using sodium sulfide and different phase transfer catalysts in liquid–liquid and solid–liquid modes. Tetrabutylammonium bromide (TBAB) was reported to be the most effective out of six catalysts they tried

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Abbreviations: BM, benzyl mercaptan; DBS, dibenzyl sulfide; PTC, phase transfer catalyst; TBAB, tetrabutylammonium bromide

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under solid–liquid mode of operation. A detailed study was reported using the best catalyst, TBAB. Use of ammonium hydrosulfide (NH_4SH) for the preparation of BM is also reported in the literature. As for example, Bittell and Speier [5] prepared BM by using the solution of NH_3 and methanol saturated with H_2S at $0\,°C$. The benzyl chloride was added to this methanolic ammonium hydrosulfide (NH_4SH) solution at $0\,°C$ while slowly bubbling H_2S through the solution. The reaction was completed in 1 h with BM (92%) and DBS (8%) as the detectable products. Labat [4] prepared BM of more than 99% purity by reacting benzyl chloride and ammonium hydrosulfide in a molar ratio ($NH_4SH/C_6H_5CH_2Cl$) of at least 1, preferably between about 1.05 and 1.5 under autogenous pressure in a closed reactor in two steps. The first step comprised adding the benzyl chloride to an aqueous solution of ammonium hydrosulfide at a temperature below $80\,°C$. The second step involved heating the reaction mixture to a temperature in the range of $80–100\,°C$ for about 2 h.

There is no report in the literature on the use of aqueous ammonium sulfide (having more industrial relevance) for selective preparation of dibenzyl sulfide. The present work was, therefore, undertaken to synthesize dibenzyl sulfide in high selectivity by reacting benzyl chloride with aqueous ammonium sulfide in the presence of a phase transfer catalyst, TBAB. A further objective of this work was to study the kinetics of this commercially important reaction and to propose a suitable mechanism for the same.

2. Experimental

2.1. Chemicals

Toluene ($\geq 99\%$) of LR grade, and liquor ammonia ($\sim 26\%$) of analytical grade were procured from S. D. Fine Chemicals Ltd., Mumbai, India. Synthesis grade benzyl chloride ($\geq 99\%$) was obtained from Merck (India) Limited, Mumbai, India. Tetrabutylammonium bromide (TBAB) was obtained from SISCO Research Laboratories Private Limited, Mumbai, India.

2.2. Experimental set-up

The reactions of benzyl chloride with aqueous ammonium sulfide were carried out in batch mode in a 6.5 cm i.d. fully baffled mechanically agitated glass reactor (capacity $250\,cm^3$). A 2.0 cm diameter six-bladed glass disk turbine impeller (with the provision for stirring speed regulation), located at a height of 1.5 cm from the reactor bottom was used for stirring the reaction mixture. The reactor was kept in a constant temperature bath whose temperature could be controlled within $\pm 1\,°C$.

2.3. Preparation of ammonium sulfide solution

About 10% ammonia solution was prepared by adding suitable quantity of liquor ammonia in distilled water. H_2S gas was bubbled through the ammonia solution kept in a $250\,cm^3$ standard gas-bubbler. Since, the reaction of H_2S with ammonium hydroxide is exothermic [1], the gas-bubbler containing ammonia solution was kept immersed in an ice-water bath in order to

prevent the oxidation of ammonium sulfide formed and thus formation of ammonium disulfide. The unabsorbed H_2S gas from the first bubbler was sent to another bubbler containing 1 M aqueous sodium hydroxide solution whose outlet was kept open to the atmosphere. The gas bubbling was continued until the desired sulfide concentration was obtained.

2.4. Experimental procedure

In a typical experimental run, $50\,cm^3$ of the aqueous phase containing a known concentration of sulfide was charged into the reactor and kept well stirred until steady-state temperature was reached. Then the organic phase containing measured volume of benzyl chloride, catalyst (TBAB) and solvent (toluene) kept separately at the reaction temperature was charged into the reactor. Samples were withdrawn from the organic layer at regular intervals after stopping the stirring and allowing the two phases to separate.

2.5. Analysis

All the samples from the organic phase were analyzed by gas–liquid chromatography (GLC) using a $2\,m \times 3\,mm$ stainless steel column packed with 10% OV-17 on Chromosorb W (80/100). A Chemito Model 8610 GC interfaced with Shimadzu C-R1B Chromatopac data processor was used for analysis. The column temperature was programmed with an initial temperature of $150\,°C$ for 50 s, increased at a rate of $20\,°C/min$ up to $300\,°C$, and maintained at $300\,°C$ for 2 min. Nitrogen was used as carrier gas with a flow rate of $20\,cm^3/min$. An injector temperature of $250\,°C$ was used during the analysis. An FID detector was used at a temperature of $320\,°C$. The products were characterized by GC and by IR spectra. The initial sulfide concentration was determined by the standard iodometric titration method [6]. The aqueous phase sulfide concentrations during the reaction were obtained from the overall mass balance. The concentration of ammonia was determined by standard Kjeldahl method.
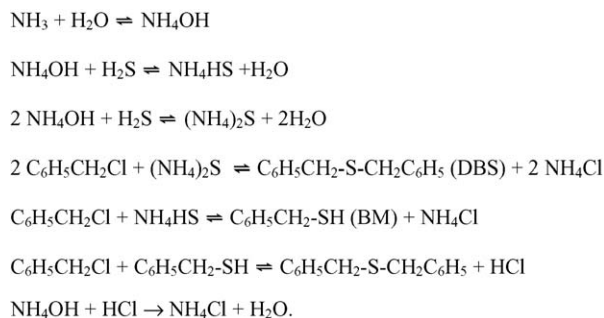
The term selectivity of the two products, DBS and BM, used in this study are defined as the fraction of benzyl chloride converted to a particular product divided by the total conversion of benzyl chloride.

3. Results and discussion

The reaction of benzyl chloride with aqueous ammonium sulfide was carried out in batch mode both in the absence and in the presence of PTC. Dibenzyl sulfide (DBS) and benzyl mercaptan (BM) were detected as products from the reaction mixture by gas–liquid chromatography (GLC). No benzyl alcohol was detected in the reaction mixture even after a batch time of 10 h. Accordingly, the reaction system may be represented by the following scheme (Scheme 1).

3.1. Effect of stirring speed

The effect of speed of stirring on the conversion of benzyl chloride was studied in the range 1000–2000 rev/min in the
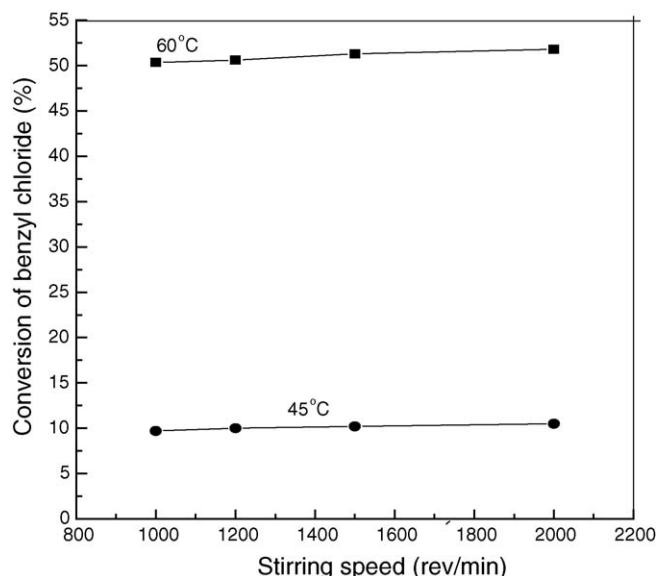
$$NH_3 + H_2O \rightleftharpoons NH_4OH$$

$$NH_4OH + H_2S \rightleftharpoons NH_4HS + H_2O$$

$$2\,NH_4OH + H_2S \rightleftharpoons (NH_4)_2S + 2H_2O$$

$$2\,C_6H_5CH_2Cl + (NH_4)_2S \rightleftharpoons C_6H_5CH_2\text{-}S\text{-}CH_2C_6H_5\ (DBS) + 2\,NH_4Cl$$

$$C_6H_5CH_2Cl + NH_4HS \rightleftharpoons C_6H_5CH_2\text{-}SH\ (BM) + NH_4Cl$$

$$C_6H_5CH_2Cl + C_6H_5CH_2\text{-}SH \rightleftharpoons C_6H_5CH_2\text{-}S\text{-}CH_2C_6H_5 + HCl$$

$$NH_4OH + HCl \rightarrow NH_4Cl + H_2O.$$

<div align="center">Scheme 1.</div>

Fig. 1. Effect of stirring speed on the conversion of benzyl chloride. Volume of organic phase = 5.0×10^{-5} m^3; concentration of benzyl chloride = 2.0 kmol/m^3; volume of aqueous phase = 5.0×10^{-5} m^3; concentration of catalyst = 8.83×10^{-2} kmol/m^3 of organic phase; concentration of sulfide = 1.32 kmol/m^3; NH$_3$/H$_2$S mole ratio = 4.2; batch time = 50 min.

presence of phase transfer catalyst, TBAB as shown in Fig. 1. As it is evident from the figure, the variation of conversion of benzyl chloride with speed of agitation is so small that the mass transfer factors become unimportant and the reaction is controlled by the kinetics only. Therefore, all other experiments were performed at a stirring speed of 1500 rev/min in order to ensure that the system is free from mass transfer resistance.

Table 2
Selectivity of DBS at different NH$_3$/H$_2$S mole ratios[a]

NH$_3$/H$_2$S mole ratio	DBS selectivity (%) at a benzyl chloride conversion of		
	30%	50%	70%
2.46	9.33	16.65	30.35
4.21	13.06	22.49	36.29
5.10	16.5	28.12	42.9

[a] Volume of organic phase = 5.0×10^{-5} m^3; concentration of benzyl chloride = 2.6 kmol/m^3; volume of aqueous phase = 5.0×10^{-5} m^3; concentration of sulfide = 1.6 kmol/m^3; concentration of catalyst = 0.11 kmol/m^3 of organic phase; temperature = 60 °C; stirring speed = 1500 rev/min.

3.2. Effect of temperature

The effect of temperature was studied at four different temperatures in the range 30–70 °C. Table 1 shows the effect of temperature on reaction rate and selectivity of DBS. For a specific conversion of benzyl chloride, the reaction rate increases with increase in the temperature. However, the selectivity of DBS is almost unaffected by the temperature. Therefore, with increase in temperature, the reaction rate increases without significantly affecting the selectivity of the products. Initial rate of reaction of benzyl chloride was calculated at different temperatures and an Arrhenius plot of Ln (initial rate) versus 1/*T* was made. The apparent activation energy for the reaction of benzyl chloride was calculated from the slope of the straight line as 12.3 kcal/mol. This further confirms that the reaction is kinetically controlled.

3.3. Effect of NH$_3$/H$_2$S mole ratio

The effect of NH$_3$/H$_2$S mole ratio on the conversion of benzyl chloride and selectivities of various products were studied in two different ways, i.e., by varying the concentration of one and keeping the initial concentration of other constant. Accordingly, the concentration of ammonia in the aqueous phase was varied maintaining a constant initial sulfide concentration of 1.6 kmol/m^3. With increase in NH$_3$/H$_2$S mole ratio, the conversion of benzyl chloride increases as shown in Fig. 2. The selectivity of DBS increases with increase in NH$_3$/H$_2$S mole ratio as shown in Fig. 3. Therefore, the selectivity of BM decreases with increase in NH$_3$/H$_2$S mole ratio. It is seen from Table 2 that the selectivity of DBS for a fixed conversion of benzyl chloride

Table 1
Effect of temperature on reaction rate and selectivity of DBS[a]

Temperature (°C)	Reaction rate $\times 10^5$ (kmol/m^3 s) at a conversion of benzyl chloride (%) of			Selectivity of DBS (%) at a conversion of benzyl chloride (%) of		
	10	20	30	10	20	30
30	3.43	2.44	1.46	7.6	17.4	28.2
45	18.14	8.86	6.9	7.9	18.1	29.5
60	38.94	33.01	27.1	8.2	16.7	26.2
70	51.92	44.26	36.6	9.0	18.4	28.2

[a] Volume of organic phase = 6.5×10^{-5} m^3; concentration of benzyl chloride = 2.0 kmol/m^3; volume of aqueous phase = 5.0×10^{-5} m^3; concentration of sulfide = 1.06 kmol/m^3; NH$_3$/H$_2$S mole ratio = 5.3; concentration of catalyst = 8.92×10^{-2} kmol/m^3; stirring speed = 1500 rev/min.
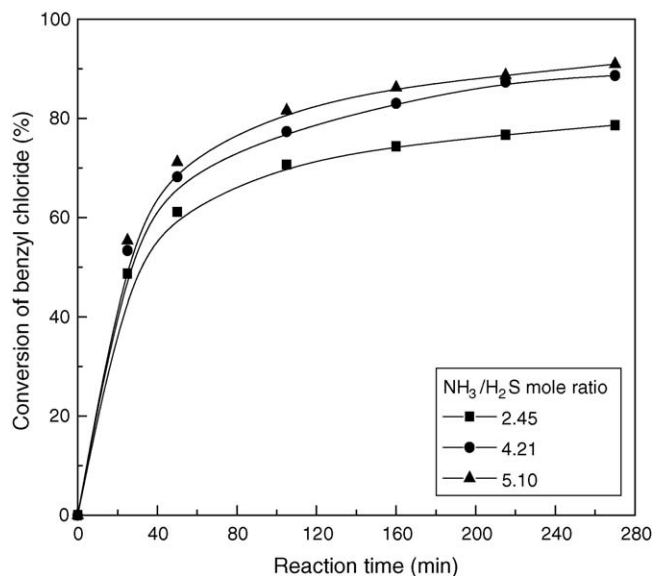
Fig. 2. Effect of ammonia concentration on the conversion of benzyl chloride. Volume of organic phase $= 5.0 \times 10^{-5}$ m^3; concentration of benzyl chloride $= 2.6$ kmol/m^3; volume of aqueous phase $= 5.0 \times 10^{-5}$ m^3; concentration of sulfide $= 1.6$ kmol/m^3; concentration of catalyst $= 0.11$ kmol/m^3 of organic phase; temperature $= 60\,^\circ$C; stirring speed $= 1500$ rev/min.

Fig. 4. Effect of sulfide concentration on conversion of benzyl chloride. Volume of organic phase $= 5.0 \times 10^{-5}$ m^3; concentration of benzyl chloride $= 2.0$ kmol/m^3; volume of aqueous phase $= 5.0 \times 10^{-5}$ m^3; concentration of ammonia $= 5.62$ kmol/m^3; concentration of catalyst $= 8.83 \times 10^{-2}$ kmol/m^3 of organic phase; temperature $= 60\,^\circ$C; stirring speed $= 1500$ rev/min.

increases with increase in the NH$_3$/H$_2$S mole ratio. Although ammonia does not take part in the reaction with benzyl chloride, it affects the equilibrium among ammonia, hydrogen sulfide, and water that results two active anions, sulfide and hydrosulfide, in the aqueous phase. The concentration of sulfide ions relative to hydrosulfide ions in the aqueous phase increases with increase in NH$_3$/H$_2$S mole ratio, which results in the higher selectivity of DBS. As it is observed from Scheme 1, 1 mole of sulfide reacts with 2 mole of benzyl chloride to form 1 mole DBS whereas it requires only 1 mole of benzyl chloride to form 1 mole BM. Although the initial concentration as well as the amount of sulfide in the aqueous phase remains same, yet the conversion of
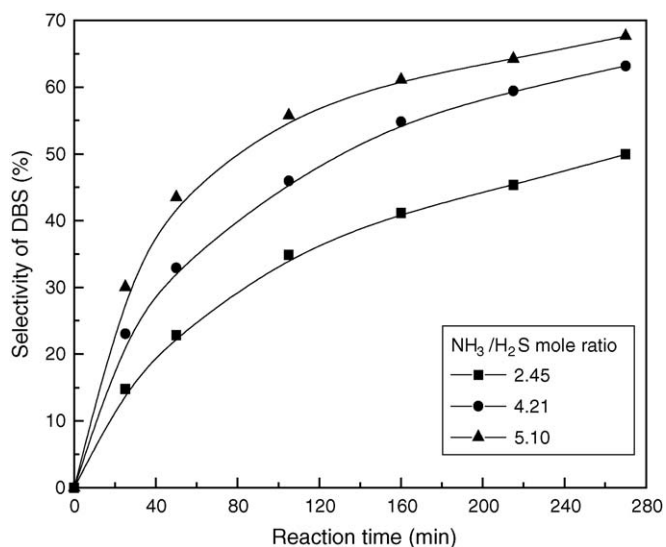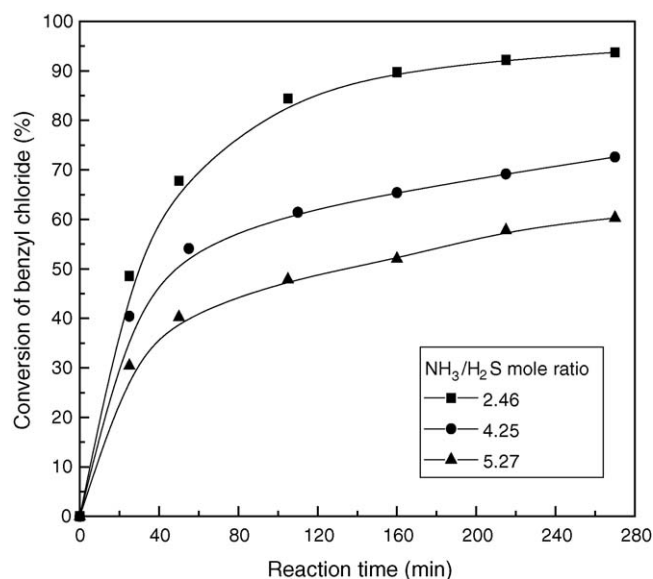
benzyl chloride increases with increase in NH$_3$/H$_2$S mole ratio because of the higher selectivity of DBS at higher NH$_3$/H$_2$S mole ratio.

The effect of NH$_3$/H$_2$S mole ratio was also studied by varying the initial sulfide concentration in the aqueous phase keeping ammonia concentration fixed at 5.62 kmol/m^3. For a fixed ammonia concentration, with increase in NH$_3$/H$_2$S mole ratio, the conversion of benzyl chloride decreases because of the limited quantity of sulfide in the aqueous phase as shown in Fig. 4. The selectivity of DBS increases with increase in NH$_3$/H$_2$S mole ratio.

3.4. Effect of catalyst (TBAB) loading

The effect of catalyst loading was studied at four different catalyst concentrations in the range of 0.0–0.14 kmol/m^3 as shown in Fig. 5. With increase in catalyst concentration, the conversion of benzyl chloride as well as reaction rate increases. Only by increasing the catalyst concentration, benzyl chloride conversion of more than 90% was achieved whereas it was only about 70% without catalyst even after 445 min of reaction under otherwise identical conditions. The maximum rate enhancement factor of 2.45 was obtained with catalyst concentration of 0.14 kmol/m^3 of organic phase. The selectivity of DBS increases with increase in catalyst concentration as shown in Fig. 6. Therefore, the selectivity of BM decreases with catalyst loading. From the plot of selectivity of DBS versus conversion of benzyl chloride (Fig. 7), it is observed that for a fixed conversion of benzyl chloride, the selectivity of DBS increases with increase in the catalyst concentration up to a value of 0.09 kmol/m^3 of organic phase. Beyond this concentration, the selectivity of DBS is almost independent of the catalyst concentration. This trend was observed up to about 70% conversion of benzyl chloride. Above this conversion, the
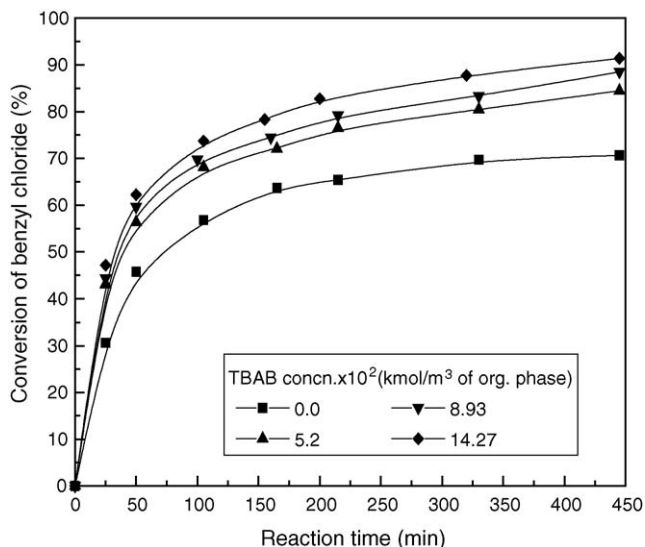

Fig. 3. Effect of ammonia concentration on selectivity. All conditions are same as in Fig. 2.

Fig. 5. Effect of catalyst loading on conversion of benzyl chloride. Volume of organic phase $= 5.0 \times 10^{-5}$ m^3; concentration of benzyl chloride $= 1.44$ kmol/m^3; volume of aqueous phase $= 5.0 \times 10^{-5}$ m^3; concentration of sulfide $= 1.06$ kmol/m^3; NH$_3$/H$_2$S mole ratio $= 5.27$; temperature $= 60\,^{\circ}$C; stirring speed $= 1500$ rev/min.

Fig. 7. Relationship between conversion of benzyl chloride and selectivity of DBS under different catalyst loading. All conditions are same as in Fig. 5.

3.5. Effect of concentration of benzyl chloride

selectivity of DBS was not found to be affected by the catalyst concentration.

With increased catalyst concentration, more amount of $[Q^+]_2S^{2-}$ ion pair is formed and transferred to the organic phase and reacts with benzyl chloride to form DBS. The selectivity of DBS, therefore, increases with increase in catalyst concentration. Beyond a catalyst concentration of 0.09 kmol/m^3 of organic phase, the reaction of QSQ with benzyl chloride in the organic phase controls the rate of formation of DBS by direct reaction and the selectivity of DBS remains almost constant.
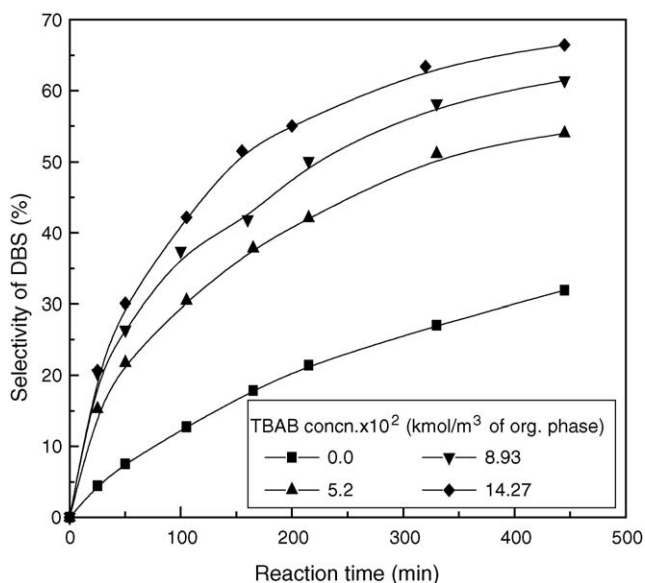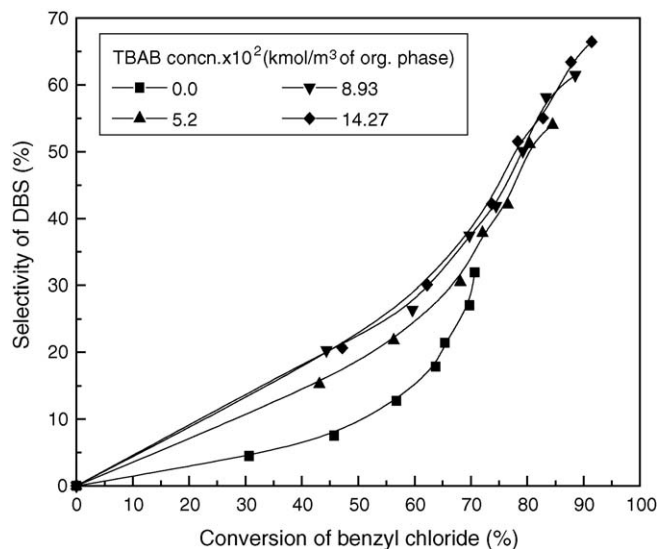
The effect of the concentration of benzyl chloride on conversion and selectivity was studied at three different concentrations in the range of 0.78–2.0 kmol/m^3. The selectivity of DBS increases with increase in the concentration of benzyl chloride as shown in Fig. 8. Therefore, the selectivity of BM decreases with the concentration of benzyl chloride. From the plot of selectivity of DBS versus conversion of benzyl chloride (Fig. 9), it is seen that there is a sharp increase of slope of the curve with increase in the concentration of benzyl chloride. Since the reaction leading to the formation of BM is very fast compared to that of DBS, at low benzyl chloride concentration there will be insufficient quantity of benzyl chloride present to produce
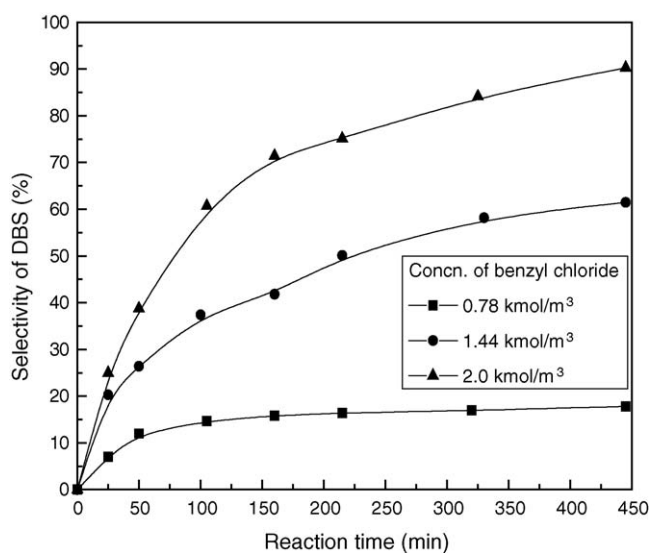

Fig. 6. Effect of catalyst loading on selectivity. All conditions are same as in Fig. 5.

Fig. 8. Effect of benzyl chloride concentration on selectivity. Volume of organic phase $= 5.0 \times 10^{-5}$ m^3; TBAB $= 5.8 \times 10^{-3}$ mol; volume of aqueous phase $= 5.0 \times 10^{-5}$ m^3; concentration of sulfide $= 1.06$ kmol/m^3; NH$_3$/H$_2$S mole ratio $= 5.27$; temperature $= 60\,^{\circ}$C; stirring speed $= 1500$ rev/min.
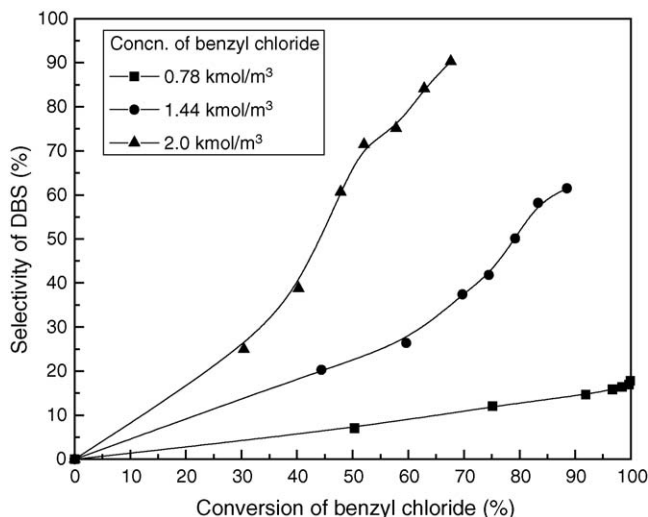
Fig. 9. Relationship between conversion of benzyl chloride and selectivity of DBS under different benzyl chloride concentration. All conditions are same as in Fig. 8.

Fig. 10. Effect of volume of aqueous phase on selectivity. Volume of organic phase $= 5.0 \times 10^{-5}$ m^3; concentration of benzyl chloride $= 1.44$ kmol/m^3; concentration of sulfide $= 1.06$ kmol/m^3; NH$_3$/H$_2$S mole ratio $= 5.27$; concentration of catalyst $= 8.92 \times 10^{-2}$ kmol/m^3; temperature $= 60\,^\circ$C; stirring speed $= 1500$ rev/min.

DBS, which results low selectivity of DBS. It is also seen from Fig. 9 that with increase in the concentration of benzyl chloride, the conversion of benzyl chloride decreases because of limited quantity of sulfide present in the aqueous phase.

With low benzyl chloride concentration in the organic phase, almost complete conversion of benzyl chloride was achieved. This resulted in very low selectivity of DBS, i.e., high selectivity of BM. With excess benzyl chloride, higher DBS selectivity was achieved with efficient utilization of sulfide in the aqueous phase although the benzyl chloride conversion remained low. Therefore, a question of optimisation among the opposing factors (conversion of benzyl chloride, utilization of sulfide, and selectivity of DBS) arises.

3.6. Effect of volume of aqueous phase

It is seen from Fig. 10 that the selectivity of DBS increases from about 30% to 88% for change in the volume of aqueous phase from 75 to 25 cm^3 after 445 min of reaction under identical experimental conditions. Therefore, the selectivity of BM decreases with decrease in the volume of aqueous phase. From the plot of selectivity of DBS versus conversion of benzyl chloride (Fig. 11), it is seen that the slope of the curve drops drastically with increase in the volume of aqueous phase. Similar argument can be used to explain this phenomenon as in the case of concentration of benzyl chloride. It is also seen from the same figure that the conversion of benzyl chloride increases with increase in volume of aqueous phase. This is due to the deficient quantity of sulfide in the aqueous phase at lower volume of aqueous phase.

3.7. Mechanism

Generally, the reactions in the aqueous phase are fast compared to the reactions in the organic phase. Therefore, there exists an ionic equilibrium among ammonia, hydrogen sulfide
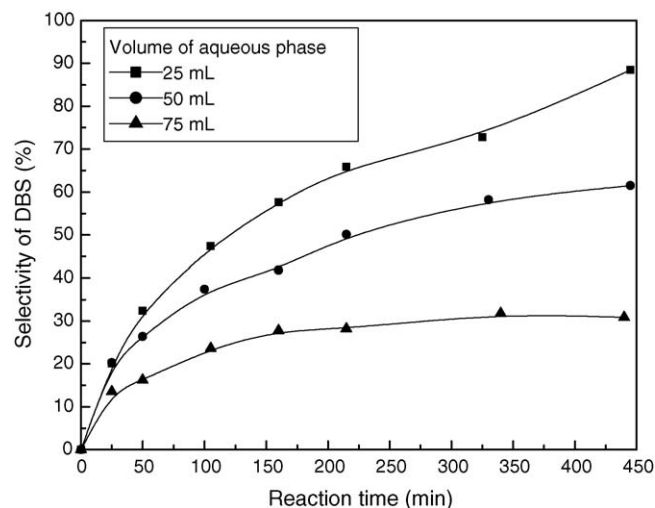
and water, which results three active anions: hydroxide (HO$^-$), hydrosulfide (HS$^-$), and sulfide (S^{2-}) as represented by Eqs. (1)–(4) in Scheme 2. These ions are capable of producing the ion pairs (QOH, QSH, and QSQ) with quaternary ammonium cation, Q$^+$ [(C$_4$H$_9$)$_4$N$^+$]. However, no benzyl alcohol, C$_6$H$_5$CH$_2$OH (substitution product of QOH), was identified in the GC analysis from the two-phase reaction in the presence of TBAB. This is because of the fact that the active catalyst, QOH, is more hydrophilic in nature and not easily transferred to the organic phase [7] and therefore the hydrolysis of benzyl chloride under weak alkaline medium of aqueous ammonium hydroxide is slow [8]. However, only two species (QSH and QSQ) are generated and transferred to the organic phase where the reaction takes place.
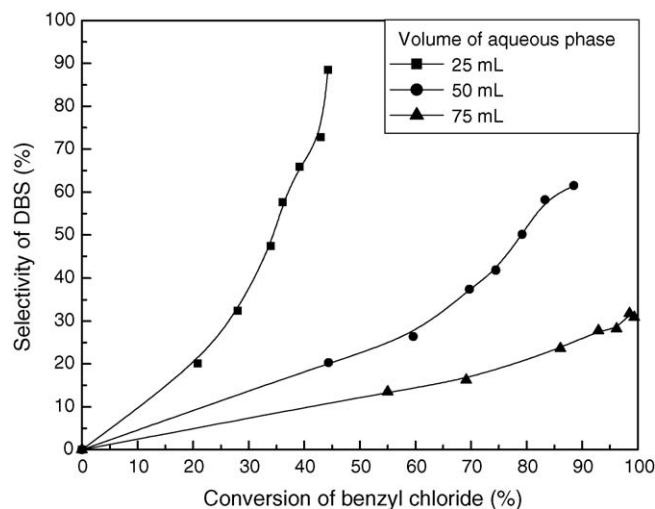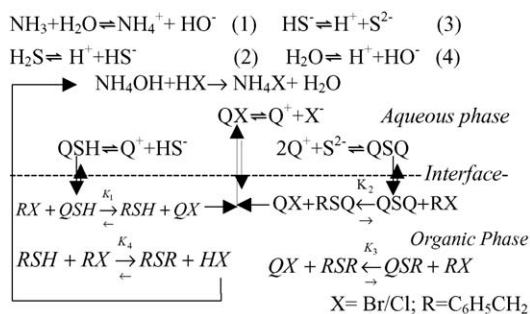

Fig. 11. Relationship between conversion of benzyl chloride and selectivity of DBS under different volume of aqueous phase. All conditions are same as in Fig. 10.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + HO^- \quad (1) \qquad HS^- \rightleftharpoons H^+ + S^{2-} \quad (3)$$

$$H_2S \rightleftharpoons H^+ + HS^- \quad (2) \qquad H_2O \rightleftharpoons H^+ + HO^- \quad (4)$$

$$\longrightarrow NH_4OH + HX \rightarrow NH_4X + H_2O$$

$$QX \rightleftharpoons Q^+ + X^- \qquad \textit{Aqueous phase}$$

$$QSH \rightleftharpoons Q^+ + HS^- \qquad 2Q^+ + S^{2-} \rightleftharpoons QSQ$$

----Interface-

$$RX + QSH \overset{K_1}{\underset{\leftarrow}{\rightarrow}} RSH + QX \quad \blacktriangleright\blacktriangleleft \quad QX + RSQ \overset{K_2}{\underset{\rightarrow}{\leftarrow}} QSQ + RX$$

$$\textit{Organic Phase}$$

$$RSH + RX \overset{K_4}{\underset{\leftarrow}{\rightarrow}} RSR + HX \qquad QX + RSR \overset{K_3}{\underset{\rightarrow}{\leftarrow}} QSR + RX$$

$$X = Br/Cl; \; R = C_6H_5CH_2$$

Scheme 2.

No BM was identified in the GC analysis during the reaction of benzyl chloride with sodium sulfide under two-phase condition using TBAB as PTC. Therefore, the sulfide ions (S^{2-}) present in the aqueous phase form ion pair with quaternary ammonium cation (Q^+) to produce QSQ (instead of converting into hydrosulfide ion by reacting with water, $S^{2-} + H_2O \rightleftharpoons HS^- + OH^-$), which in turn is transferred to the organic phase and reacts with benzyl chloride to produce DBS. This is supported by the fact that the selectivity of DBS increases with increase in NH_3/H_2S mole ratio as discussed previously. Therefore, it can be concluded that the active catalysts (QSQ and QSH) formed from the sulfide ions and hydrosulfide ions present in the aqueous phase are transferred to the organic phase and react with benzyl chloride to produce DBS and BM, respectively.

Fig. 12 shows the concentration profile for a typical batch. It is seen from the figure that concentration of BM reaches a maximum and then falls gradually with time. Therefore, BM is converted to DBS whose concentration increases with time. Probably, benzyl chloride reacts with BM to produce DBS and hydrochloric acid. Since, the hydrochloric acid (strong acid) is formed from a weak acid, BM, this reaction is expected to be slow and is favored only due to the presence of ammonium
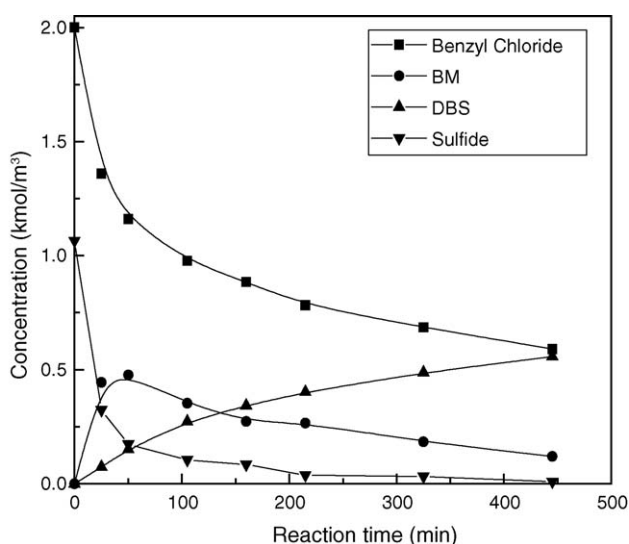

Fig. 12. Concentration profile for a typical run. Volume of organic phase $= 5.0 \times 10^{-5} \, m^3$; concentration of benzyl chloride $= 2.0 \, kmol/m^3$; concentration of catalyst $= 8.92 \times 10^{-2} \, kmol/m^3$; volume of aqueous phase $= 5.0 \times 10^{-5} \, m^3$; concentration of sulfide $= 1.06 \, kmol/m^3$; NH_3/H_2S mole ratio $= 5.27$; temperature $= 60\,°C$; stirring speed $= 1500 \, rev/min$.

hydroxide, which reacts with hydrochloric acid irreversibly to produce ammonium chloride in the aqueous phase.

Two mechanisms, interfacial and bulk, are generally used for liquid–liquid phase-transfer catalysis based on the lipophilicity of the quaternary cation. The bulk mechanism, suggested by Starks [9] and Starks and Liotta [10], is applicable to catalysts that are not highly lipophilic or that can distribute themselves between the organic and the aqueous phases. In the interfacial model, catalyst remains entirely in the organic phase because of its high lipophilicity and exchanges anions across the liquid–liquid interface [11].

Even without phase transfer catalyst, there is a significant conversion of benzyl chloride as it is seen in the effect of catalyst loading. Therefore, the reaction proceeds through both the un-catalyzed and catalyzed pathway. Based on the above facts, the catalytic pathway is pictorially represented by Scheme 2. The reaction proceeds through the un-catalyzed pathway is similar to that of catalytic pathway except that the anions (S^{2-} and HS^-) in the form of ammonium sulfide and ammonium hydrosulfide are directly transferred to organic phase from aqueous phase instead of transferring via the formation of active catalyst as in the case of catalytic pathway and react with benzyl chloride to produce DBS and BM, respectively, as shown previously in Scheme 1.

4. Conclusions

The reaction of benzyl chloride with ammonium sulfide is of great industrial relevance, which could lead to different products of high commercial value. This reaction was studied in detail under liquid–liquid phase transfer catalysis conditions. The reaction was found to be kinetically controlled with an apparent activation energy value of 12.3 kcal/mol. The NH_3/H_2S mole ratio was found to have enormous effect on the selectivity of DBS and BM. The higher ratio favors DBS where as the lower ratio favors BM. The change in the temperature and the catalyst concentration (beyond a certain value) only changes the reaction rate without significantly affecting the selectivity. The selectivity of DBS increases with excess benzyl chloride in the organic phase and low ammonium sulfide volume with the efficient sulfide utilization although the conversion of benzyl chloride remains low. However, the opposite trend was observed for BM.

The process involves a complex mechanism. The existence of ionic equilibriums among ammonia, hydrogen sulfide, and water producing sulfide (S^{2-}) and hydrosulfide (HS^-) ions in the aqueous phase was established. The two active ion pairs ($Q^+S^{-2}Q^+$ and Q^+SH^-) formed in the aqueous phase are first transferred to the organic phase and the react with benzyl chloride to produce DBS and BM, respectively. The DBS is also formed by the reaction of BM and benzyl chloride.

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