Kinetics of phase transfer catalyzed reduction of nitrochlorobenzenes by aqueous ammonium sulfide: Utilization of hydrotreater off-gas for the production of value-added chemicals

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Abstract

The reduction of nitrochlorobenzenes (NCBs) was carried out in an organic solvent, toluene, under liquid–liquid mode with phase transfer catalyst, tetrabutylammonium bromide (TBAB). The selectivity of chloroanilines (CANs) was found to be 100%. The reaction rate of \( m \)-nitrochlorobenzene (MNCB) was found to be highest among the three NCBs followed by \( o \)- and \( p \)-nitrochlorobenzene (ONCB and PNCB). The reactions were found to be kinetically controlled with apparent activation energies of 22.8, 19.6 and 9.4 kcal/mol for ONCB, PNCB and MNCB, respectively. The effects of different parameters such as TBAB concentration, NCB concentration, sulfide concentration, ammonia concentration, and elemental sulfur loading on the conversion and reaction rate of NCBs were studied to establish the mechanism of the reaction. The rate of reaction of NCBs was found to be proportional to the concentrations of the catalyst and NCBs and to the cube of the concentration of sulfide. A generalized empirical kinetic model was developed to correlate the experimentally obtained conversion versus time data for the three NCBs.

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1. Introduction

The importance of hydrotreatment is ever increasing in the refining industry. This is because of the fact that the supply of light and easy-to-process crude oils is gradually declining and the refiners throughout the world are forced to process heavy crudes containing high amount of sulfur and nitrogen. With stringent environmental regulations, refiners are also forced to hydrotreat such crude to bring down the sulfur and nitrogen concentrations to the prescribed levels. 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). Moreover, several disadvantages of air oxidation of hydrogen sulfide, including loss of a valuable hydrogen source, precise air rate control, removal of trace sulfur compounds from exhaust gas, and an upper limit on the ratio of carbon dioxide to hydrogen sulfide, provide driving force for the development of alternative processes for better utilization of the low value component of the gaseous streams, i.e., hydrogen sulfide. Since, ammonia is present as non-hydrocarbon co-impurity in most of the gases, it was thought desirable to use ammonium hydroxide to absorb the hydrogen sulfide and to produce some commercially important chemicals utilizing this H\(_2\)S-rich aqueous ammonia called ammonium sulfide. The simultaneous absorption of hydrogen sulfide and ammonia into water and the use of ammonium hydroxide for the removal of hydrogen sulfide and ammonia from gas stream are well documented [3–5]. However, there is no information in the literature on the
The reduction of nitrochlorobenzenes (NCBs) to the corresponding amines is commercially very important, because the products chloroanilines (CANS) have wide commercial applications as intermediates for the preparation of polyanilines and substituted phenyl carbamates [6], and organic fine chemicals, such as dyes, drugs, herbicides and pesticides [7,8]. The use of ammonium sulfide as a reducing agent is of considerable practical value due to some inherent advantages of the method over other conventional processes. For example, catalytic hydrogenation requires more expensive equipment and hydrogen handling facility; additional problems arise due to catalyst preparation, catalyst poisoning hazards and the risk of reducing other groups. Although the reduction by iron is reserved for small-scale commercial applications, it cannot be used for reduction of a single nitro group in a polynitro compound, nor it can be used on substrates harmed by acid media (e.g., some ethers and thioethers). Metal hydrides, e.g., lithium aluminum hydride, generally convert nitro compounds to mixtures of azoxy and azo compounds, besides being expensive. The present work is concerned with the reduction of NCBs (o−, m− and p−) by aqueous ammonium sulfide as the reducing agent under two-phase condition in the presence of a phase transfer catalyst (PTC).

PTCs are widely used to intensify otherwise slow heterogeneous reactions involving an organic substrate and an ionic reactant, either dissolved in water (liquid−liquid) or present in solid state (liquid−solid) [9,10]. Phase transfer catalysis is now an attractive technique for organic synthesis because of its advantages of simplicity, reduced consumption of organic solvent and raw materials, mild operating conditions, and enhanced reaction rates and selectivity. Among several varieties of PTCs, quaternary ammonium salts are most preferred for their better activity and ease of availability. Tetrabutylammonium bromide (TBAB) has been reported to be the most active PTC among six different catalysts used to intensify the reaction of benzyl chloride with solid sodium sulfide [11]. In the present work, the TBAB was therefore used as PTC to enhance the otherwise slow reduction rate of NCBs by aqueous ammonium sulfide.

The reduction reaction of nitroarenes by negative divalent sulfur (sulfide, hydrosulfide and polysulfides) is called Zinin reduction [12]. Sodium sulfide, sodium disulfide and ammonium sulfide are most commonly used for this purpose. Several researchers studied the kinetics of the reduction of various nitroarenes using sodium sulfide and disulfide both in the absence and presence of PTC and in different modes (solid−liquid and liquid−liquid) [13−18]. The preparation of ary1 amines using aqueous ammonium sulfide [19], alcoholic ammonium sulfide [20,21], and ammonium sulfide prepared from the equivalent amounts of ammonium chloride and crystalline sodium sulfide dissolved in ammonium hydroxide or alcohol [22,23] has also been reported in the literature. However, there is no reported work in the literature on detail kinetic study of reduction of any nitroarenes using such an industrially relevant reducing agent, aqueous ammonium sulfide, in presence of PTC.

In aqueous ammonium sulfide, the sulfide ions (S2−) and the hydrosulfide ions (HS−) remain in equilibrium, as represented by Scheme 1 [3,24]. Due to the existence of two different ions (sulfide and hydrosulfide) in the aqueous ammonium sulfide, the properties of this reducing agent is expected to be different from the other reducing agents like sodium sulfide and disulfide.

The overall stoichiometry of the Zinin’s original reduction of nitrobenzene by aqueous ammonium sulfide as proposed by Zinin in 1842 is given by Eq. (1) [12]. This stoichiometry is also applicable for reduction of nitrobenzenes by sodium sulfide [14−18].

\[
4\text{ArNO}_2^- + 6\text{S}^{2-} + 7\text{H}_2\text{O} \rightarrow 4\text{ArNH}_2^- + 3\text{S}_2\text{O}_3^{2-} + 6\text{HO}^-
\]

(1)

For the preparation of p-aminophenylacetic acid from p-nitrophenylacetic acid using aqueous ammonium sulfide, it is reported that the sulfide ions are oxidized to elemental sulfur instead of thiosulfate following stoichiometry of Eq. (2) [19]. A similar stoichiometry is reported for the reduction of 2-bromo-4-nitrotoluene by alcoholic ammonium sulfide [21]. The formation of elemental sulfur is also reported for the preparation of 3-amino-5-nitrobenzyl-alcohol using ammonium sulfide prepared from ammonium chloride and crystalline sodium sulfide dissolved in methanol [23].

\[
\text{ArNO}_2^- + 3\text{HS}^- + \text{H}_2\text{O} \rightarrow \text{ArNH}_2^- + 3\text{S}^- + 3\text{HO}^-
\]

(2)

The overall stoichiometry of the reduction reaction using sodium disulfide as the reducing agent is as follows [13,14]:

\[
\text{ArNO}_2^- + 2\text{S}_2^{2-} + \text{H}_2\text{O} \rightarrow \text{ArNH}_2^- + 2\text{S}_2\text{O}_3^{2-}
\]

(3)

\[
\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{HO}^-
\]

\[
\text{HS}^- \rightleftharpoons \text{H}^- + \text{S}^-.
\]

Scheme 1
Therefore, the two different reactions leading to the formation of either elemental sulfur or thiosulfate may be operative for the reduction of nitroarenes with aqueous ammonium sulfide. A detailed study of such reactions is, therefore, not only commercially important, it is academically interesting too.

Present work is, therefore, concerned with the reduction of NCBs (α, m-, and p-) by aqueous ammonium sulfide in the presence of PTC to produce commercially important CANs (α-, m-, and p-). The effects of various parameters such as speed of agitation, temperature, TBAB concentration, concentration of NCB, sulfide concentration, ammonia concentration, and elemental sulfur loading on the reaction rate and conversion were studied to establish a mechanism and stoichiometry of the reaction. A generalized empirical kinetic model applicable for all the NCBs was also developed to correlate the experimental data.

2. Experimental

2.1. Chemicals

Toluene (≥99%) of LR grade and LIQR ammonia (~26%) of analytical grade were procured from S.D. Fine Chemicals Ltd., Mumbai, India. Nitrochlorobenzenes were purchased from Central Drug House (P) Ltd., New Delhi, India. Tetrabutylammonium bromide was obtained from SISCO Research Laboratories Pvt. Ltd., Mumbai, India.

2.2. Equipment

The reactions of NCBs with aqueous ammonium sulfide were carried out batch-wise in a fully baffled mechanically agitated glass reactor of capacity 250 cm³ (6.5 cm i.d.). A 2.0 cm-diameter six-bladed glass disk turbine impeller with the provision of speed regulation, located at a height of 1.5 cm from the bottom, was used for stirring the reaction mixture. The reactor was kept in a constant temperature water bath whose temperature could be controlled within ±1 °C.

2.3. Preparation of aqueous ammonium sulfide

For the preparation of aqueous ammonium sulfide, around 15 wt% ammonia solution was prepared first by adding a suitable quantity of LIQR ammonia in distilled water. Then H₂S gas was bubbled through this ammonia solution in a 250 cm³ standard gas-bubbler. The gas bubbling was continued until the desired sulfide concentration was obtained in the aqueous ammonia solution.

2.4. Experimental procedure

In a typical run, 50 cm³ of the aqueous phase containing a known concentration of sulfide was charged into the reactor and kept well agitated until the steady-state temperature was reached. Then the organic phase containing a measured amount of NCB, catalyst (TBAB) and solvent (toluene), kept separately at the reaction temperature, was charged into the reactor. The reaction mixture was then agitated at a constant speed. About 0.5 cm³ of the organic layer was withdrawn at a regular interval after stopping the agitation and allowing the phases to separate.

2.5. Analysis

All the samples from the organic phase were analyzed by gas–liquid chromatography (GLC) using a 2 m × 3 mm stainless steel column packed with 10% OV-17 on Chromosorb W (80/100). Nitrogen was used as the carrier gas with a flow rate of 15 cm³/min. An injector temperature of 250 °C was used during the analysis. An FID detector was used at a temperature of 270 °C. A Chemito Model 8610 GC interfaced with a Shimadzu C-R6A Chromatopac data processor was used for the analysis.

Initial sulfide concentrations were determined by the standard iodometric titration method [25].

3. Results and discussion

3.1. Effect of speed of agitation

The effect of speed of agitation on the rate of reaction of NCBs (α-, m- and p-) was studied in the range 1000–2500 rpm under otherwise identical experimental conditions in the presence of PTC, TBAB as shown in Fig. 1. As it is evident from the figure, the variation of reaction rate with speed of agitation is so small that the mass transfer factors become unimportant and the reactions may be considered as kinetically controlled for all the NCBs. All other experiments were performed at 1500 rpm so as to neglect the effects of mass transfer resistance on the reaction kinetics.

Fig. 1. Effect of speed of agitation on reaction rate of NCBs. Matching conversion = 5%; volume of organic phase = 5 × 10⁻³ m³; NCB concentration = 1.27 kmol/m³; TBAB concentration = 3.1 × 10⁻³ kmol/m³ of organic phase; volume of aqueous phase = 5 × 10⁻³ m³; concentration of ammonia = 8.54 kmol/m³; concentration of sulfide = 2.25 kmol/m³; temperature = 323 K.
Table 1
Effect of temperature on reaction rate of NCBs

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Reaction rate ( \times 10^3 ) (kmol/m³ s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PNCBa ONCBb MNCBb</td>
</tr>
<tr>
<td>303</td>
<td>1.20 1.27 7.82</td>
</tr>
<tr>
<td>313</td>
<td>1.88 3.28 12.21</td>
</tr>
<tr>
<td>323</td>
<td>4.72 7.05 16.64</td>
</tr>
<tr>
<td>333</td>
<td>8.53 26.8 36.4</td>
</tr>
</tbody>
</table>

Matching conversion = 5%; volume of organic phase = 5 \( \times 10^{-3} \) m³; NCB concentration = 1.01 kmol/m³; TBAB concentration = 3.1 \( \times 10^{-2} \) kmol/m³ of organic phase; volume of aqueous phase = 5 \( \times 10^{-3} \) m³; concentration of ammonia = 6.22 kmol/m³; speed of agitation = 1500 rpm.

Table 2
Effect of TBAB concentration on reaction rate of NCBs

<table>
<thead>
<tr>
<th>Organic substrates</th>
<th>Reaction rate ( \times 10^3 ) (kmol/m³ s)</th>
<th>Enhancement factor (A/B)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In presence of TBAB (A)</td>
<td>In absence of TBAB (B)</td>
</tr>
<tr>
<td>PNCB</td>
<td>6.44</td>
<td>0.90</td>
</tr>
<tr>
<td>ONCB</td>
<td>11.00</td>
<td>1.20</td>
</tr>
<tr>
<td>MNCB</td>
<td>35.00</td>
<td>2.60</td>
</tr>
</tbody>
</table>

Matching conversion = 5%; volume of organic phase = 5 \( \times 10^{-3} \) m³; NCB concentration = 1.27 kmol/m³; TBAB concentration = 3.1 \( \times 10^{-2} \) kmol/m³ of organic phase; volume of aqueous phase = 5 \( \times 10^{-3} \) m³; concentration of ammonia = 8.54 kmol/m³; concentration of sulfide = 2.25 kmol/m³; temperature = 323 K; speed of agitation = 1500 rpm.

3.2. Effect of temperature

The effect of temperature on the rate of reaction of NCBs (o-, m- and p-) with aqueous ammonium sulfide was studied in the range of 303–333 K in the presence of catalyst, TBAB, as shown in Table 1. The reaction rate increases with increase in temperature for all the NCBs, as observed from the table. The initial rates were calculated at different temperatures and an Arrhenius plot of \( \ln (\text{rate}) \) against \( 1/T \) (K⁻¹) was made. The apparent activation energies for this kinetically controlled reaction were calculated from the slopes of the straight lines as 22.8, 19.6 and 9.4 kcal/mol for o-nitrochlorobenzene (ONCB), p-nitrochlorobenzene (PNCB) and m-nitrochlorobenzene (MNCB), respectively. The high values of apparent activation energy again confirm that the reactions are kinetically controlled.

3.3. Effect of catalyst concentration

The effect of catalyst (TBAB) concentration on the conversion of PNCB was studied in the concentration range of 1.57 \( \times 10^{-2} \) to 6.23 \( \times 10^{-2} \) kmol/m³ of organic phase as shown in Fig. 2. The study was also conducted in the absence of catalyst as shown in the figure. As it is observed from the figure, the conversion of PNCB is only about 10% in the absence of catalyst whereas it is around 51% with maximum concentration of catalyst tried after 200 min of reaction under otherwise identical experimental conditions. From Table 2, it is observed that the rate of reaction of NCBs in the absence of TBAB is low compared to that in the presence of TBAB. This shows the importance of PTC in enhancing the rate of the reaction under investigation.

In order to determine the order of reaction with respect to TBAB concentration, the initial reaction rate was calculated at different TBAB concentration and a plot of \( \ln \) (initial rate) against \( \ln \) (TBAB concentration) was made (Fig. 3). From the slope of the linear fit line, the order of the reaction with respect to TBAB concentration was obtained as 1.06, which is close to unity. Yadav et al. have also reported a similar observation for the reduction of p-nitroanisole by sodium sulfide in presence of PTC, TBAB [17].

3.4. Comparison of reactivity of nitrochlorobenzenes

It is worthy to mention here that the rate of reduction of MNCB is highest among the three NCBs followed by ONCB and PNCB as observed from Fig. 1 as well as from Tables 1 and 2. The presence of electron donating group in the aromatic ring is reported to reduce the rate of reduction of nitroarenes and the rate of reduction increases in presence of electron withdrawing group [26]. In case of NCBs, the electron donating (due to resonance by lone pair electron of chlorine atom) as well as electron withdrawing (due to high electron negativity of chlorine atom) effect is felt by the nitro group due to the presence of chloride group in the aromatic ring. The resonance theory predicts the same degree of electron donation by chloride group for ortho and para isomers and this effect is absent in case of meta isomer. Therefore, the rate of reduction of MNCB is expected to be higher compared to PNCB and ONCB as observed in the present study. The electron withdrawing effect...
is felt more when chloride group is present at ortho position compared to para position resulting in higher rate of reduction of ONCB compared to PNCB.

3.5. Effect of p-nitrochlorobenzene concentration

The effect of concentration of PNCB on the conversion was studied in the presence of TBAB under otherwise identical experimental conditions as shown in Fig. 4. As the concentration of PCNB increased, the conversion of PCNB, as well as the reaction rate (Fig. 5), was observed to increase up to a certain reaction time; beyond that time, an opposite trend was observed, i.e., with lower PCNB concentration, higher PCNB conversion was achieved. The increase in reaction rate during the initial stage of the reaction is due to the increase in

concentration of PCNB as expected. Since the amount of sulfide in the aqueous phase remained same for all the runs, the conversion of PCNB dropped beyond a certain concentration as shown in Fig. 4. From the plot of ln (initial rate) against ln (initial PCNB concentration) (Fig. 5) the order of the reaction with respect to PCNB concentration was obtained as 1.2, which is close to unity. Similar observations were reported for the reduction of p-nitroanisole [17] and nitroaromatics [14] by aqueous sodium sulfide. The rate was also reported to be proportional to the concentration of nitrobenzene for its reduction with sodium disulfide under two-phase conditions [13].

3.6. Effect of sulfide concentration

Fig. 6 shows the effect of aqueous phase sulfide concentration on the conversion of PNCB. With increase in the concentration of sulfide, the conversion of PNCB as well as the reaction rate increases, as evident from the figure. From the plot of ln (initial rate) against ln (initial sulfide concentration) (Fig. 7), the order of the reaction with respect to sulfide concentration was obtained as 2.88. Since this value is closer to 3, the reaction was, therefore, considered as third order with respect to sulfide concentration. However, for the reduction of nitroarenes with aqueous sodium sulfide, the reaction rate was reported to be first order with respect to sulfide concentration [14,17]. The rate was also reported to be proportional to the square of the concentration of sodium disulfide [13].

3.7. Effect of ammonia concentration

Although ammonia as such does not take part in the reaction with NCBs, it affects the equilibrium among itself, hydrogen sulfide, and water, which results in two active anions, sulfide (S²⁻) and hydrosulfide (HS⁻), in the aqueous phase as shown in Scheme 1. These two active anions participate in two different reactions (Eqs. (1) and (2)). In the presence of a base, ammonia,
the dissociation equilibrium shifts toward more ionization [24] and the concentration of sulfide ions relative to hydrosulfide ions in the aqueous phase increases with increase in ammonia concentration. Therefore, only by changing the ammonia concentration with constant sulfide concentration in the aqueous phase, one can more easily prove the existence of two different reactions.

To study the effect of ammonia concentration, aqueous ammonium sulfide of different ammonia concentrations (but constant sulfide concentration) were prepared by taking first 30 cm$^3$ of aqueous ammonium sulfide (with known sulfide and ammonia concentrations). Then various proportions of LIQR ammonia and distilled water were added to it in such a way that the total volume became 50 cm$^3$ in all the cases.

The effect of ammonia concentration on the conversion of PNCB is shown in Fig. 8. As the concentration of ammonia increased, the conversion of PCNB was observed to decrease up to a certain reaction time; beyond that point, an opposite trend was observed, i.e., with higher ammonia concentration, higher PCNB conversion was achieved.

If the conversion of sulfide in the aqueous phase is assumed to be complete and the reduction of PNCB follows the stoichiometry of Eq. (2) solely, the conversion of PNCB will be around 55% as calculated from the material balance. On the other hand, the sulfide concentration in the aqueous phase may be kept sufficiently high to get complete conversion of PNCB if the reaction solely follows the stoichiometry of Eq. (1). However, after long reaction run, maximum of about 60% conversion of PNCB was achieved with the maximum ammonia concentration used in this study as shown in the figure. From this result it is clear that the first reaction (Eq. (1)) is also operative in the reduction NCBs by aqueous ammonium sulfide as proposed by Zinin in 1842 [12]. These results are in complete disagreement with some other works with ammonium sulfide [19,21,23] that proposed reaction of Eq. (2) to be solely operative. From the same figure, it is also observed that the overall conversion of PNCB remains closer to the value as governed by the stoichiometry of Eq. (2). Therefore, it can be concluded that the reaction follows the stoichiometry of Eq. (2) predominantly. It can also be concluded from these results that it is preferred to carry out the reaction with high sulfide loading (low ammonia concentration) in the aqueous phase in order to get the elemental sulfur predominantly as the desired coproduct instead of thiosulfate at the cost of low overall conversion of NCBs.

Since the formation of elemental sulfur was not reported anywhere in the literature for the reduction of nitroarene with sodium sulfide, it could be thought that the reaction via the transfer of sulfide ions follows the stoichiometry of Eq. (1). The concentration of sulfide ions ($S^{2-}$) increases with increase in the concentration of ammonia for fixed sulfide concentration.

Fig. 6. Effect of sulfide concentration. Volume of organic phase = $5 \times 10^{-5}$ m$^3$; PNCB concentration = 1.27 kmol/m$^3$; TBAB concentration = $3.1 \times 10^{-2}$ kmol/m$^3$ of organic phase; volume of aqueous phase = $5 \times 10^{-5}$ m$^3$; concentration of ammonia = 8.54 kmol/m$^3$; temperature = 323 K; speed of agitation = 1500 rpm.

Fig. 7. ln (initial rate) vs. ln (initial sulfide concentration). All conditions are same as in Fig. 6.

Fig. 8. Effect of ammonia concentration. Volume of organic phase = $5 \times 10^{-5}$ m$^3$; PNCB concentration = 1.01 kmol/m$^3$; TBAB concentration = $3.1 \times 10^{-2}$ kmol/m$^3$ of organic phase; volume of aqueous phase = $5 \times 10^{-5}$ m$^3$; concentration of sulfide = 1.68 kmol/m$^3$; temperature = 323 K; speed of agitation = 1500 rpm.
Thus, with increase in ammonia concentration, there is an increase in the reaction via the transfer of sulfide ions following the stoichiometry of Eq. (1), which results higher conversion of PNCB at higher ammonia concentration.

It is worthy to mention here that the nature of the curve obtained in this reaction is ‘S’ type which is typical of autocatalytic reaction where the rate of reaction increases with increase in the concentration of catalyst formed by the reaction and then the rate of reaction decreases with the depletion of the reactants as observed from the figure. This nature of curve is also observed for other NCBs as well. This phenomenon was only observed for low concentration of one of the components: NCBs, sulfide and catalyst or the conditions that favor low initial reaction rate. However, for high concentration, this phenomenon could not be observed as it occurred within a very short period of time. The exact reason for this nature of curve will be explained when the effect of elemental sulfur loading on the reaction will be discussed.

3.8. Effect of elemental sulfur loading

Elemental sulfur in the solution of ammonia and hydrogen sulfide is known to form ammonium polysulfides [27], (NH₄)₂Sₙ where 2 ≤ n ≤ 6, which is also one of the reducing agents of the Zinin reduction. Since, the formation of elemental sulfur was reported for the reduction of nitroarenes by ammonium sulfide [19,21,23], here we examined the effect of externally added elemental sulfur on conversion of PNCB.

In this experiment, elemental sulfur was first dissolved in the aqueous ammonium sulfide, which was then used for the reaction following the same procedure as described earlier. The color of the aqueous ammonium sulfide is greenish yellow. However, after dissolution of elemental sulfur to the aqueous ammonium sulfide, the color of the solution becomes reddish brown. Also during the reaction with aqueous ammonium sulfide, initially the color of the solution was unaffected but later on it changed rapidly from greenish yellow to reddish brown. This color change indicates the formation of elemental sulfur (polysulfides) during the reaction. The characteristic reddish brown color of the polysulfide, which develops as the reaction proceeds, is useful in indicating the extent of the reaction. Lucas and Scudder [21] also used similar argument to explain the lower conversion.

The rise in rate of reaction with elemental sulfur loading may be due to the fact that the reaction via the transfer of hydroxysulfide and sulfide ions is slow compared to disulfide ions formed by the reaction of elemental sulfur with ammonium sulfide. It was observed that disulfide reduced nitrobenzene much more rapidly than did sulfide as reported by Hojo et al. [13].

4. Reaction mechanism and kinetic modeling

The kinetics and mechanism of a variety phase transfer catalyzed SN₂ type of reactions, in liquid–liquid [28], solid–liquid [29], and liquid–liquid–liquid [30] mode, and some oxidation reactions [28,31] are well documented. However, such information on Zinin reduction is very limited. Although, a lot of published works are there in the literature on Zinin reduction, the exact mechanism of this important reaction is still not clear. Probably the first product is a nitroso compound, which is rapidly reduced to hydroxylamine and then to amine [12]. The rate-determining step is considered to be the attack of negative divalent sulfur on the nitro group as no intermediate compounds are observed to form during the reaction. The mechanism and kinetic scheme developed by Yadav et al. [17] for the reduction of p-nitroanisole by aqueous sodium sulfide.
under liquid–liquid mode in the presence of PTC, TBAB, was found to be not applicable in the case of reduction of NCBs by aqueous ammonium sulfide.

The tetrabutylammonium cation [Q+] is not highly lipophilic and therefore, can distribute itself between the organic and the aqueous phase. The phase transfer catalyst, TBAB therefore follows the extraction mechanism of phase transfer catalysis as proposed by Starks and Liotta [9]. The sulfide (S^{2−}) and hydrosulfide (HS^{−}) ions present in the aqueous phase readily form ion pairs (Q’S^{2−} Q^{+} and Q’HS^{−}) with tetrabutylammonium cation and are transferred to the organic phase and reduce the NCBs following the stoichiometry of Eqs. (1) and (2), respectively. The elemental sulfur formed according to the stoichiometry of Eq. (2) reacts with aqueous ammonium sulfide forming ammonium polysulfide. It is observed in the earlier discussion that the overall conversion of PNCB decreases with increase in elemental sulfur loading because of the formation of higher amount of polysulfides (other than disulfide), which are not easily transferred to the organic phase. Only disulfide ions form ion pair, [Q’S^{2−} Q^{+}] and are transferred to the organic phase and reduce the NCBs following Eq. (3).

Development of a fundamental kinetic model for this system is a difficult task because of these complexities involved and poor knowledge of the system. In this work, an empirical kinetic model applicable for all the NCBs was, therefore, developed to correlate the experimentally obtained time versus conversion data. The order of the reaction was determined to be the cube of the concentration of sulfide. It was also proved that the elemental sulfur formed in this reaction enhanced the reaction rate resulting in ‘S’ nature of time versus conversion curve. Therefore, the rate of reduction of NCBs (−r_{A}) is expressed by the following equation.

\[
-\dot{r}_A = k_1 C_A C_S^3 C_C + k_2 C_A C_S^2 C_C C_B
\]

(4)

Table 3
Rate constants of the model Eq. (4)

<table>
<thead>
<tr>
<th>NCBs</th>
<th>Rate constants</th>
<th>Temperatures (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k_1 × 10^3 [(kmol/m^3) s^{-1}]</td>
<td>0.85</td>
</tr>
<tr>
<td>PNCB</td>
<td>k_2 × 10^3 [(kmol/m^3) s^{-1}]</td>
<td>0.69</td>
</tr>
<tr>
<td>ONCB</td>
<td>k_1 × 10^4 [(kmol/m^3) s^{-1}]</td>
<td>0.28</td>
</tr>
<tr>
<td>MNCB</td>
<td>k_2 × 10^4 [(kmol/m^3) s^{-1}]</td>
<td>0.029</td>
</tr>
</tbody>
</table>

where C_A and C_C are the concentrations of NCBs and catalyst, TBAB, respectively, in the organic phase. The second term in the above rate expression takes care of ‘S’ nature of curves due to the formation of elemental sulfur during the reaction as discussed previously. Since, the concentration of ammonia in the aqueous phase was kept around 15 wt%, its effect was not incorporated in this kinetic model.

Since, the course of the reduction follows the stoichiometry of Eq. (2) predominantly; the concentration of sulfide (C_S) and elemental sulfur (C_B) in the aqueous phase are obtained from the overall mass balance based on the same stoichiometry as given by the following expressions.

\[
C_S = C_{SO} - 3 f(C_{AO} - C_A)
\]

(5)

\[
C_B = 3 f(C_{AO} - C_A)
\]

(6)

where C_{SO} and C_{AO} represent the initial concentrations of sulfide and NCBs, respectively, and f is the ratio of volume of organic phase to that of aqueous phase. A non-linear regression algorithm was used for parameter estimation. The optimum values of the rate constants (k_1 and k_2) of the NCBs reactions were estimated by minimizing the objective function (E) as given by the equation.

\[
E = \sum_{i=1}^{n} [\{(−r_{A})_{pred} i - \{(−r_{A})_{exp} i\}]^2
\]

(7)

Table 4
Activation energy and pre-exponential factors for various rate constants

<table>
<thead>
<tr>
<th></th>
<th>k_1 = A_{10} \exp(−AE_1/RT)</th>
<th>k_2 = A_{20} \exp(−AE_2/RT)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A_{10} [(kmol/m^3) s^{-1}]</td>
<td>AE_1 (kcal/mol)</td>
</tr>
<tr>
<td>PNCB</td>
<td>2.6 × 10^{13}</td>
<td>25.6</td>
</tr>
<tr>
<td>ONCB</td>
<td>3.7 × 10^{10}</td>
<td>19.6</td>
</tr>
<tr>
<td>MNCB</td>
<td>1.1 × 10^{10}</td>
<td>6.4</td>
</tr>
</tbody>
</table>

Fig. 10. Comparison of calculated and experimental conversions of NCBs. All conditions are same as in Table 1.
The optimum values of the rate constants, $k_1$ and $k_2$, for all the NCBs (m-, o- and p-) at different temperatures were estimated as listed in Table 3. Both the rate constants increased with temperature for all NCBs as expected. The activation energy and pre-exponential factor of the rate constants were evaluated from the slopes and intercepts of the Arrhenius plots of $\ln(k)$ against $1/T$, as shown in Table 4. Fig. 10 represents the comparison of the calculated conversions of NCBs based on these rate constants and experimentally obtained conversions. The mean errors between the experimental and predicted conversions of NCBs were observed to be 2.25, 2.32, 3.29% for MNCB, ONCB, and PNCB, respectively. A good correlation was therefore observed.

5. Conclusions

The reduction of NCBs by aqueous ammonium sulfide to the corresponding CANs was studied under liquid–liquid mode in presence of PTC, TBAB. The selectivity of CANs was 100%. The MNCB was found to be the most reactive among the NCBs followed by ONCB and PNCB. The reaction was found to be kinetically controlled with apparent activation energies of 22.8, 19.6 and 9.4 kcal/mol for ONCB, PNCB and MNCB, respectively. The rate of reduction of NCBs was found to be proportional to the concentration of catalyst and NCBs and to the cube of the concentration of sulfide. The process was found to follow a complex mechanism involving three different reactions. Based on the detailed kinetic study and proposed mechanism, a general empirical kinetic model was developed. The developed model, applicable to all NCBs, predicts conversions of NCBs reasonably well.

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References