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Kinetics of Reduction of Nitrochlorobenzenes by Aqueous Ammonium Sulfide under Liquid–Liquid Phase Transfer Catalysis

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ABSTRACT

The reduction of nitrochlorobenzenes (NCBs) by aqueous ammonium sulfide to the corresponding chloroanilines (CANs) was carried out in an organic solvent, toluene, under liquid-liquid mode with phase transfer catalyst, tetrabutylammonium bromide (TBAB). The selectivity of 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 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 effects of different parameters such as TBAB concentration, concentration of NCB, sulfide concentration, ammonia concentration, and elemental sulfur loading on the reaction rate and conversion were studied to establish the mechanism of the reaction. The rate of reaction of NCBs was found to be proportional to the concentration of catalyst and NCBs and to the cube of the concentration of sulfide.

Keywords: Hydrogen sulfide; Chloroanilines; Liquid-liquid phase transfer catalysis, Kinetics.

INTRODUCTION

With stringent environmental regulations, refiners are forced to hydrotreat heavy crudes containing high amount of sulfur and nitrogen 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]. Moreover, several disadvantages of air oxidation of 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 ammonia simultaneously present in the gas streams and to produce some commercially important chemicals like chloroanilines (CANs) utilizing this H₂S-rich aqueous ammonia solution called ammonium sulfide. CANs have wide commercial applications as intermediates for the preparation of polyanilines and substituted phenyl carbamates, and organic fine chemicals, such as dyes, drugs, herbicides and pesticides [2].

The reduction reaction of nitroarenes by negative divalent sulfur (sulfide, hydrosulfide and polysulfides) is called Zinin reduction [3]. The Zinin reduction 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.

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) [4]. PTC 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 [5]. In the present work, the TBAB was therefore used as PTC to enhance the otherwise slow reduction rate of NCBs by aqueous ammonium sulfide.

In aqueous ammonium sulfide, the sulfide ions (S^2) and the hydrosulfide ions (HS⁻) remain in equilibrium, as represented by Scheme 1 [6]. Due to the existence of two different ions in aqueous ammonium sulfide, the properties of this reducing agent are expected to be different from the other reducing agents like sodium sulfide and disulfide. $\begin{aligned} \mathsf{NH}_3 + \mathsf{H}_2\mathsf{O} &\rightleftharpoons \mathsf{NH}_4^+ + \mathsf{HO}^- \\ \mathsf{H}_2\mathsf{S} &\rightleftharpoons \mathsf{H}^+ + \mathsf{HS}^- \\ \mathsf{HS}^- &\rightleftharpoons \mathsf{H}^+ + \mathsf{S}^{2-} \\ \mathbf{Scheme 1} \end{aligned}$

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 [3]. This stoichiometry is also applicable for reduction of nitroarenes by sodium sulfide [7-10].

$$4ArNO_2 + 6S^{2-} + 7H_2O \rightarrow 4ArNH_2 + 3S_2O_3^{2-} + 6HO^{-}$$
(1)

However, some of the recent works on the reduction of nitroarenes by ammonium sulfide, it was reported that the sulfide ions were oxidized to elemental sulfur instead of thiosulfate following stoichiometry of Eq. 2 [11-13].

$$ArNO_2 + 3HS^- + H_2O \rightarrow ArNH_2 + 3S + 3HO^-$$
(2)

The overall stoichiometry of the reduction reaction using sodium disulfide as the reducing agent is as follows [7,14]:

$$ArNO_2 + S_2^{2^-} + H_2O \to ArNH_2 + S_2O_3^{2^-} + HO^-$$
(3)

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.

EXPERIMENTAL

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 $\pm 1^{\circ}$ C.

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 H_2S 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.

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, TBAB, and 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 and were analyzed by gas-liquid chromatography (GLC). The sulfide concentrations were determined by the standard iodometric titration method [15].

RESULTS AND DISCUSSION

Effect of Speed of Agitation. The effect of speed of agitation on the rate of reaction of NCBs (o-, m- and p-) was studied in the range 1000-2500 rev/min 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 rev/min so as to neglect the effects of mass transfer resistance on the reaction kinetics.

Table 1.	Effect of	f tempera	ature on	-	
reaction ra	ate of NCBs	S ^a			
Reaction rate $\times 10^{5}$, kmol/m ³ s					
Temp., K		ONCB ^c	MNCB		
303	1.20	1.27	7.82	9	
313	1.88	3.28	12.21		
323	4.72	7.03	16.64		
333	8.53	26.8	36.4		
^a Matching	conversior	n = 5%;	volume of		
organic phase = 5×10^{-5} m ³ ; NCB = 1.01					
$kmol/m^3$; TBAB = 3.1×10^{-2} kmol/m ³ of org.					
phase: volume of aqueous phase = 5×10^{-5}					
m^3 ; ammonia = 6.22 kmol/ m^3 ; speed of					
agitation = 1500 rev/min. ^b sulfide = 1.66					
kmol/m3; ^c sulfide = 2.30 kmol/m ³ .					

Table 2. Effect of TBAB concentration on reaction rate of NCBs ^a					
Reaction rate × 10 ⁵ , kmol/m ³ s					
Organic	In	In	Enhancem		
substrates	presence	absence	ent factor		
	of TBAB	of TBAB	(A/B)		
	(A)	(B)			
PNCB	6.44	0.90	7.2		
ONCB	11.0	1.2	9.2		
MNCB	35.0	2.60	13.5		
^a Matching conversion = 5%; volume of organic					
phase = 5×10^{-5} m ³ ; NCB = 1.27 kmol/m ³ ; TBAB =					
3.1×10^{-2} kmol/m ³ of org. phase; volume of					
aqueous phase = 5×10^{-5} m ³ ; ammonia = 8.54					
kmol/m ³ ; sulfide = 2.25 kmol/m ³ ; temperature =					
323 K; speed of agitation = 1500 rev/min.					

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 303-333K in the presence of catalyst, TBAB, as shown in Table 1. The reaction rate increases with increase in temperature for all the NCBs, as it is observed from the table. The apparent activation energies for this kinetically controlled reaction were calculated from the slopes of an Arrhenius plot of Ln (initial rate) against 1/T (K⁻¹) as 22.8, 19.6 and 9.4 kcal/mol for o-nitrochlorobenzene (ONCB), p-nitrochlorobenzene (PNCB) and m-nitrochloro-benzene (MNCB), respectively. The high values of apparent activation energy again confirm that the reaction systems are kinetically controlled.

Effect of catalyst concentration. The effect of catalyst (TBAB) concentration on the conversion of PNCB was studied in the concentration range of 1.57×10^{-2} to 6.23×10^{-2} kmol/m³ of organic phase as shown in Table 2. The study was also conducted in the absence of catalyst. As it is observed from table, 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. From the plot of Ln(initial rate) against Ln(TBAB concentration), 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 [10].



Fig. 1. Effect of speed of agitation on reaction rate of NCBs. Matching conversion =5%; volume of organic phase = 5×10^{-5} m³; NCB = 1.27 kmol/m³; TBAB = 3.1×10^{-2} kmol/m³ of org. phase; volume of aqueous phase= 5×10^{-5} m³; ammonia= 8.54 kmol/m³; sulfide= 2.25 kmol/m³; temperature= 323 K.



Fig. 2. Effect of PNCB concentration. Volume of organic phase = 5×10^{-5} m³; TBAB = 3.1×10^{-2} kmol/m³ of org. phase; volume of aqueous phase= 5×10^{-5} m³; ammonia= 8.54 kmol/m³; sulfide =2.25 kmol/m³; temperature= 323 K; Speed of agitation= 1500 rev/min.



Fig. 3. Effect of sulfide concentration. Volume of organic phase = 5×10^{-5} m³; PNCB = 1.27 kmol/m³; TBAB = 3.1×10^{-2} kmol/m³ of org. phase; volume of aqueous phase= 5×10^{-5} m³; ammonia= 8.54 kmol/m³; temperature= 323 K; Speed of agitation= 1500 rev/min.



Fig. 4. Effect of ammonia concentration. Volume of organic phase = 5×10^{-5} m³; PNCB = 1.01 kmol/m³; TBAB = 3.1×10^{-2} kmol/m³ of org. phase; volume of aqueous phase= 5×10^{-5} m³; sulfide= 1.68 kmol/m³; temperature= 323 K; speed of agitation = 1500 rev/min.

Comparison of Reactivity of NCBs. 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 Table 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 [16]. 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 electro negativity of chlorine atom) effect is felt by the nitro group due to the presence 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.

Effect of p- nitrochlorobenzene concentration. The effect of concentration of PNCB on the conversion was studied in presence of TBAB under otherwise identical experimental conditions as shown in Fig. 2. The overall conversion of PNCB decreases with increase in concentration of PNCB as expected. However, the initial rate of reaction of PNCB increases with increase in concentration of PNCB as observed from the figure. The order of the reaction with respect to PNCB concentration was obtained as 1.2, which is close to unity. Similar observations were reported for the reduction of p-nitroanisole [10] and nitroaromatics [7] 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 [14].

Effect of sulfide concentration. Fig. 3 shows the effect of sulfide concentration in the aqueous phase on the conversion of PNCB. With increase in the concentration of sulfide, the conversion of PNCB as well as the reaction rate increases, as it is evident from the figure. From the plot of Ln(initial rate) against Ln(initial sulfide concentration), 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 3rd 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 of sodium disulfide [14].

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 the 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 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.

The effect of ammonia concentration on the conversion of PNCB is shown in the Fig. 4. As it is observed from the figure, the overall conversion of PNCB (after prolonged reaction run) increases with increase in ammonia concentration although at the initial stage the rate of reduction of PNCB (or conversion of PNCB) decreases with increase in ammonia concentration.

It is expected to get around 55% conversion of PNCB if the reaction solely follows the stoichiometry of Eq. 2 for complete conversion of sulfide in the aqueous phase. On the other hand, the sulfide concentration in the aqueous phase



Fig. 5. Effect of elemental sulfur loading. Volume of organic phase = 5×10^{-5} m³; PNCB = 1.01 kmol/m³; TBAB = 3.1×10^{-2} kmol/m³ of org. phase; volume of aqueous phase= 5×10^{-5} m³; sulfide= 1.68 kmol/m³; ammonia= 8.88 kmol/m³; temperature= 323 K; speed of agitation = 1500 rev/min.

was 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. 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 [11-13] 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.

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. 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. The exact reason for this nature of curve will be explained when the effect of elemental sulfur loading on the reaction will be discussed.

Effect of elemental sulfur loading. Elemental sulfur in the solution of ammonia and hydrogen sulfide is known to form ammonium polysulfides [17], $(NH_4)_2S_n$ where $2 \le n \le 6$, 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 [11-13], here we examined the effect of externally added elemental sulfur on conversion of PNCB.

The effect of elemental sulfur loading on conversion of PNCB is shown in Fig. 5. It is clearly observed from the figure that initially the reaction rate (or conversion of PNCB) increases with increasing elemental sulfur loading. However, the overall conversion of PNCB decreases with increase in the elemental sulfur loading. As it is observed from the nature of the curves in the figure, the reaction rate gradually decreases with conversion of PNCB in the presence of elemental sulfur whereas the nature of the curve is 'S' type in the absence of elemental sulfur.

These observations are in support of the formation of elemental sulfur and can also be used to explain the 'S' type of curve as discussed in the previous section. Therefore, it can be said that the

reaction rate increases with the build up of elemental sulfur concentration (Eq. 2) as the reaction proceeds and then falls with the depletion of the reactants resulting in 'S' type of curve.

The conversion of PNCB decreases with increase in elemental sulfur loading as observed from the figure. This may be due to the formation of polysulfide in addition to disulfide (which is only transferred to the organic phase and reacts with NCBs there to form thiosulfate and CANs according to the stoichiometry of Eq. 3). Lucas and Scudder [12] 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 hydrosulfide 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. [14].

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.

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