Kinetics of the Reduction of Nitrotoluenes by Aqueous Ammonium Sulfide under Liquid-Liquid Phase Transfer Catalysis

Sunil K. Maity, Narayan C. Pradhan* and Anand V. Patwardhan

Department of Chemical Engineering, Indian Institute of Technology,

Kharagpur – 721 302, INDIA

Abstract

The reduction of nitrotoluenes (o-, m- and p-) using aqueous ammonium sulfide as the reducing agent was carried out in an organic solvent, toluene, under liquid-liquid mode with a phase transfer catalyst (PTC), tetrabutylammonium bromide (TBAB). The selectivity of toluidines was found to be 100%. The reaction rate of m-nitrotoluene was found to be highest among the three nitrotoluenes, followed by p- and o-nitrotoluene. The effects of different parameters, such as speed of agitation, temperature, ammonia concentration, elemental sulfur loading, catalyst concentration, sulfide concentration, and concentration of nitrotoluene, on the conversion and reaction rate of nitrotoluene were studied to establish the mechanism of the reaction. The rate of reaction of nitrotoluene was found to be proportional to the concentration of catalyst, to the square of the concentration of sulfide, and to the cube of the concentration of nitrotoluene. The apparent activation energy for this kinetically controlled reaction was estimated as 19.43, 21.45 and 25.54 kcal/mol for ONT, PNT and MNT, respectively. A generalized empirical kinetic model was developed to correlate the experimentally obtained conversion *versus* time data for the three nitrotoluenes.

Keywords: Kinetics; Ammonium sulfide; Nitrotoluene; Zinin reduction; Liquid-liquid phase transfer catalysis.

1. Introduction

The reduction of nitrotoluenes to the corresponding amines is commercially very important, because the product toluidines have wide commercial applications as intermediates for dyes, agrochemicals and pharmaceutical products. 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 nitrotoluenes (o-, m- and p-) by using aqueous ammonium sulfide as the reducing agent under two-phase condition with tetrabutylammonium bromide (TBAB) as the phase transfer catalyst (PTC).

Phase transfer catalysts (PTC) 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). 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 phase

transfer catalysts, quaternary ammonium salts are most preferred for their better activity and availability.

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, as suggested by Starks [1] and Starks and Liotta [2], is applicable to catalysts that are not highly lipophilic or that can distribute themselves between the organic and the aqueous phase, such as benzyltriethylammonium, dodecyltrimethylammonium, and tetrabutylammonium salts. In the interfacial model, catalysts such as tetrahexylammonium and trioctylmethylammonium salts remain entirely in the organic phase because of their high lipophilicity, and they exchange anions across the liquid-liquid interface [3]. 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 [4]. Several researchers have also carried out reduction of nitroarenes by sodium sulfide using TBAB as PTC [5-8]. However, there is no report in the literature on the preparation of aryl amines using aqueous ammonium sulfide in presence of a phase transfer catalyst, TBAB.

The reduction reaction of nitroarenes by negative divalent sulfur (sulfide, hydrosulfide and polysulfides) is called Zinin reduction [9]. Sodium sulfide, sodium disulfide and ammonium sulfide are most commonly used for this purpose. In aqueous ammonium sulfide solution, the sulfide ions (S^{2-}) and the hydrosulfide ions (HS^-) remain in equilibrium, as represented by Scheme 1 [10]. This property of ammonium sulfide makes it different from the others. The rates of these biphasic reductions, especially with

aqueous ammonium sulfide and sodium sulfide, are so low that the use of a phase transfer

catalyst is essential to make the process commercially viable.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + HO^-$$

$$H_2S \rightleftharpoons H^+ + HS^-$$

$$HS^- \rightleftharpoons H^+ + S^{2-}$$
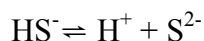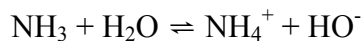
Scheme 1

The overall stoichiometry of the Zinin original reduction of nitrobenzene by

aqueous ammonium sulfide is given by Eq. 1. This stoichiometry is also applicable for

reduction of nitroarenes with sodium sulfide [11].

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

For the preparation of p-aminophenylacetic acid from p-nitrophenylacetic acid

using aqueous ammonium sulfide, Gilman [12] reported that the sulfide ions were

oxidized to elemental sulfur instead of to thiosulfate, following the stoichiometry of Eq.

2. Lucas and Scudder [13] also reported similar observations for the reduction of 2-

bromo-4-nitrotoluene to the corresponding 2-bromo-4-aminotoluene by an alcoholic

solution of ammonium sulfide.

$$ArNO_2 + 3HS^- + H_2O \rightarrow ArNH_2 + 3S + 3HO^- \qquad (2)$$
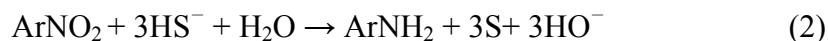
The overall stoichiometry of the reduction reaction using disulfide as the reducing

agent is as follows [11]:

$$ArNO_2 + S_2^{2-} + H_2O \rightarrow ArNH_2 + S_2O_3^{2-} + HO^- \qquad (3)$$
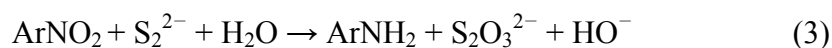
Therefore, the two different reactions leading to the formation of either elemental sulfur or thiosulfate may be operative for the reduction of nitroarenes with ammonium sulfide. A detailed study of such reactions is, therefore, not only commercially important, it is academically interesting too.

Development of ammonium sulfide- or hydrogen sulfide-based processes is also very much welcome in the refining industry. With gradual decline of the supply of light and easy-to-process crude oils, refiners throughout the world are forced to process heavy crudes containing high amounts 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 an amine treating unit to remove hydrogen sulfide, which is further processed in the Claus unit to produce elemental sulfur [14]. 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 of the elemental sulfur produced in their sulfur recovery units (SRUs). Therefore, any process that could consume hydrogen sulfide will be very much helpful to the refining industry in alleviating the sulfur disposal problem.

Several researchers used sodium sulfide and disulfide for the reduction of nitroarenes to corresponding amines in both the presence and the absence of PTC and also under different modes (liquid-liquid or solid–liquid). Hojo et al. [15] studied the kinetics of the reduction of nitrobenzene by aqueous methanolic solutions of sodium

disulfide. Bhave and Sharma [11] studied the kinetics of two-phase reduction of aromatic nitro compounds (e.g., m-nitrochlorobenzene, m-dinitrobenzene and p-nitroaniline) by aqueous solutions of sodium monosulfide and sodium disulfide. Pradhan and Sharma [5] studied the reaction of nitrochlorobenzene with sodium sulfide in both the presence and the absence of a PTC. In the solid-liquid mode, the reactions of o- and p-nitrochlorobenzene gave 100% chloroanilines in the absence of a catalyst and 100% dinitrodiphenyl sulfides in the presence of a catalyst. The reaction of m-nitrochlorobenzene with solid sodium sulfide, however, was reported to give m-chloroaniline as the only product even in the presence of a catalyst. In the liquid-liquid mode, all three substrates gave only amine as the product in both the presence and the absence of a catalyst. Pradhan [6] has studied the reduction of nitrotoluenes (o-, m- and p-) by sodium sulfide to the corresponding aminotoluenes, both in the liquid-liquid and solid-liquid modes with a phase transfer catalyst, TBAB. In the liquid-liquid mode, the reactions of all three nitrotoluenes were reported to be kinetically controlled. In solid-liquid mode, the reactions of o- and p-nitrotoluenes were kinetically controlled, whereas that of m-nitrotoluene was reported as mass-transfer-controlled. Yadav et al. [7] have reported the kinetics and mechanisms of L–L PTC reduction of p-nitroanisole by sodium sulfide to p-anisidine.

It is evident from the above discussion that there is hardly any information in the literature on the reduction of nitrotoluenes by aqueous ammonium sulfide. Considering the importance of the system, a detailed study was therefore performed, and is reported in the present work, on the reduction of nitrotoluenes to produce commercially important toluidines. The effects of various parameters on the reaction rate and conversion were

studied to establish the mechanism and the stoichiometry of the reaction. A generalized empirical kinetic model applicable for all the nitrotoluenes 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. Nitrotoluenes (>99%) of synthesis grade were purchased from Loba Chemie Pvt. Ltd., Mumbai, India. Tetrabutylammonium bromide (TBAB) was obtained from SISCO Research Laboratories Pvt. Ltd., Mumbai, India.

2.2 Equipment

The reactions of nitrotoluenes with aqueous ammonium sulfide were carried out batch-wise in a fully baffled mechanically agitated glass reactor of capacity 250 cm^3 (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 $\pm 1^{o}C$.

2.3 Preparation of ammonium sulfide solution

For the preparation of ammonium sulfide solution, around 15% 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 cm^3 standard gas-

bubbler. The gas bubbling was continued until the desired sulfide concentration was obtained in the aqueous ammonia solution.

2.4 Procedure

In a typical run, 50 cm^3 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 nitrotoluene, 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 cm^3 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 x 3 mm stainless steel column packed with 10% OV-17 on Chromosorb W (80/100). A Chemito Model 8610 GC interfaced with a Shimadzu C-R6A Chromatopac data processor was used for the analysis. The column temperature was programmed with an initial temperature at 130^{0}C, increased at 20^{0}C/min to 170^{0}C, maintained at 170^{0}C for 1 min, and then increased at 10^{0}C/min to 240^{0}C. Nitrogen was used as the carrier gas with a flow rate of 15 cm^3/min. An injector temperature of 250^{0}C was used during the analysis. An FID detector was used at the temperature of 270^{0}C.

Initial sulfide concentrations were determined by the standard iodometric titration method [16].

3. Results and discussion

3.1 Comparison of reactivities of nitrotoluenes

The rates of reduction of the three nitrotoluenes (o-, m- and p-) by aqueous ammonium sulfide were compared in both the presence and the absence of PTC (TBAB) under liquid-liquid mode under otherwise identical experimental conditions. The reaction rate, both in the presence and absence of TBAB, was found to be in the order of m-nitrotoluene (MNT) > p-nitrotoluene (PNT) > o-nitrotoluene (ONT), as shown in Table 1. From this observation, it can be concluded that the presence of an electron donating group like methyl group in the aromatic ring reduces the reaction rate more when it is present at the ortho and para positions, i.e., positions of high electron density, compared to its presence at the meta position (site of low electron density). Pradhan [6] also reported a similar trend of reactivity for the reduction of nitrotoluenes by sodium sulfide using TBAB in the liquid-liquid mode. The rates of reduction of nitrotoluenes are very low in the absence of PTC, which results in high enhancement factors as shown in Table 1.

3.2 Effect of speed of agitation

The effect of speed of agitation on the rate of reaction of nitrotoluenes (o-, m- and p-) was studied in the range 1000-2500 rev/min in the presence of a phase transfer catalyst, TBAB, as shown in Figure 1. As it is evident from the figure, the variation of reaction rate with speed of agitation is so small that the reactions may be considered as kinetically controlled for all the nitrotoluenes. All other experiments were performed at

1500 rev/min in order to avoid the effects of mass transfer resistance on the reaction kinetics.

3.3 Effect of temperature

The effect of temperature on the rate of reaction of nitrotoluenes with aqueous ammonium sulfide was studied in the range of 303-333K in the presence of a catalyst, TBAB, as shown in Table 2. The reaction rate increases with temperature for all the nitrotoluenes, as it is observed from the table. The initial rates were calculated at different temperatures and an Arrhenius plot of Ln (initial 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 19.43, 21.45 and 25.54 kcal/mol for ONT, PNT and MNT, respectively. The high values of apparent activation energy confirm that the reaction systems are kinetically controlled.

The effects of various parameters on the reactions of nitrotoluenes were studied to determine the dependencies of the reaction rates on the concentrations of various species present in the reaction system. Such knowledge is essential for proposing a rate expression for the reaction systems. The following sections report the effects of different parameters on the rates of nitrotoluenes reduction by aqueous ammonium sulfide in the presence of a phase transfer catalyst, TBAB.

3.4 Effect of ammonia concentration

Although ammonia as such does not take part in the reaction with nitrotoluenes, it affects the equilibrium among ammonia, hydrogen sulfide, and water, which results in

two active anions, sulfide (S^{2-}) 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 [17] 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, we prepared aqueous ammonium sulfide solutions of different ammonia concentrations (but constant sulfide concentration) by taking 30 cm^3 of aqueous ammonium sulfide solution (with known sulfide and ammonia concentrations). Then we added various proportions of LIQR ammonia and distilled water to it in such a way that the total volume became 50 cm^3 in all the cases. Figure 2 shows the effect of ammonia concentration on the conversion of MNT at a constant initial sulfide concentration of 1.27 $kmol/m^3$. With increase in concentration of ammonia, the conversion of MNT was found to decrease up to a certain reaction time; beyond that the opposite trend was observed, i.e., with higher ammonia concentration, a higher MNT conversion was achieved (Figure 2).

One should get around 62% conversion of MNT if the reaction follows the stoichiometry of Eq. 1 and the value would be around 31% if the stoichiometry of Eq. 2 is considered, for complete conversion of sulfide in the two cases. However, after long reaction run, a maximum 23% conversion of MNT was achieved, which was still much lower than that expected based on stoichiometry of Eq. 2. Similar results were also obtained in the subsequent experiments with other nitrotoluenes as well. Lucas and

Scudder [13] also reported similar observations. Therefore, it can be concluded that the reaction follows stoichiometry of Eq. 2 predominantly. This is in complete disagreement with Zinin's original work [9]. The lower conversion of MNT based on the stoichiometry of Eq. 2 will be explained further when the effect of elemental sulfur loading will be discussed later.

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 in higher conversion of MNT at higher reaction time.

The nature of the curve obtained is 'S' type, which is typical of autocatalytic reactions where the rate of reaction increases with increase in concentration of catalyst formed by the reaction and then the rate of reaction decreases with the depletion of the reactants, as shown in the figure. This phenomenon was observed only for low concentration of one of the components: MNT, 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. This phenomenon was also observed for other nitrotoluenes as well. But for o- and p-nitrotoluenes, this phenomenon was found to occur even at relatively high concentrations because of their

slow reaction rates. The exact reason for this phenomenon will be explained when the effect of elemental sulfur loading on the reaction will be discussed.

3.5 Effect of elemental sulfur loading

Elemental sulfur in the solution of ammonia and hydrogen sulfide is known to form ammonium polysulfides [10], $(NH_4)_2S_n$ where $2 \leq n \leq 6$ such a material is also one of the reducing agents of the Zinin reduction. Since elemental sulfur was reported to be formed in the reaction [12, 13], here we examined the effect of externally added elemental sulfur on the reaction rate and conversion of PNT. In this experiment, elemental sulfur was first dissolved in the aqueous ammonium sulfide solution, which was then used for the reaction following the same procedure as described earlier.

The effect of elemental sulfur loading on conversion of PNT is shown in Figure 3. From the figure, it is clear that the overall conversion of PNT decreases with increase in the elemental sulfur loading, although the initial rate of reaction is higher in the presence of elemental sulfur compared to the rate with no elemental sulfur present. As one can observe from the nature of the curves in the figure, the reaction rate gradually increases with conversion of PNT in the absence of elemental sulfur, whereas the rate decreases with conversion of PNT in the presence of elemental sulfur.

These observations are in support of the formation of elemental sulfur and can also be used to explain the lower conversion of nitrotoluene than expected by both the stoichiometry (Eq. 1 & 2) and '*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 an '*S*' type of curve.

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 the transfer of polysulfide 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. [15]. The lowering of conversion may be due to the formation of polysulfide in addition to disulfide (which is only transferred), such polysulfides react with nitrotoluene to form thiosulfate and aminotoluene according to the stoichiometry of Eq. 3. Lucas and Scudder [13] also used a similar argument to explain the lower conversion.

With increase in elemental sulfur loading, the initial rate and the overall conversion decrease. This may be due to higher amounts of polysulfide (other than disulfide) formed with higher amounts of elemental sulfur loading.

3.6 Effect of sulfide concentration

Figure 4 shows the effect of sulfide concentration in the aqueous phase on the conversion of MNT. With increase in the concentration of sulfides, the conversion of MNT as well as the reaction rate increases, as it is evident from the figure. In order to determine the order of the reaction with respect to sulfide concentration, the plot of Ln(initial rate) against Ln(initial sulfide concentration) was made (Figure 5). From the slope of the linear fit line, the order of reaction with respect to sulfide concentration was obtained as 1.67. Since this value is closer to 2, the reaction was, therefore, considered as 2nd 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 the

sulfide concentration [7, 11]. The rate was also reported to be proportional to the square of the concentration of sodium disulfide [15].

3.7 Effect of catalyst concentration

The effect of catalyst (TBAB) concentration on conversion of MNT was studied in the concentration range of 0.031 to 0.155 $kmol/m^3$ of organic phase, as shown in Figure 6. The study was also conducted in the absence of catalyst. As one can observe from the figure, the conversion of MNT is only 1.48% in absence of catalyst, whereas it is around 64% with maximum concentration of catalyst tried after 260 minutes of reaction under otherwise identical experimental conditions. 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) (Figure 7), the order of the reaction with respect to TBAB concentration was obtained as 1.03, which is close to unity. Yadav et al. [7] also reported similar observations.

3.8 Effect concentration of nitrotoluene

The effect of concentration of MNT and ONT on the reaction rate is shown in Figure 8. The reaction rate increases with increase in concentration of both the nitrotoluenes. The order of the reaction with respect to nitrotoluenes concentration was obtained as 3.18 and as 3.16 for MNT and ONT, respectively, which is close to third order. However, for the reduction of nitroarenes by aqueous sodium sulfide, the reported order is unity with respect to the concentration of p-nitroanisole [7] and nitroaromatics [11]. The rate was also reported as proportional to the concentration of nitrobenzene for its reduction with sodium disulfide [15].

3.9 Kinetic modeling

Much work has been done on Zinin reduction but the exact mechanism of the reaction is still not known. Probably the first product is a nitroso compound, which is rapidly reduced to hydroxylamine and then to amine [9]. 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 kinetics and mechanisms of a variety of SN^2 type of liquid-liquid phase transfer-catalyzed (L–L PTC) reactions and some alkylation reactions are well documented. However, such information on nitroarene reductions using ammonium sulfide is very limited. The mechanism and kinetic scheme developed by Yadav et al. [7] are found to be not applicable in the case of reduction of nitrotoluenes by aqueous ammonium sulfide. The hydrosulfide (HS^-) and sulfide (S^{2-}) ions present in the aqueous phase readily form ion pairs [Q^+HS^- and $Q^+S^{2-}Q^+$], with quaternary cations, [Q^+] and are transferred to the organic phase and reduce the nitrotoluenes following the stoichiometry of Eq.2 and Eq.1, respectively. The elemental sulfur formed (Eq.1) reacts with ammonium sulfide to form ammonium polysulfides, $(NH_4)_2S_n$ where $2 \leq n \leq 6$ [10]. It is observed in the earlier discussion that the reaction rate falls with increase in elemental sulfur loading because of the formation of higher amounts of polysulfides (other than disulfide) which are not easily transferred to the organic phase. Only disulfide ions form ion pairs, [$Q^+S_2^{2-}Q^+$], which are transferred to the organic phase and reduce the nitrotoluenes following Eq. 3.

Development of a fundamental kinetic model for this system is a difficult task because of these complexities and our poor knowledge of the system. In this work, an

empirical kinetic model applicable for all the nitrotoluenes was, therefore, developed to correlate the experimentally obtained time *versus* conversion data. Since the concentration of ammonia in the aqueous phase was kept around 15%, its effect was not incorporated in this kinetic model. Based on the experimental facts, the rate of reduction of nitrotoluenes $(-r_A)$ can be expressed by the following equation:

$$-r_A = k_1 C_A^3 C_S^2 C_C + k_2 C_A^3 C_S^2 C_C C_B \qquad (4)$$

where C_A and C_C are the concentrations of nitrotoluenes and catalyst TBAB in the organic phase, respectively. In the above rate expression, the individual orders of the reaction were taken as the nearest integer value.

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:

$$C_S = C_{SO} - 3f(C_{AO} - C_A) \qquad (5)$$

$$C_B = 3f(C_{AO} - C_A) \qquad (6)$$

where C_{SO} and C_{AO} represent the initial concentrations of sulfide and nitrotoluene, 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 nitrotoluenes reactions were estimated by minimizing the objective function (E) as given by the equation

$$E = \sum_{i=1}^{n} \left[\left\{ (-r_A)_{pred} \right\}_i - \left\{ (-r_A)_{expt} \right\}_i \right]^2 \qquad (7)$$

The optimum values of the rate constants, k_1 and k_2, are listed in Table 3. Figure 9 represents the comparison of the calculated conversions of nitrotoluenes based on these rate constants and experimentally obtained conversions. Good agreement was observed between the predicted and experimental conversions.

4. Conclusions

The reduction of nitrotoluenes by aqueous ammonium sulfide to the corresponding toluidines was studied under liquid–liquid mode in presence of PTC, TBAB. The selectivity of toluidines was 100%. The MNT was found to be the most reactive among the nitrotoluenes, followed by PNT and ONT. The reaction was found to be kinetically controlled with apparent activation energies of 25.54, 21.45 and 19.43 kcal/mol for MNT, PNT and ONT, respectively. The rate of reduction of nitrotoluene was found to be proportional to the concentration of catalyst and to the cube of the concentration of nitrotoluene. 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 nitrotoluenes, predicts conversions of nitrotoluenes reasonably well.

Acknowledgment

Nomenclature

MNT   m-nitrotoluene

ONT   o-nitrotoluene

PNT   p-nitrotoluene

TBAB   tetrabutylammonium bromide

PTC   phase transfer catalyst

References

[1] C. M. Starks, J. Am. Chem. SOC. 93 (1971) 195.

[2] C. M. Starks, C. L. Liotta, Phase-Transfer Catalysis Principles and Techniques, Academic: New York, 1978.

[3] E. V. Dehmlow, S. S. Dehmlow, Phase Transfer Catalysis, 2nd ed., Verlag Chemie Weinheim, 1983.

[4] N. C. Pradhan, M. M. Sharma, Ind. Eng. Chem. Res. 29 (1990) 1103.

[5] N. C. Pradhan, M. M Sharma, Ind. Eng. Chem. Res. 31 (1992) 1606.

[6] N. C. Pradhan, Indian J. Chem. Technol. 7 (2000) 276.

[7] G. D. Yadav, Y. B. Jadhav, S. Sengupta, Chem. Eng. Sci. 58 (2003) 2681.

[8] G. D. Yadav, Y. B. Jadhav, S. Sengupta, J. Mol. Catal. A: Chem. 200 (2003) 117.

[9] W. G. Dauben, Organic Reactions, John Wiley & Sons, Inc.: New York, 1973, Vol. 20, p455.

[10] P. Dubois, J. P. Lelieur, G. Lepoutre, Inorg. Chem. 27 (1988) 1883.

[11] R. R. Bhave, M. M. Sharma, J. Chem. Tech. Biotechnol. 31 (1981) 93.

[12] H. Gilman, Organic Syntheses. Collective volume 1, John Wiley & Sons, Inc.: NewYork, 1941, p-52.

[13] H. J. Lucas, N. F. Scudder, J. Am. Chem. Soc. 50 (1928) 244.

[14] A. L. Kohl, R. B. Nielson, Gas Purification, Gulf Publishing Company Houston: Texas, 1997.

[15] M. Hojo, Y. Takagi, Y. Ogata, J. Am. Chem. Soc. 82 (1960) 2459.

[16] W. W. Scott, Standard Methods of Chemical Analysis, Van Nostrand: New York, 1966, 6th ed., Vol. IIA, p 2181.

[17] D. Beutier, H. Renon, Ind. Eng. Chem. Process Des. Dev. 17 (1978) 220.

Table 1. Comparison of reactivities of nitrotoluenes[a]

Nitro-toluene isomer	Rate of reaction×10^5, kmol/m^3 s		Enhancement factor (B/A)
	In absence of TBAB (A)	In presence of TBAB (B)	
MNT	0.03	6.3	210
PNT	0.02	5.0	250
ONT	0.01	2.8	280

[a]Matching conversion = 5%; volume of organic phase = 5×10^{-5} m^3; nitrotoluene = 1.17 kmol/m^3; TBAB = 9.3×10^{-2} kmol/m^3 of organic phase; volume of aqueous phase = 5×10^{-5} m^3; concentration of sulfide = 2.2 kmol/m^3; concentration of ammonia = 5.62 kmol/m^3; temperature = 323 K; speed of agitation =1500 rev/min.

Table 2. Effect of temperature on the reaction rate[a]

Temperature,	Rate of reaction $\times 10^5$, kmol/m^3 s		
K	MNT[1]	PNT[2]	ONT[3]
303	1.14	0.58	0.34
313	3.96	1.75	0.82
323	9.66	5.96	2.14
333	19.8	7.35	4.32

[a]Matching conversion =5%; volume of organic phase = 5×10^{-5} m^3; volume of aqueous phase = 5×10^{-5} m^3; concentration of ammonia = 8.03 kmol/m^3; TBAB = 9.3×10^{-2} kmol/m^3 of organic phase; speed of agitation =1500 rev/min. [1]MNT = 1.35 kmol/m^3; concentration of sulfide = 2.8 kmol/m^3. [2]PNT =1.46 kmol/m^3; concentration of sulfide = 2.6 kmol/m^3. [3]ONT = 1.35 kmol/m^3; concentration of sulfide = 2.6 kmol/m^3.

Table 3. Activation energy and pre-exponential factors for

rate constants of nitrotoluenes

	$k_1 = A_{10} Exp(-AE1/T)$		$k_2 = A_{20} Exp(-AE2/T)$	
	A_{10} [(kmol/m^3)$^{-5}$s^{-1}]	AE1 (kcal/mol)	A_{20} [(kmol/m^3)$^{-6}$s^{-1}]	AE2 (kcal/mol)
MNT	4.20×10^{14}	28.46	4.14×10^8	18.09
PNT	9.05×10^{10}	23.62	3.05×10^7	16.85
ONT	1.98×10^4	14.79	9.35×10^{10}	22.22

List of Figures

Figure 1. Effect of speed of agitation. matching conversion = 20%

[1] volume of organic phase = 5×10^{-5} m^3; ONT = 1.35 kmol/m^3; TBAB = 9.3×10^{-2} kmol/m^3 of organic phase; volume of aqueous phase = 5×10^{-5} m^3; concentration of ammonia = 8.03 kmol/m^3; concentration of sulfide = 2.6 kmol/m^3; speed of agitation = 1500 rev/min; temperature = 323 K.

[2] volume of toluene = 5×10^{-5} m^3; PNT = 1.17 kmol/m^3; TBAB = 12.4×10^{-2} kmol/m^3 of organic phase; volume of aqueous phase = 5×10^{-5} m^3; concentration of sulfide = 2.9 kmol/m^3; concentration of ammonia = 8.42 kmol/m^3; temperature = 333 K.

[3] volume of organic phase = 5×10^{-5} m^3; MNT = 1.7 kmol/m^3; TBAB = 9.3×10^{-2} kmol/m^3 of organic phase; volume of aqueous phase = 5×10^{-5} m^3; concentration of sulfide= 3.5 kmol/m^3; concentration of ammonia = 8.42 kmol/m^3; temperature = 323K.

Figure 2. Effect of ammonia concentration. volume of organic phase = 5×10^{-5} m^3; MNT = 1.35 kmol/m^3; TBAB = 6.2×10^{-2} kmol/m^3 of organic phase; volume of aqueous phase = 5×10^{-5} m^3; concentration of sulfide = 1.27 kmol/m^3; temperature = 323 K; speed of agitation =1500 rev/min.

Figure 3. Effect of elemental sulfur loading. volume of organic phase = 5×10^{-5} m^3; PNT = 1.17 kmol/m^3; TBAB = 6.2×10^{-2} kmol/m^3 of organic phase; volume of aqueous phase = 5×10^{-5} m^3; concentration of sulfide = 1.68 kmol/m^3; concentration of ammonia = 5.6 kmol/m^3 ; temperature = 323 K; speed of agitation =1500 rev/min.

Figure 4. Effect of sulfide concentration. volume of organic phase = 5×10^{-5} m^3; MNT = 1.7 kmol/m^3; TBAB = 9.3×10^{-2} kmol/m^3 of organic phase; volume of aqueous phase = 5×10^{-5} m^3; concentration of ammonia = 8.42 kmol/m^3; temperature = 323 K; speed of agitation =1500 rev/min.

Figure 5. Plot of Ln(initial rate) vs. Ln(initial sulfide concentration). All conditions are the same as in Figure 4.

Figure 6. Effect of catalyst concentration. volume of organic phase = 5×10^{-5} m^3; MNT = 1.7 kmol/m^3; volume of aqueous phase = 5×10^{-5} m^3; concentration of ammonia = 8.42 kmol/m^3; concentration of sulfide = 4.02 kmol/m^3; temperature = 323 K; speed of agitation =1500 rev/min.

Figure 7. Plot of Ln(initial rate) vs. Ln(catalyst concentration). All conditions are the same as in Figure 6.

Figure 8. Effect of concentration of MNT and ONT. volume of organic phase $= 5 \times 10^{-5}$ m^3; TBAB $= 9.3 \times 10^{-2}$ kmol/m^3 of organic phase; volume of aqueous phase $= 5 \times 10^{-5}$ m^3; temperature $= 323$ K; speed of agitation $=1500$ rev/min. [1]concentration of ammonia $= 8.42$ kmol/m^3; concentration of sulfide $= 3.62$ kmol/m^3. [2] concentration of ammonia $= 8.03$ kmol/m^3; concentration of sulfide $= 2.6$ kmol/m^3.

Figure 9. Comparison of calculated and experimental conversions of nitrotoluenes. All conditions are the same as in Table 2.
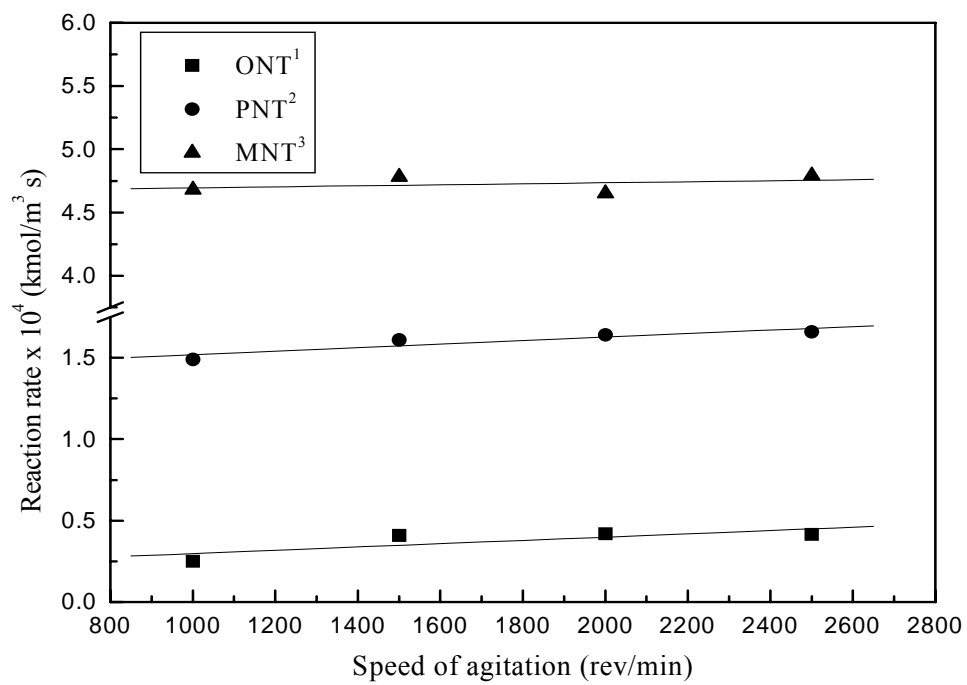
Figure 1.
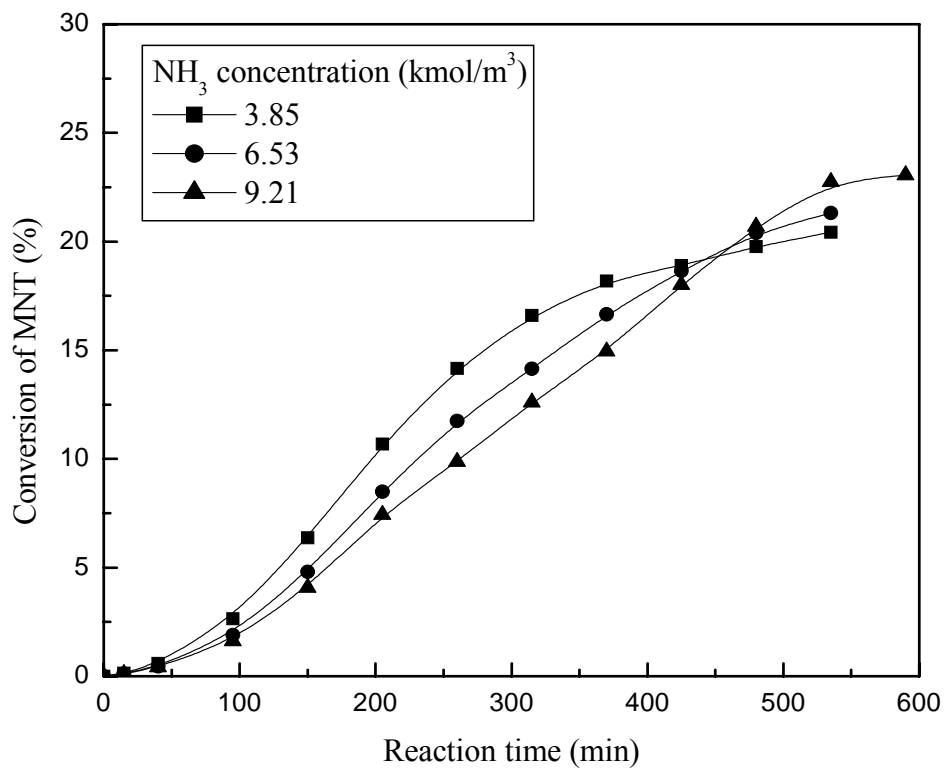
Figure 2.
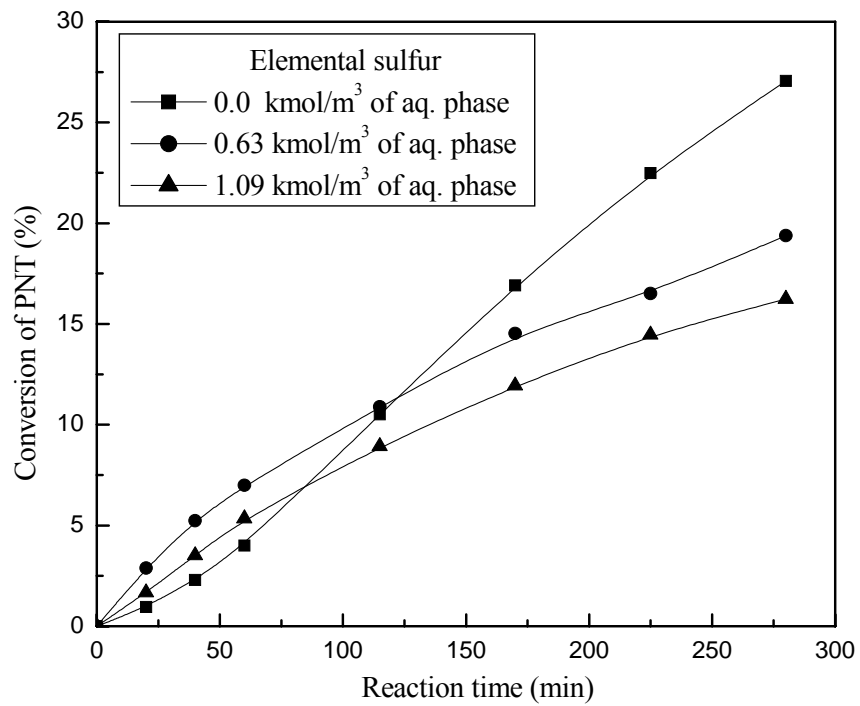
Figure 3.
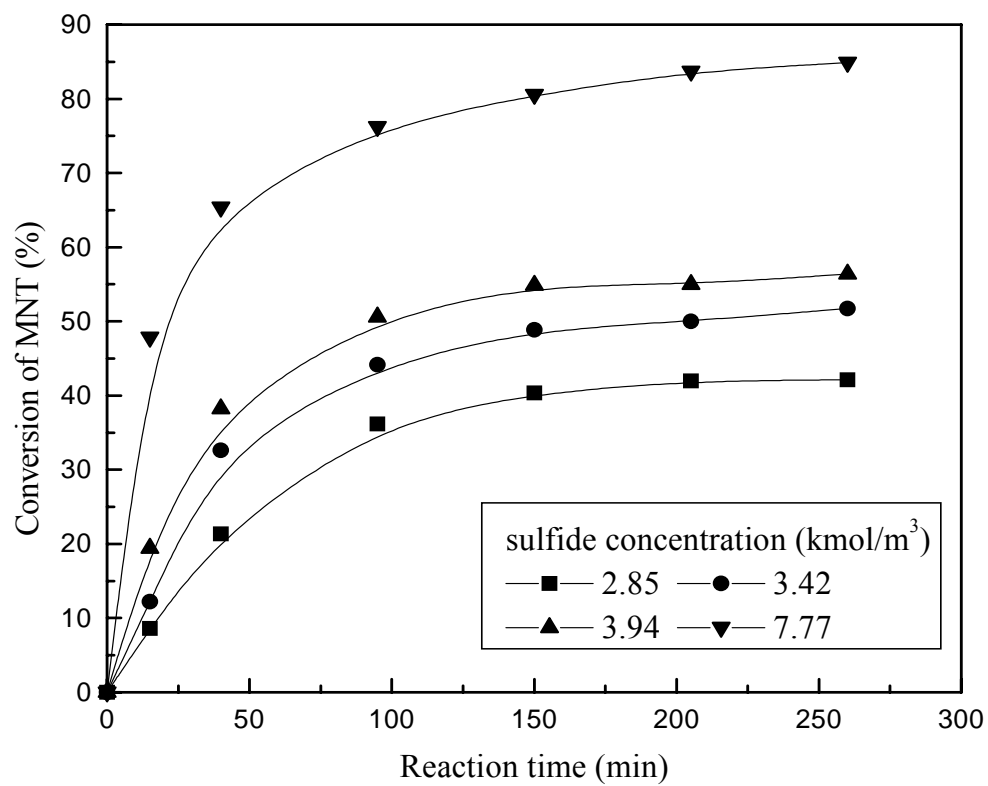
Figure 4.
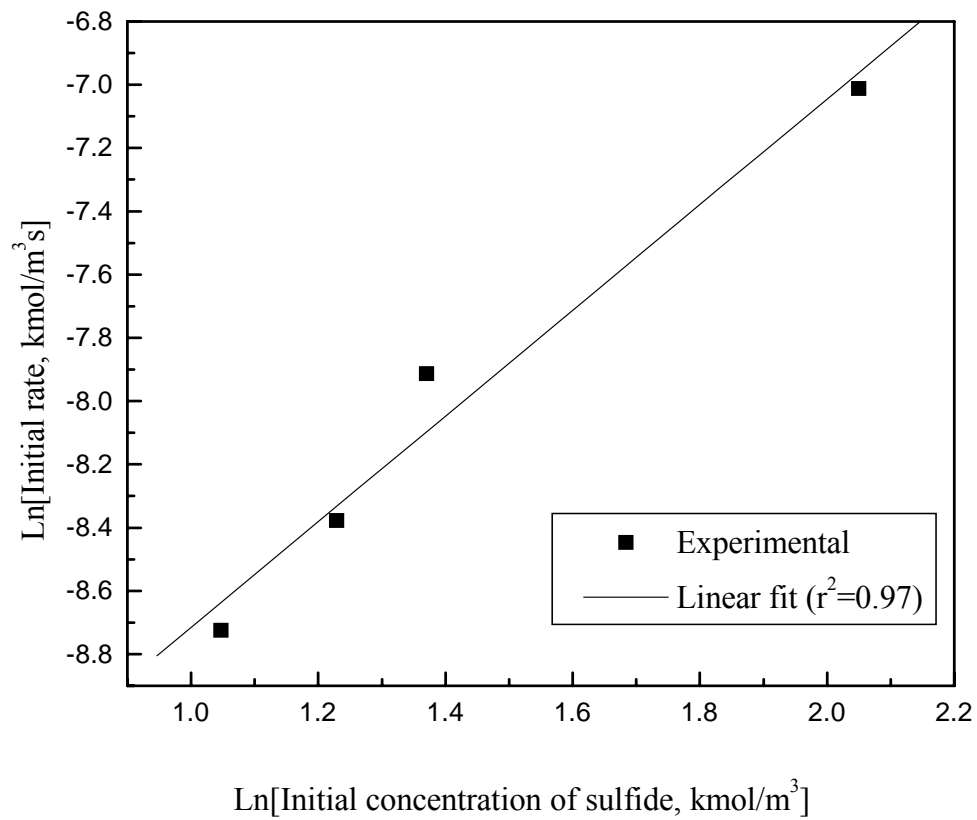
Figure 5.
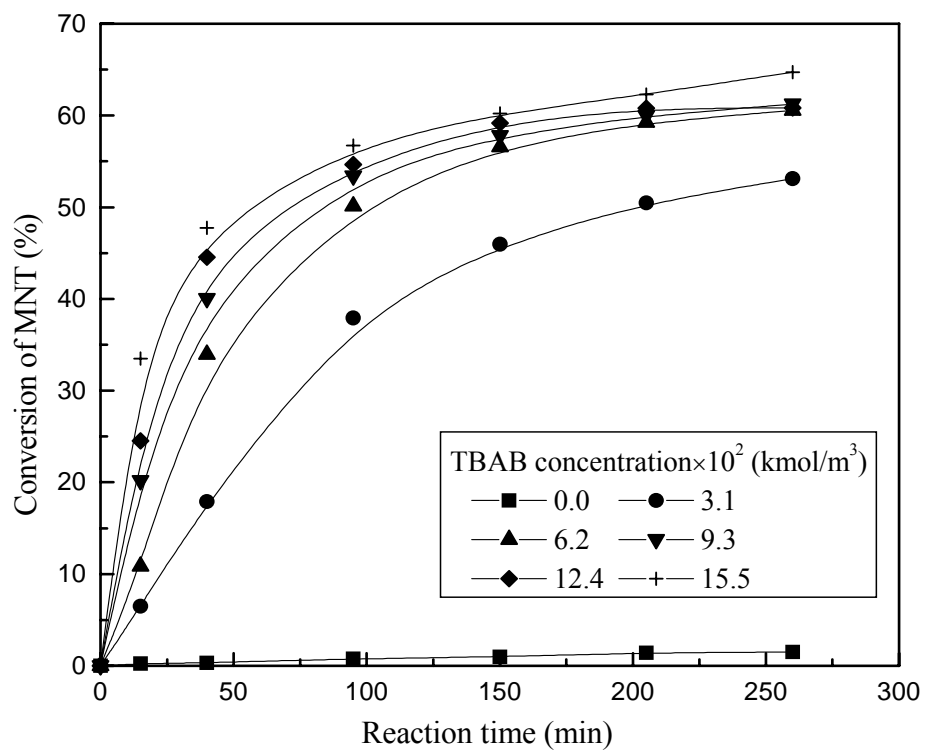
Figure 6.
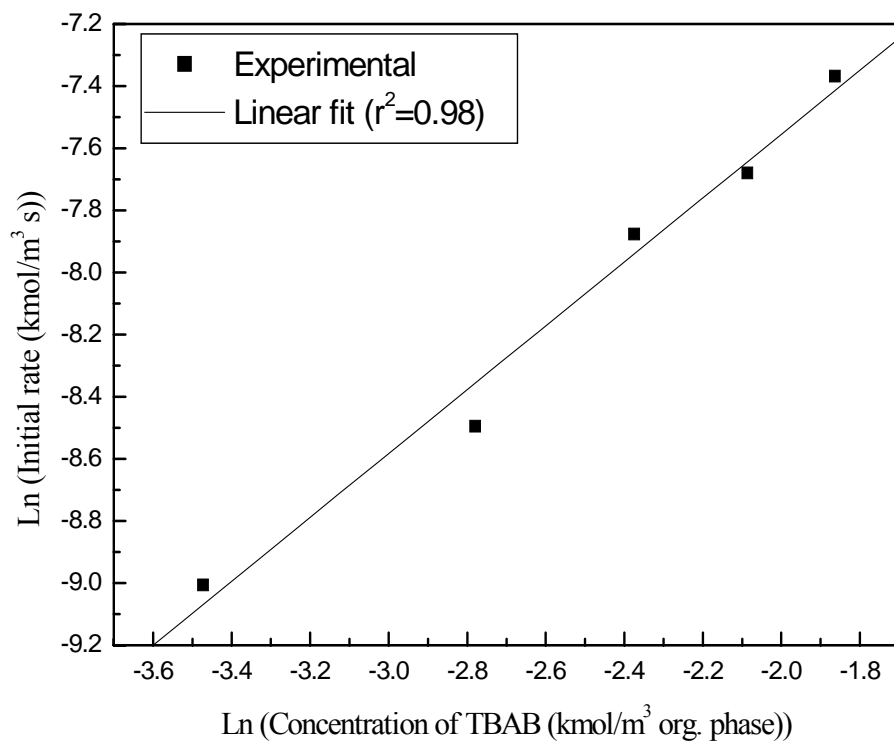
Figure 7.

Figure 8.

Figure 9.