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# Kinetics of Reduction of Nitrotoluenes by H<sub>2</sub>S-Rich Aqueous Ethanolamine

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The reduction of nitrotoluenes (*o*-, *m*-, and *p*-) by H<sub>2</sub>S-rich aqueous monoethanolamine (MEA) was conducted in an organic solvent (toluene), under liquid–liquid mode with a phase transfer catalyst (PTC) (in this study, tetrabutylammonium bromide (TBAB)). The selectivity of toluidines was determined to be 100%. The reaction rate of *m*-nitrotoluene (MNT) was determined to be highest among the three nitrotoluenes, followed by *p*- and *o*-nitrotoluene (PNT and ONT), respectively. The reaction was determined to be kinetically controlled, with apparent activation energies of 18.2, 21.1, and 21.7 kcal/mol for MNT, PNT, and ONT, respectively. The effects of different parameters such as TBAB concentration, sulfide concentration, concentration of nitrotoluenes, MEA concentration, and elemental sulfur loading on the conversions and reaction rates of nitrotoluenes were studied to establish the mechanism of the reaction. The rate of reaction of nitrotoluene was determined to be proportional to the concentration of catalyst, to the square of the concentration sulfide, and to the cube of the concentration of nitrotoluenes. A generalized empirical kinetic model was developed to correlate the experimentally obtained conversion versus time data for the three nitrotoluenes. The present work has a very high commercial importance, because it can replace the expensive Claus process, which gives elemental sulfur as the only product.

## Introduction

During the course of many processes in the petroleum and coal processing industry, one or more gaseous streams that contain hydrogen sulfide (H<sub>2</sub>S) are quite commonly produced. Also, in the natural gas industry, the H<sub>2</sub>S content of certain gas streams, recovered from natural gas deposits in many parts of the world, is often too high for commercial acceptance. The removal of H<sub>2</sub>S from these gaseous streams can be desirable for a variety of reasons:

(1) H<sub>2</sub>S is odiferous in nature, corrosive in the presence of water, and poisonous in very small concentrations.

(2) If these gaseous streams are to be burned as a fuel, the removal of H<sub>2</sub>S from the fuel gas may be necessary to prevent environmental pollution, because of the resultant sulfur dioxide.

(3) The presence of H<sub>2</sub>S in the refinery gas streams can cause several detrimental problems in subsequent processing steps, such as the corrosion of process equipment, deterioration and deactivation of catalysts, undesired side reactions, etc.

The H<sub>2</sub>S from these gaseous streams is conventionally removed through an amine treating unit and then processed in the Claus unit<sup>1</sup> to produce elemental sulfur. However, there are several disadvantages of air oxidation of H<sub>2</sub>S, which include the loss of a valuable hydrogen source, the requirement of precise air rate control, the removal of trace sulfur compounds from spent air, and a limit on the concentration of H<sub>2</sub>S in the feed gas stream, to name a few negatives. Therefore, the development of viable alternative processes for the conversion of H<sub>2</sub>S to produce commercially important chemicals (toluidines), with the coproduction of elemental sulfur (as obtained in the Claus process) is very much welcome in the process industry, particularly in the refineries that are handling sour crudes.

Although both ammonia- and alkanolamine-based processes are used for the removal of acid constituents (H<sub>2</sub>S and CO<sub>2</sub>) from gas streams, an alkanolamine-based process has received widespread commercial acceptance as the preferred gas treatment method, because of its advantages of low vapor pressure

(high boiling point) and ease of reclamation.<sup>1</sup> The low vapor pressure of alkanolamines can make the operation more flexible, in terms of operating pressure, temperature, and concentration of alkanolamine, in addition to negligible vaporization losses. Moreover, in this process, the costly regeneration of the H<sub>2</sub>S-rich amine solution can also be avoided.

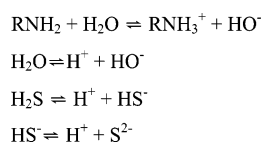
Although triethanolamine (TEA)<sup>2,3</sup> is one of the first amines used for the removal of H<sub>2</sub>S and CO<sub>2</sub> from gas streams, it is superseded by aqueous monoethanolamine (MEA) and diethanolamine (DEA), because of their higher rates of reaction with the acid gases. Aqueous MEA has been used widely, because of its high reactivity, low solvent cost, ease of reclamation, low absorption of hydrocarbons, and low molecular weight (which results in high solution capacity at moderate concentrations). On the other hand, DEA, which is less corrosive than MEA, is a better choice for treating gas streams that contain appreciable amounts of COS and CS<sub>2</sub>, because it is much less reactive with these impurities, compared to primary amines such as MEA. Much study has been conducted on the equilibrium solubility of pure H<sub>2</sub>S,<sup>4–6</sup> a mixture of acid gases (H<sub>2</sub>S and CO<sub>2</sub>),<sup>5,6</sup> and the mathematical representation of the experimental solubility data for H<sub>2</sub>S, CO<sub>2</sub>, and their mixture,<sup>7–10</sup> using aqueous MEA. Much work was also reported on the use of aqueous DEA.<sup>5,8–12</sup> However, no attempt was made in the past to utilize the H<sub>2</sub>S-rich aqueous alkanolamine to produce value-added chemicals such as toluidines. Considering the importance of the system, the present work was undertaken using the most commonly used amine, MEA.

Aqueous methyl diethanolamine (MDEA) has been reported to remove H<sub>2</sub>S selectively from a gas stream that contains both CO<sub>2</sub> and H<sub>2</sub>S.<sup>13–15</sup> The selectivity of H<sub>2</sub>S removal could be greatly improved using MDEA in nonaqueous solvents such as *N*-methyl pyrrolidone, ethylene glycol, etc.<sup>15,16</sup> The applicability of the present process for gas streams that contain both H<sub>2</sub>S and CO<sub>2</sub> is largely dependent on this selectivity. Therefore, extensive research is needed in this field, using various H<sub>2</sub>S-selective alkanolamines as the solvent.

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

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## Scheme 1

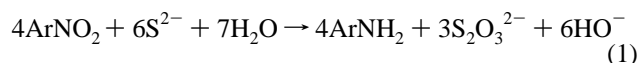


reduction.<sup>17</sup> Zinin reduction has considerable practical value, because of some inherent advantages of the method over other conventional processes. For example, catalytic hydrogenation requires more-expensive equipment and hydrogen handling facility; additional problems that are due to catalyst preparation, catalyst poisoning hazards, and the risk of reducing other groups are observed. Although the reduction by iron is reserved for small-scale commercial applications, it cannot be used for the 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 converts nitro compounds to mixtures of azoxy and azo compounds, in addition to being expensive. The reduction of nitrotoluenes (*o*-, *m*-, and *p*-) by H<sub>2</sub>S-rich aqueous MEA under liquid–liquid phase transfer catalysis conditions is commercially very important, because the products (toluidines) have widespread applications as intermediates for dyes, agrochemicals, and pharmaceutical products.

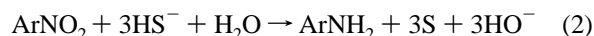
The advantages of the use of phase transfer catalysts (PTCs) in the performance of multiphase reactions efficiently are well-recognized. The use of these catalysts to enhance the otherwise slow two-phase reduction of aromatic nitro compounds may be very interesting, from a commercial point of view. Among 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.<sup>18</sup> The same catalyst, TBAB, was used in this study.

In H<sub>2</sub>S-rich aqueous MEA, the sulfide ions (S<sup>2-</sup>) and hydrosulfide ions (HS<sup>-</sup>) remain in equilibrium, as represented by Scheme 1.<sup>9</sup> A similar ionic equilibrium also exists in the aqueous ammonium sulfide. Therefore, the behavior of H<sub>2</sub>S-rich aqueous MEA is expected to be similar to that of ammonium sulfide. However, because of the existence of two different ions (sulfide and hydrosulfide) in the H<sub>2</sub>S-rich aqueous MEA and aqueous ammonium sulfide, the properties of these reducing agents are expected to be different from the other reducing agents (such as sodium sulfide and disulfide).

The overall stoichiometry of the Zinin's original reduction of nitrobenzene by aqueous ammonium sulfide is given by eq 1.<sup>17</sup>

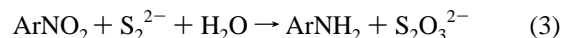


This stoichiometry is also applicable for the reduction of nitroarenes by sodium sulfide.<sup>19–23</sup> For the preparation of *p*-aminophenylacetic acid from *p*-nitrophenylacetic acid using aqueous ammonium sulfide, it has been reported that the sulfide ions were oxidized to elemental sulfur, instead of thiosulfate, following the stoichiometry of eq 2.<sup>24</sup>



A similar stoichiometry was reported for the reduction of 2-bromo-4-nitrotoluene by alcoholic ammonium sulfide.<sup>25</sup> The formation of elemental sulfur was reported for the preparation

of 3-amino-5-nitrobenzyl alcohol using ammonium sulfide prepared from ammonium chloride and crystalline sodium sulfide dissolved in methanol.<sup>26</sup> The overall stoichiometry of the reduction reaction using disulfide as the reducing agent is as follows:<sup>19,27</sup>



Therefore, two different reactions leading to the formation of either elemental sulfur or thiosulfate may be operative for the reduction of nitroarenes with H<sub>2</sub>S-rich aqueous MEA. Therefore, a detailed study of such reactions is not only commercially important, but also academically interesting.

## Experimental Section

**Chemicals.** Toluene (≥99%) and ethanolamine (≥98%) of synthesis grade were procured from Merck (India), Ltd., Mumbai, India. Nitrotoluenes (>99%) of synthesis grade were purchased from Loba Chemie Pvt., Ltd., Mumbai, India. TBAB was obtained from SISCO Research Laboratories Pvt., Ltd., Mumbai, India.

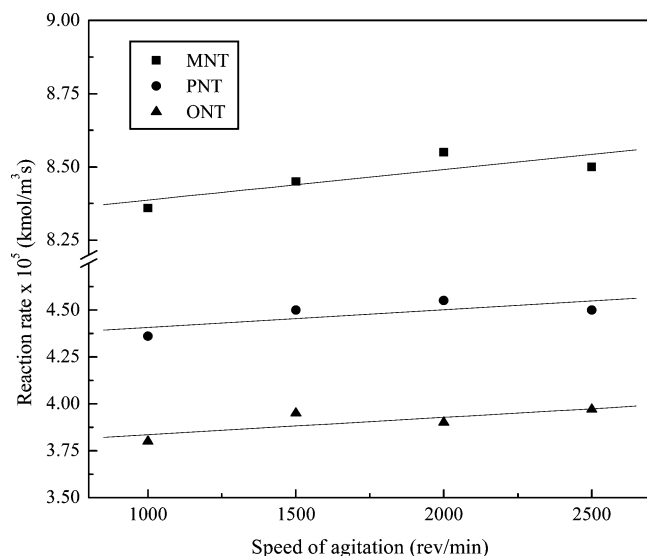
**Equipment.** The reactions of nitrotoluenes with H<sub>2</sub>S-rich aqueous MEA were performed batchwise in a fully baffled mechanically agitated glass reactor with a capacity of 250 cm<sup>3</sup> (6.5 cm i.d.). A 2.0 cm diameter six-bladed glass-disk turbine impeller with the provision of speed regulation, located at a height of 1.5 cm from the bottom, was used to stir the reaction mixture. The reactor was kept in a constant-temperature water bath, the temperature of which could be controlled to within ±1°C.

**Preparation of H<sub>2</sub>S-Rich Aqueous MEA Solution.** For the preparation of H<sub>2</sub>S-rich aqueous MEA, ~30 wt % MEA was prepared first by adding a suitable quantity of MEA in distilled water. H<sub>2</sub>S gas then was bubbled through this aqueous MEA in a 250 cm<sup>3</sup> standard gas bubbler. Liquid samples were withdrawn from time to time after the gas bubbling was stopped and the samples were analyzed for sulfide content.<sup>28</sup> The gas bubbling was then continued until the desired sulfide concentration was obtained in the aqueous MEA solution.

**Experimental Procedure.** In a typical run, 50 cm<sup>3</sup> of the aqueous phase that contained a known concentration of sulfide was charged into the reactor and kept well-agitated until the steady-state temperature was attained. The organic phase that contained a measured amount of nitrotoluene, catalyst (TBAB), and solvent (toluene), kept separately at the reaction temperature, then was charged into the reactor. The reaction mixture was then agitated at a constant speed. Approximately 0.5 cm<sup>3</sup> of the organic layer was withdrawn at a regular interval after the agitation was stopped and the phases were allowed to separate.

**Analysis.** All the samples from the organic phase were analyzed via gas–liquid chromatography (GLC) using a 2 m × 3 mm stainless steel column packed with 10% OV-17 on Chromosorb W (80/100). A gas chromatograph (Chemito Model 8610 GC) that was interfaced with a data processor (Shimadzu C-R6A Chromatopac) was used for the analysis. The column temperature was programmed with an initial temperature at 423 K and increased at a rate of 15 K/min to 513 K. Nitrogen was used as the carrier gas, with a flow rate of 15 cm<sup>3</sup>/min. An injector temperature of 543 K was used during the analysis. A flame ionization detector (FID) was used at the temperature of 543 K.

The initial sulfide concentrations were determined by the standard iodometric titration method.<sup>28</sup>



**Figure 1.** Effect of speed of agitation. Conditions were as follows: volume of organic phase,  $5 \times 10^{-5} \text{ m}^3$ ; nitrotoluenes concentration,  $1.46 \text{ kmol/m}^3$ ; TBAB concentration,  $6.2 \times 10^{-2} \text{ kmol/m}^3$  of organic phase; volume of aqueous phase,  $5 \times 10^{-5} \text{ m}^3$ ; concentration of MEA,  $5.01 \text{ kmol/m}^3$ ; sulfide concentration,  $1.85 \text{ kmol/m}^3$ ; and temperature,  $343 \text{ K}$ .

**Table 1.** Effect of Temperature on the Reaction Rate of Nitrotoluenes<sup>a</sup>

temperature (K)	reaction rate ( $\times 10^5 \text{ (kmol/m}^3 \text{ s)}$ )		
	MNT	PNT	ONT
313	7.2	2.8	1.1
323	22.0	11.0	3.5
333	39.3	27.3	15.6
343	82.5	54.1	31.3

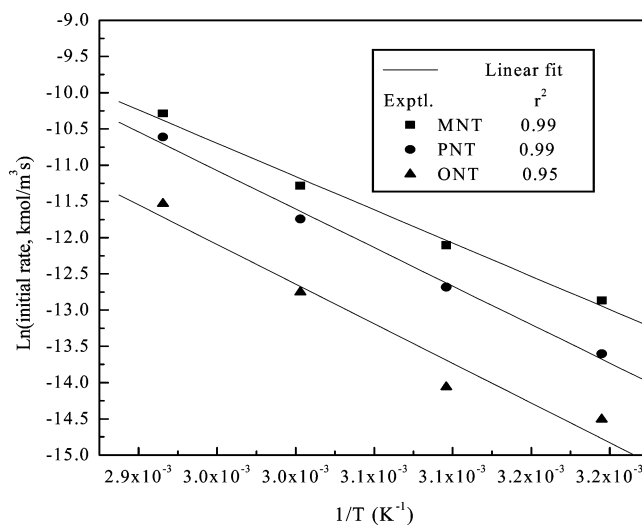
<sup>a</sup> Matching conversion, 5%; speed of agitation, 1500 rpm; all other conditions are the same as those in Figure 1.

## Results and Discussion

The reduction of nitrotoluenes (*o*-, *m*-, and *p*-) was performed in liquid–liquid mode with an aqueous MEA solution. In all cases, 100% selectivity for the corresponding amines was obtained. The effects of various parameters on the rates of reaction of the nitrotoluenes were studied and reported below.

**Effect of Speed of Agitation.** The effect of speed of agitation on the rate of reaction of nitrotoluenes (*o*-, *m*-, and *p*-, denoted hereafter as ONT, MNT, and PNT, respectively) was studied in the range of 1000–2500 rpm under otherwise identical experimental conditions in the presence of PTC (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 to be kinetically controlled for all the nitrotoluenes. All other experiments were performed at 1500 rpm, to avoid the effects of mass-transfer resistance on the reaction kinetics.

**Effect of Temperature.** The effect of temperature on the rate of reaction of nitrotoluenes with  $\text{H}_2\text{S}$ -rich aqueous MEA was studied in the temperature range of 313–343 K under identical experimental conditions in the presence of a catalyst (TBAB), as shown in Table 1. As the table shows, the reaction rate increases with temperature for all the nitrotoluenes. The initial rates were calculated at different temperatures and an Arrhenius plot of the natural logarithm of the initial rate versus  $1/T \text{ (K}^{-1}\text{)}$  was made, as shown in Figure 2. The apparent activation energy for this kinetically controlled reaction was calculated from the slope of the straight lines as 18.2, 21.1, and 21.7 kcal/mol for MNT, PNT, and ONT, respectively. For



**Figure 2.** Arrhenius plot. All conditions are the same as those given in Table 1.

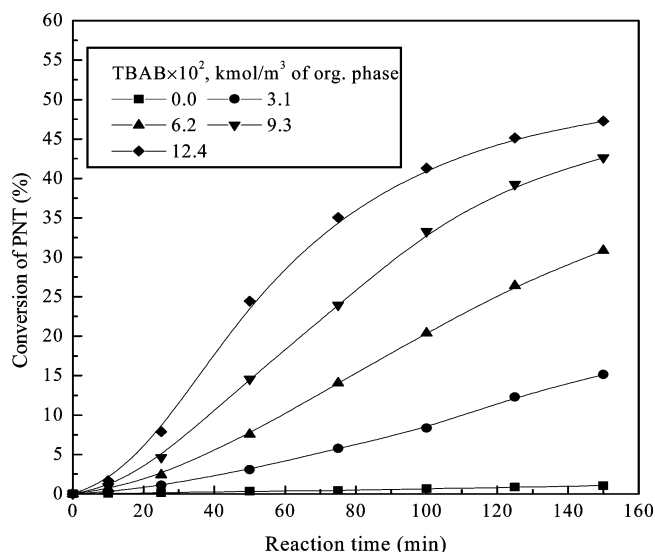
the kinetically controlled reductions of nitroarenes by sodium sulfide under liquid–liquid phase transfer catalysis, the reported activation energies are 11.25, 12.54, and 9.36 kcal/mol for ONT, MNT, and PNT, respectively,<sup>21</sup> 8.04 kcal/mol for *m*-nitrochlorobenzene,<sup>20</sup> and 47.36 kcal/mol for *p*-nitroanisole.<sup>22</sup>

**Comparison of Reactivities of Nitrotoluenes.** As shown in Table 1, the reaction rates of nitrotoluenes follow the order of  $\text{MNT} > \text{PNT} > \text{ONT}$  in the presence of PTC (TBAB), in the temperature range studied. From this observation, it can be concluded that the presence of an electron-donating group such as the 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 (which is a site of low electron density). Pradhan<sup>21</sup> also reported a similar trend of reactivity for the reduction of nitrotoluenes by sodium sulfide using TBAB in the liquid–liquid mode.

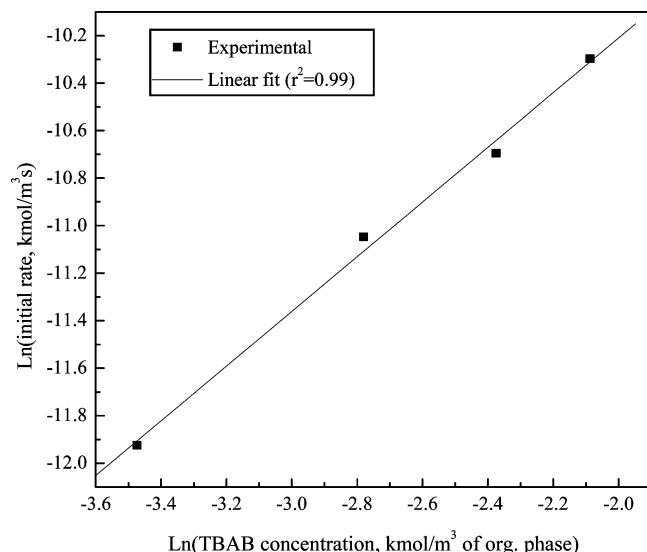
**Effect of Catalyst Loading.** The effect of catalyst (TBAB) loading on the conversion of PNT was studied in the concentration range of  $3.1 \times 10^{-2}$ – $12.4 \times 10^{-2} \text{ kmol/m}^3$  of organic phase, as shown in Figure 3. The study was also conducted in the absence of catalyst, as shown in the same figure. As shown in the figure, the conversion of PNT is only ~1% in the absence of catalyst, whereas it is ~47% with the maximum concentration of catalyst tried after 150 min of reaction under otherwise identical experimental conditions. Table 2 shows that the rate of reaction of PNT in the absence of TBAB is very low, compared to that in the presence of TBAB, resulting in a very high enhancement factor. This shows the importance of PTC in enhancing the rate of the reaction under investigation.

To determine the order of the reaction, with respect to the TBAB concentration, the initial reaction rate was calculated at different TBAB concentrations and the plot of the natural logarithm of the initial rate versus the natural logarithm of the TBAB concentration was made (Figure 4). From the slope of the linearly fitted line, the order of the reaction, with respect to the TBAB concentration, was obtained as 1.12, which is close to unity. Yadav et al.<sup>22</sup> also reported a similar observation for the reduction of *p*-nitroanisole by sodium sulfide in the presence of PTC (TBAB).

**Effect Concentration of *p*-Nitrotoluene.** The effect of concentration of PNT on the conversion was studied at four different concentrations in the range of 0.87–1.75 kmol/m<sup>3</sup> in the presence of TBAB under otherwise identical experimental



**Figure 3.** Effect of TBAB loading. Conditions were as follows: volume of organic phase,  $5 \times 10^{-5} \text{ m}^3$ ; PNT concentration,  $1.46 \text{ kmol/m}^3$ ; volume of aqueous phase,  $5 \times 10^{-5} \text{ m}^3$ ; concentration of MEA,  $5.01 \text{ kmol/m}^3$ ; sulfide concentration,  $2.25 \text{ kmol/m}^3$ ; temperature,  $333 \text{ K}$ ; and speed of agitation,  $1500 \text{ rpm}$ .



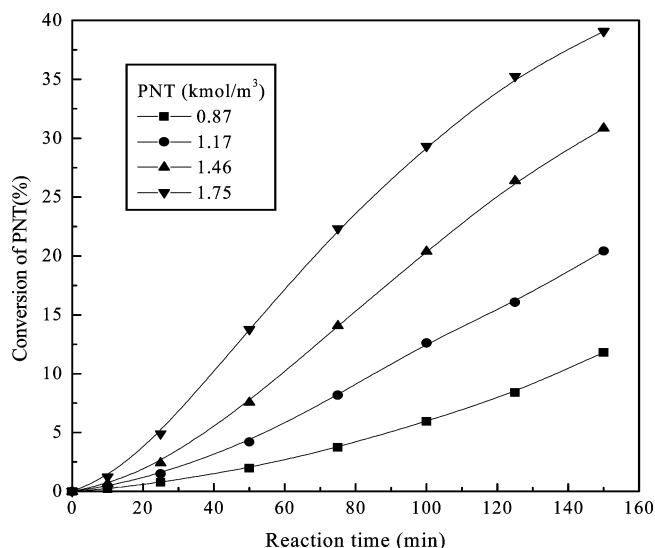
**Figure 4.** Plot of the natural logarithm of the initial rate versus the natural logarithm of the TBAB concentration. All conditions are the same as those in Figure 3.

**Table 2.** Effect of TBAB Loading on the Reaction Rate of PNT<sup>a</sup>

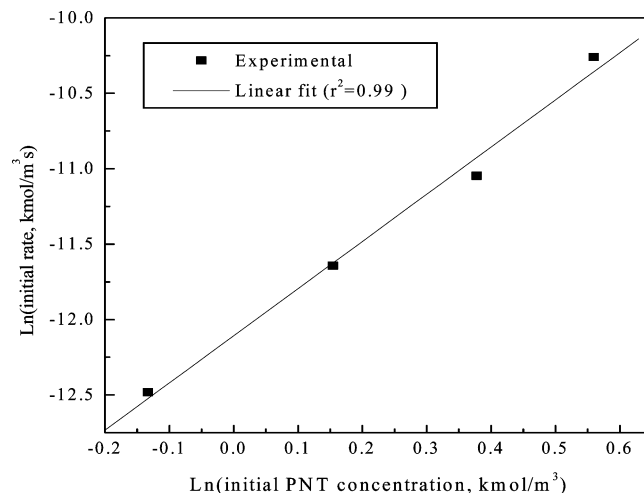
TBAB concentration ( $\times 10^2 \text{ kmol/m}^3$ of org. phase)	reaction rate ( $\times 10^4 \text{ kmol/m}^3 \text{ s}$ )	enhancement factor
0.0	0.01	-
3.1	0.26	26
6.2	0.50	50
9.3	0.79	79
12.4	1.00	100

<sup>a</sup> Matching PNT conversion, 5%; all other conditions are the same as those in Figure 3.

conditions, as shown in Figure 5. The conversion (and, thus, the reaction rate) of PNT increases as the concentration of the PNT increases. From the plot of the natural logarithm of the initial rate versus the natural logarithm of the PNT concentration (Figure 6), the order of the reaction, with respect to PNT concentration, was obtained as 3.12 (which is close to 3). The same order also was observed for other two nitrotoluenes (MNT and ONT). However, for the reduction of nitroarenes by aqueous sodium sulfide, the reported order is unity, with respect to the



**Figure 5.** Effect of PNT concentration. Conditions were as follows: volume of organic phase,  $5 \times 10^{-5} \text{ m}^3$ ; TBAB concentration,  $6.2 \times 10^{-2} \text{ kmol/m}^3$  of organic phase; volume of aqueous phase,  $5 \times 10^{-5} \text{ m}^3$ ; concentration of MEA,  $5.01 \text{ kmol/m}^3$ ; sulfide concentration,  $2.25 \text{ kmol/m}^3$ ; temperature,  $333 \text{ K}$ ; and speed of agitation,  $1500 \text{ rpm}$ .



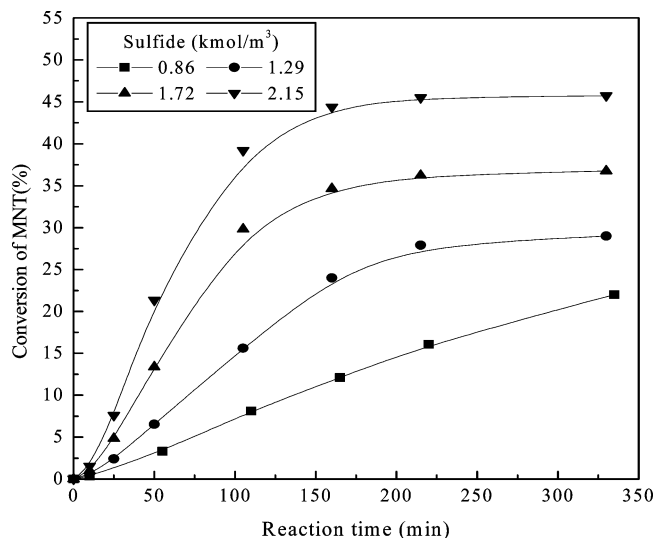
**Figure 6.** Plot of the natural logarithm of the initial rate versus the natural logarithm of the PNT concentration. All conditions are the same as those in Figure 5.

concentration of *p*-nitroanisole<sup>22</sup> and nitroaromatics.<sup>19</sup> The rate was also reported to be proportional to the concentration of nitrobenzene for its reduction with sodium disulfide under two-phase conditions.<sup>27</sup>

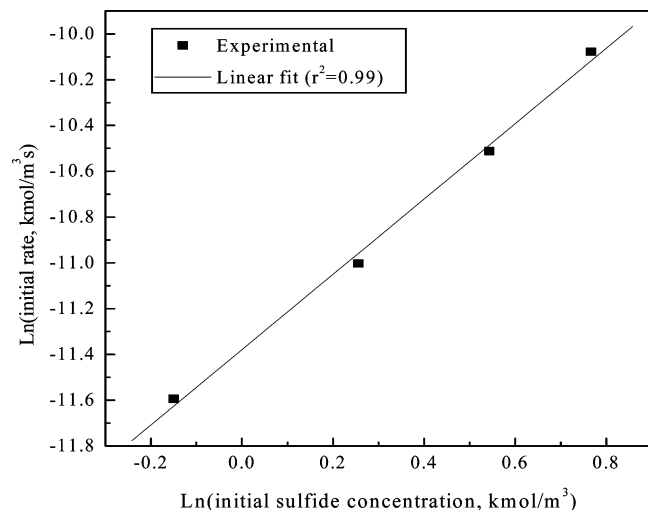
**Effect of Sulfide Concentration.** Figure 7 shows the effect of sulfide concentration in the aqueous phase on the conversion of MNT. As the concentration of sulfides increases, the conversion of MNT as well as the reaction rate increases, which is evident from the figure. From the plot of the natural logarithm of the initial rate versus the natural logarithm of the initial sulfide concentration (Figure 8), the order of the reaction, with respect to the sulfide concentration, was obtained as 1.64. Because this value is closer to the integer 2, the reaction was, therefore, considered to be second 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 the sulfide concentration.<sup>19,22</sup> The rate was also reported to be proportional to the square of the concentration of sodium disulfide.<sup>27</sup>

It is worthy to mention here that the nature of the curve obtained in this reaction is "S"-type, which is typical of an





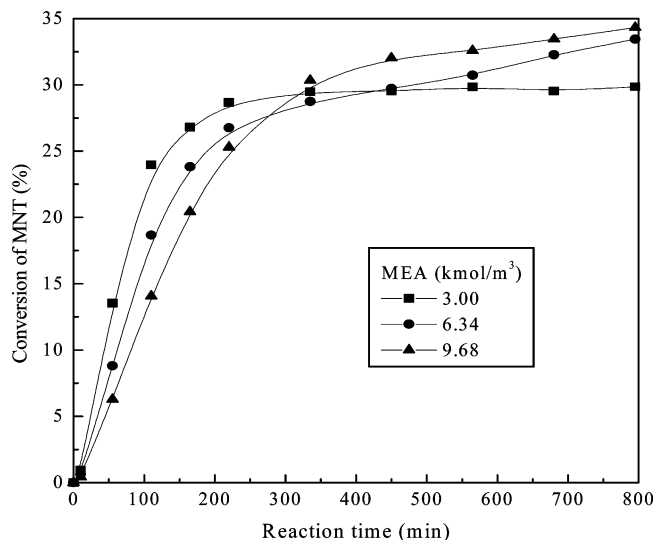
**Figure 7.** Effect of sulfide concentration. Conditions were as follows: volume of organic phase,  $5 \times 10^{-5} \text{ m}^3$ ; MNT concentration,  $1.60 \text{ kmol/m}^3$ ; TBAB concentration,  $9.3 \times 10^{-2} \text{ kmol/m}^3$  of organic phase; volume of aqueous phase,  $5 \times 10^{-5} \text{ m}^3$ ; concentration of MEA,  $5.01 \text{ kmol/m}^3$ ; temperature,  $333 \text{ K}$ ; and speed of agitation,  $1500 \text{ rpm}$ .



**Figure 8.** Plot of the natural logarithm of the initial rate versus the natural logarithm of the sulfide concentration. All conditions are the same as those in Figure 7.

autocatalytic reaction, where the rate of reaction increases as the concentration of catalyst formed by the reaction increases and then the rate of reaction decreases with the depletion of the reactants, as observed in Figures 3, 5, and 7. This phenomenon was only observed for a low concentration of one of the components: nitrotoluenes, sulfide, and catalyst or the conditions that favor low initial reaction rate. However, for high concentration, this phenomenon could not be observed, because it occurred within a very short period of time. For ONT and PNT, this phenomenon was determined to occur even at relatively high concentrations, because of their slow reaction rates. The exact reason for the nature of this curve will be explained when the effect of elemental sulfur loading on the reaction will be discussed.

**Effect of MEA Concentration.** Although MEA, as such, does not participate in the reaction with nitrotoluenes, it does affect the equilibrium among MEA,  $\text{H}_2\text{S}$ , and water, which results in two active anions, sulfide ( $\text{S}^{2-}$ ) and hydrosulfide ( $\text{HS}^-$ ), in the aqueous phase, as shown in Scheme 1. These two active anions participate in two different reactions (eqs 1 and



**Figure 9.** Effect of MEA concentration. Conditions were as follows: volume of organic phase,  $5 \times 10^{-5} \text{ m}^3$ ; MNT concentration,  $1.60 \text{ kmol/m}^3$ ; TBAB concentration,  $9.3 \times 10^{-2} \text{ kmol/m}^3$  of organic phase; volume of aqueous phase,  $5 \times 10^{-5} \text{ m}^3$ ; concentration of sulfide,  $1.29 \text{ kmol/m}^3$ ; temperature,  $333 \text{ K}$ ; and speed of agitation,  $1500 \text{ rpm}$ .

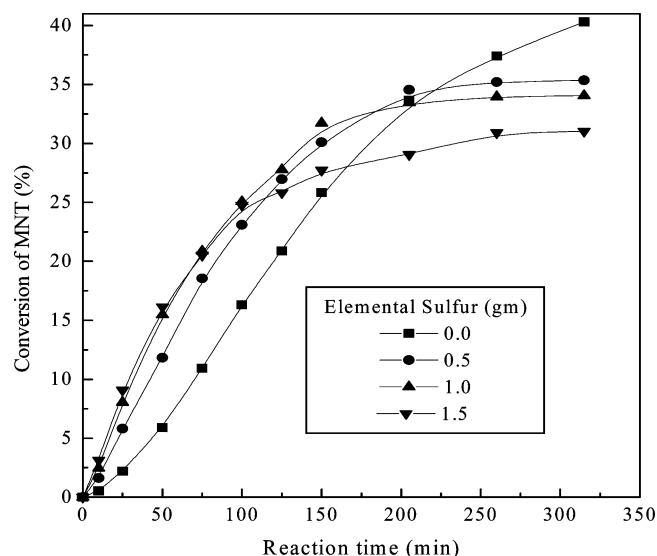
2). In the presence of a base (MEA), the dissociation equilibrium shifts toward more ionization and the concentration of sulfide ions, relative to hydrosulfide ions in the aqueous phase, increases as the MEA concentration increases. Therefore, only by changing the MEA concentration with constant sulfide concentration in the aqueous phase, it would be easy to prove the existence of two different reactions.

To study the effect of MEA concentration,  $\text{H}_2\text{S}$ -rich aqueous MEA of different MEA concentrations (but constant sulfide concentration) was prepared by taking  $30 \text{ cm}^3$  of  $\text{H}_2\text{S}$ -rich aqueous MEA (with known sulfide and MEA concentration) and then adding various proportions of pure MEA and distilled water to it in such a way that the total volume became  $50 \text{ cm}^3$  in all the cases.

The effect of MEA concentration on the conversion of MNT is shown in Figure 9. As the concentration of MEA increased, the conversion of MNT was observed to decrease up to a certain reaction time; beyond that point, the opposite trend was observed, i.e., with higher MEA concentration, higher MNT conversion was achieved (see Figure 9).

The conversion of MNT is expected to reach  $\sim 54\%$  if the reaction follows the stoichiometry of reaction 1, and it would be  $\sim 27\%$  if the stoichiometry of reaction 2 is considered, for complete conversion of sulfide in both cases. However, after a long reaction run, a maximum conversion of MNT of  $34\%$  was achieved with the maximum MEA concentration used in this study, as shown in the figure. This result clearly indicates that the first reaction (reaction 1) is also operative in the Zinin reduction, as proposed by Zinin in 1842.<sup>17</sup> These results are in complete disagreement with some of the recent works with ammonium sulfide<sup>24–26</sup> that propose reaction 2 to be the solely operative reaction. From the same figure, it is also observed that the reaction reaches equilibrium well before the expected conversion from stoichiometry of reaction 1. The reduction in conversion may be due to the existence of reaction 2 in addition to reaction 1. The formation of elemental sulfur will be confirmed when the effect of elemental sulfur loading will be discussed.

Because of the fact that 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



**Figure 10.** Effect of elemental sulfur loading. Conditions were as follows: volume of organic phase,  $5 \times 10^{-5}$  m<sup>3</sup>; MNT concentration, 1.46 kmol/m<sup>3</sup>; TBAB concentration,  $6.2 \times 10^{-2}$  kmol/m<sup>3</sup> of organic phase; volume of aqueous phase,  $5 \times 10^{-5}$  m<sup>3</sup>; concentration of MEA, 5.01 kmol/m<sup>3</sup>; sulfide concentration, 1.85 kmol/m<sup>3</sup>; temperature, 333 K; and speed of agitation, 1500 rpm.

reaction via the transfer of sulfide ions follows the stoichiometry of reaction 1. The concentration of sulfide ions ( $S^{2-}$ ) increases as the concentration of MEA increases for a fixed sulfide concentration. Thus, with increase in MEA concentration, there is an increase in the reaction rate via the transfer of sulfide ions, following the stoichiometry of reaction 1, which results in higher conversion of MNT at higher MEA concentrations.

**Effect of Elemental Sulfur Loading.** Elemental sulfur in the solution of ammonia and hydrogen sulfide is known to form ammonium polysulfides<sup>29</sup>  $((NH_4)_2S_n$ , where  $2 \leq n \leq 6$ ), which is also one of the reducing agents of the Zinin's reduction. Similar behavior is also expected with aqueous MEA. Because the formation of elemental sulfur was reported for this reaction,<sup>24–26</sup> here, we have examined the effect of externally added elemental sulfur on the reaction rate and conversion of MNT.

In this experiment, elemental sulfur was first dissolved in the  $H_2S$ -rich aqueous MEA and then used for the reaction, following the same procedure as that described earlier. The color of the  $H_2S$ -rich aqueous MEA is greenish yellow. However, after dissolution of elemental sulfur into this solution, the color of the solution became reddish brown. Also during the reaction run, initially the color of the solution was unaffected but later, it changed rapidly from greenish yellow to reddish brown. This color change indicates the formation of elemental sulfur (and polysulfides) during the reaction.

The effect of elemental sulfur loading on the conversion of MNT is shown in Figure 10. It is clearly observed from the figure that the conversion of MNT increases as the elemental sulfur loading increases, up to a certain reaction time; beyond that point, an opposite trend was observed (i.e., the conversion of MNT decreases as the elemental sulfur loading increases). It is also observed from the nature of the curves in the figure that the reaction rate gradually decreases with reaction time 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 curve, as discussed in the previous section.

Therefore, it can be said that the reaction rate increases with the buildup of the elemental sulfur concentration (reaction 2)

as the reaction proceeds and then falls with the depletion of the reactants, resulting in an S-type curve.

The increase in the rate of reaction with increased elemental sulfur loading may be due to the fact that the reaction via the transfer of hydrosulfide and sulfide ions is slow, compared to polysulfide ions formed by the reaction of elemental sulfur with  $H_2S$ -rich aqueous MEA. As reported by Hojo et al.,<sup>27</sup> disulfide reduces nitrobenzene much more rapidly than sulfide.

The final conversion of MNT decreases as the elemental sulfur loading increases, as observed from the figure. This may be due to the formation of polysulfide in addition to disulfide (which is only transferred and reacts with nitrotoluenes to form thiosulfate and toluidines, according to the stoichiometry of reaction 3).<sup>25</sup>

From the results of Figure 9, it is observed that the conversion of MNT remains more similar to the value as governed by stoichiometry of reaction 2. Therefore, it can be concluded that the reaction follows the stoichiometry of reaction 2 predominantly. It can also be concluded from these results that it is preferred to conduct the reaction with a high sulfide loading (low MEA concentration) in the aqueous phase to get the elemental sulfur predominantly, instead of thiosulfate, at the cost of low overall conversion of nitrotoluenes.

### Kinetic Modeling

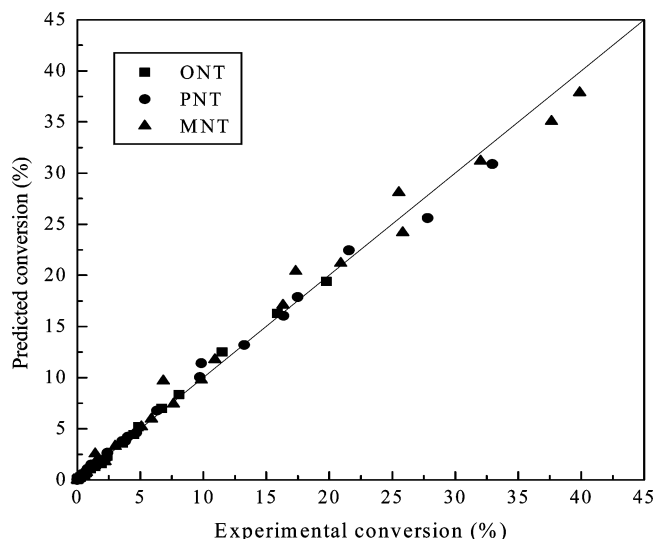
The kinetics and mechanism of a variety of phase transfer catalyzed  $SN^2$  type of reactions, in liquid–liquid,<sup>30</sup> solid–liquid,<sup>31</sup> and liquid–liquid–liquid<sup>32</sup> mode, and some oxidation reactions<sup>30,33</sup> are well-documented. However, such information on Zinin reduction is very limited. Although many published works on Zinin reduction exist, the exact mechanism of this important reaction is still not clear. The first product probably is a nitroso compound, which is rapidly reduced to hydroxylamine and then to amine.<sup>17</sup> The rate-determining step is considered to be the attack of negative divalent sulfur on the nitro group, because no intermediate compounds are observed to be formed during the reaction. The mechanism and kinetic scheme developed by Yadav et al.<sup>22</sup> for the reduction of *p*-nitroanisole by aqueous sodium sulfide under liquid–liquid mode in the presence of PTC (TBAB) was determined to be not applicable in the case of reduction of nitrotoluenes by  $H_2S$ -rich aqueous MEA.

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 reactions 2 and 1, respectively. The polysulfide is formed by the reaction of elemental sulfur (formed by reaction 2) with  $H_2S$ -rich aqueous MEA. It is mentioned in the earlier discussion that the overall conversion of MNT decreases as the elemental sulfur loading increased, because of the formation of a greater amount of polysulfides (other than disulfide), which are not easily transferred to the organic phase. Only disulfide ions form an ion pair,  $[Q^+S_2^{2-}Q^+]$ , and are transferred to the organic phase and reduce the nitrotoluenes following reaction 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 nitrotoluenes was, therefore, developed to correlate the experimentally obtained time versus conversion data. Since, the concentration of MEA in the aqueous phase was maintained at  $\sim 30$  wt %, its effect was not incorporated in this kinetic model. Based on the experimental facts, the rate of reduction of nitrotoluenes ( $-r_A$ ) is expressed by the following equation:

**Table 3.** Activation Energies and Pre-exponential Factors for Reactions of Nitrotoluenes

	$k_1 = A_{10} \exp(-AE_1/RT)$		$k_2 = A_{20} \exp(-AE_2/RT)$	
	$A_{10} ((\text{kmol}/\text{m}^3)^{-5} \text{ s}^{-1})$	$AE_1 (\text{kcal}/\text{mol})$	$A_{20} ((\text{kmol}/\text{m}^3)^{-6} \text{ s}^{-1})$	$AE_2 (\text{kcal}/\text{mol})$
<i>m</i> -nitrotoluene, MNT	$1.26 \times 10^7$	18.0	$1.94 \times 10^9$	19.2
<i>p</i> -nitrotoluene, PNT	$1.17 \times 10^9$	21.2	$1.95 \times 10^5$	13.6
<i>o</i> -nitrotoluene, ONT	$7.50 \times 10^8$	21.4	$8.76 \times 10^4$	13.4

**Figure 11.** Comparison of calculated and experimental conversions of nitrotoluenes. All conditions are the same as those given in Table 1.

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

where  $C_A$  and  $C_C$  are the concentrations of nitrotoluenes and catalyst (TBAB) in the organic phase, respectively. The second term in the aforementioned rate expression addresses the S-type nature of the curves, which are due to the formation of elemental sulfur during the reaction, as discussed previously. The course of the reduction follows the stoichiometry of reaction 2 predominantly; therefore, 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 that given by the following expressions:

$$C_S = C_{S_0} - 3f(C_{A_0} - C_A) \quad (5)$$

$$C_B = 3f(C_{A_0} - C_A) \quad (6)$$

where  $C_{S_0}$  and  $C_{A_0}$  represent the initial concentrations of sulfide and nitrotoluenes, respectively, and  $f$  is the ratio of volume of organic phase to that of the aqueous phase. A nonlinear 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

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

The optimum values of the rate constants  $k_1$  and  $k_2$  are listed in Table 3. Figure 11 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.

## Conclusions

The reduction of nitrotoluenes by  $\text{H}_2\text{S}$ -rich aqueous MEA to the corresponding toluidines was studied under liquid–liquid

mode in the presence of a phase transfer catalyst (PTC) (in this study, tetrabutylammonium bromide, TBAB). The selectivity of toluidines was 100%. The *m*-nitrotoluene (MNT) was determined to be the most reactive among the nitrotoluenes, followed by *p*-nitrotoluene (PNT) and *o*-nitrotoluene (ONT). The reactions were also observed to be kinetically controlled, with apparent activation energies of 18.2, 21.1, and 21.7 kcal/mol for MNT, PNT, and ONT, respectively. The rate of reduction of nitrotoluene was established to be proportional to the concentration of catalyst, to the square of the concentration of sulfide, and to the cube of the concentration of nitrotoluenes. The process was observed to follow a complex mechanism that involved three different reactions. Under certain experimental conditions, elemental sulfur was determined to be formed at a very high selectivity. Based on the detailed kinetic study and proposed mechanism, a general empirical kinetic model was developed. The developed model, which is applicable to all nitrotoluenes, predicts the conversions of nitrotoluenes reasonably well.

The proposed process could be considered to be a viable alternative to the Claus process, because it is possible to produce commercially important products, together with elemental sulfur (the only product of Claus process), in a cost-effective way.

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## Nomenclature

DEA = diethanolamine  
MDEA = methyldiethanolamine  
MEA = monoethanolamine  
MNT = *m*-nitrotoluene  
ONT = *o*-nitrotoluene  
PNT = *p*-nitrotoluene  
PTC = phase transfer catalyst  
TBAB = tetrabutylammonium bromide  
TEA = triethanolamine

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