Reactions of nitrotoluenes with sodium sulphide :Phase transfer catalysis and role of Ω phase

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The reactions of nitrotoluenes (o-, m- and p-) with sodium sulphide were carried out both in the liquid-liquid and solid-liquid modes with phase transfer catalyst, tetrabutylammonium bromide (TBAB). In the liquid-liquid mode, the reactions of all three nitrotoluenes were found to be kinetically controlled with activation energy values of 4.71×10^4, 5.25×10^4 and 3.92×10^4 kJ mol^{-1} with o-, m- and p-nitrotoluenes respectively as the organic substrates. In solid-liquid mode, the reactions of o- and p-nitrotoluenes were kinetically controlled whereas that of m-nitrotoluene was found to be mass transfer controlled with an activation energy of 1.16×10^4 kJ mol^{-1}. The effect of Ω phase on the rate of solid-liquid reaction was also studied and a maximum six-fold enhancement in rate was observed with m-nitrotoluene as the organic substrate.

The reduction of nitrotoluenes to the corresponding amines is commercially very important as the products—toludines have wide commercial applications as intermediates for dyes, agrochemicals and pharmaceutical products. The use of sodium sulphide 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 can it be used on substrates harmed by acid media (e.g., some ethers and thioethers). Metal hydrides (e.g., lithium aluminium hydride) generally convert nitro compounds to mixtures of azoxy and azo compounds, besides being expensive.

The advantages of the use of phase transfer catalysts in carrying out multiphase reactions efficiently are well recognized. The use of these catalysts in the two phase reductions of nitrotoluenes by sodium sulphide may be very interesting from commercial as well as academic point of view.

Different researchers have carried out the reductions of nitrotoluenes with different reagents and catalysts. Anilines have been prepared in good to excellent yields by the treatment of nitroarenes with $Fe_3(CO)_{12}$, aqueous NaOH, benzene and benzyltriethyl ammonium chloride as the catalyst[1]. Alper and Amaratunga[2] have prepared a number of amines by the treatment of corresponding nitrocompounds with CO, at room temperature and atmospheric pressure, with $Ru_3(CO)_{12}$ as catalyst and in the presence of benzyltriethyl ammonium chloride as phase transfer catalyst. $RuCl_2(PPh_3)_3$ has also been reported to catalyze the phase transfer reduction of m- and p-nitrotoluenes by synthesis gas at room temperature and atmospheric pressure with 20 to 71% yield of toludines[3].

Hashimoto and Fiji[4] have carried out reduction of p-nitrotoluene with sodium sulphide and bisulphide and have got p-toludine as the only product. Ogata et al.[5] have carried out reaction of p-nitrotoluene with sodium polysulphide and have reported 100% yield of p-toludine in 3 h. Reductions of nitroaromatics such as m-nitrochlorobenzene, m-dinitrobenzene and p-nitroaniline by aqueous solutions of sodium monosulphide and disulphide has also been carried out without using any catalyst[6]. Pradhan and Sharma[7] have carried out the phase transfer catalyzed reactions of nitrochlorobenzenes with solid sodium sulphide and have reported a change in product selectivity (from amine to diaryl sulphide) with catalyst concentration.

From the above discussion, it is clear that the information on the sulphide reduction of nitrotoluenes is very limited. Moreover, there is hardly any information on the use of phase transfer catalyst to facilitate the reaction and the role of mass transfer in such cases. It was, therefore, thought desirable to

study the phase transfer catalyzed reduction of nitrotoluenes with sodium sulphide in liquid-liquid and solid-liquid modes and to assess the role of mass transfer in the system. It was also thought desirable to assess the role of small amount of water (Ω phase) in the solid-liquid phase transfer catalyzed reactions.

Experimental Procedure
Materials

All nitrotoluenes used in this study, namely o- m- and p-nitrotoluenes were obtained from Fluka Chemica. Catalyst tetrabutylammonium bromide (TBAB) was also of Fluka grade. Sodium sulphide (extra pure) was obtained from Loba Chemie Pvt Ltd, India. Solvent toluene (99.5%) was obtained from S D Fine Chemicals Pvt Ltd, India.

Method

The reactions of nitrotoluenes (o-, m- and p-) with sodium sulphide were carried out batchwise in a 0.05 m i.d. fully baffled mechanically agitated glass reactor. A six-bladed glass disk turbine impeller of 0.015 m diameter was used for agitation. The reactor was placed in a constant-temperature polyethylene glycol 400 bath whose temperature could be controlled within $\pm$ 0.5°C. The reactions were studied in both liquid-liquid and solid-liquid modes, and toluene was used as the solvent.

In the liquid-liquid mode, 5.0×10^{-5} m^3 of aqueous phase containing known concentration of sodium sulphide was charged into the reactor and kept well-agitated until the steady-state temperature was reached. Then 5.0×10^{-5} m^3 of organic phase containing 1.0 mol m^{-3} of organic substrate and 0.025 mol m^{-3} of catalyst, TBAB, in solvent toluene, kept separately at the reaction temperature, was charged into the reactor. The speed of agitation was varied from 16.67 to 33.33 rev s^{-1}. Samples from the organic phase were withdrawn at regular intervals after stopping the agitation and complete separation of the phases.

In a typical run in the solid-liquid mode, 5.0×10^{-5} m^3 of organic phase, containing same concentrations of organic reactants and catalyst as in the liquid-liquid mode, was kept in the reactor at a predetermined temperature. Then solid sodium sulphide (Na_2S, $3.5H_2O$) of a particular size range was added in one lot and the mixture was agitated at a fixed speed of agitation. Samples from the organic phase were withdrawn as earlier after stopping the agitation and settling of the solid particles.

All the samples from the organic phase were analyzed by gas-liquid chromatography (GLC) using a 2×0.003 m stainless steel column packed with 10% OV-17 on Chromosorb W (80/100) and nitrogen as the carrier gas. The rates of reaction of organic reactants were calculated knowing the time required for a fixed conversion (20%) from the concentration versus time plot. The sodium sulphide content of the solid salt and also the concentration of the sulphide in aqueous phase were determined by the standard iodometric titration procedure[8].

Results and Discussion

The reactions of o-, m- and p-nitrotoluenes (ONT, MNT and PNT) with sodium sulphide were carried out both in the liquid-liquid and solid-liquid mode. In both the cases, 100% yields of the reduction products, i.e., toludines, were observed as reported in the literature[4,5]. The role of mass transfer in the system was assessed for both liquid-liquid and solid-liquid modes of reaction.

Liquid-liquid phase transfer catalysis (L-LPTC)

The reactions ONT, MNT and PNT with saturated of aqueous sodium sulphide were carried out in the presence of phase transfer catalyst tetrabutyl-ammonium bromide (TBAB). The effects of speed of agitation and temperature on the rates of reactions were studied with the following observations.

Effect of speed of agitation

The effect of speed of agitation on the rate of reaction of nitrotoluenes with aqueous sodium sulphide was studied by varying the speed of agitation from 16.67 to 33.33 rev s^{-1}. The rates of reactions of all the three nitrotoluenes were found to be practically independent of the speed of agitation as shown in Fig. 1. The mass transfer resistance is, therefore, negligible in case of liquid-liquid phase transfer catalyzed reduction of nitrotoluenes.

Effect of temperature

The rate of reaction of nitrotoluenes with aqueous sodium sulphide in presence of catalyst TBAB was determined at five different temperatures in the range 40-80°C as shown in Table 1. A linear regression analysis of the data obtained gives the activation energies for these kinetically controlled reactions as 4.71×10^4, 5.25×10^4 and 3.92×10^4 kJ mol^{-1} with ONT, MNT and PNT respectively as the organic substrates.

Solid-liquid phase transfer catalysis (S-LPTC)

The reactions of nitrotoluenes with solid sodium sulphide (Na_2S, $3.5H_2O$) were also carried out in the
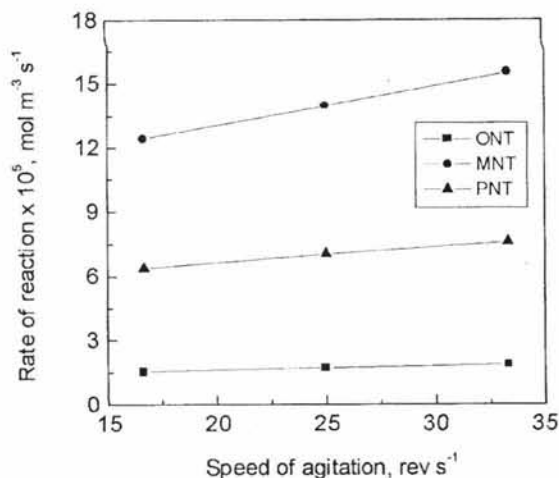
Fig. 1—Effect of speed of agitation on the rate of reaction of nitrotoluenes with aqueous sodium sulphide. Reaction conditions: Volume of organic phase = volume of aqueous phase = 5.0×10^{-5} m^3; concentration of nitrotoluenes in the organic phase = 1.0 mol m^{-3}; concentration of catalyst TBAB = 0.025 mol m^{-3} of organic phase; sodium sulphide concentration in the aqueous phase = 2.75 mol m^{-3}; temperature = 60°C; matching conversion = 20%.

Table 1—Effect of temperature on the reactions of nitrotoluenes with aqueous sodium sulphide[a]

Temperature, °C	Rate of reaction × 10^5, mol m^{-3} s^{-1} of		
	o-nitrotoluene	m-nitrotoluene	p-nitrotoluene
40	0.47	3.05	2.45
50	0.82	6.48	3.94
60	1.54	12.43	6.38
70	2.40	19.47	9.44
80	3.60	30.47	13.36

[a]Reaction conditions: Volume of organic phase = volume of aqueous phase = 5.0×10^{-5} m^3; concentration of nitrotoluenes in the organic phase = 1.0 mol m^{-3}; concentration of catalyst TBAB = 0.025 mol m^{-3} of organic phase; sodium sulphide concentration in the aqueous phase = 2.75 mol m^{-3}; speed of agitation = 16.67 rev s^{-1}; matching conversion = 20%.

presence of catalyst TBAB and the role of mass transfer in the system was assessed.

Effect of speed of agitation

The effect of speed of agitation on the rate of reaction of nitrotoluenes with solid sodium sulphide was studied by varying the speed from 16.67 to 33.33 rev s^{-1}. It can be seen from Fig. 2 that the speed of agitation has negligible effect on the rate of reaction of ONT and PNT whereas it has strong effect on the reaction of MNT as there is almost a two-fold variation in rate as the speed of agitation varies from 16.67 to 33.33 rev s^{-1}. Therefore, the reaction of MNT with solid sodium sulphide is mass transfer controlled whereas the reactions of ONT and PNT are free from mass transfer resistance.
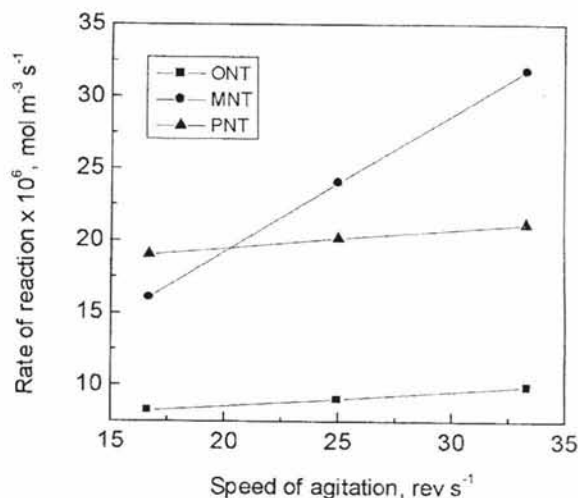

Fig. 2—Effect of speed of agitation on the rate of reaction of nitrotoluenes with solid sodium sulphide. Reaction conditions: Volume of organic phase = 5.0×10^{-5} m^3; concentration of nitrotoluenes in the organic phase = 1.0 mol m^{-3}; concentration of catalyst TBAB = 0.025 mol m^{-3} of organic phase; solid sodium sulphide ($Na_2S, 3.5H_2O$) loading = 30% (w/v); average particle size of solid sulphide = 9.25×10^{-4}m; temperature = 60°C; matching conversion = 20%.

Table 2—Effect of temperature on the reactions of nitrotoluenes with solid sodium sulphide[a]

Temperature, °C	Rate of reaction × 10^5, mol m^{-3} s^{-1} of		
	o-nitrotoluene	m-nitrotoluene	p-nitrotoluene
40	0.38	1.24	0.99
50	0.56	1.37	1.37
60	0.82	1.60	1.90
70	1.08	1.81	2.51
80	1.37	2.03	3.39

[a]Reaction conditions: Volume of organic phase = 5.0×10^{-5} m^3; concentration of nitrotoluenes in the organic phase = 1.0 mol m^{-3}; concentration of catalyst TBAB = 0.025 mol m^{-3} of organic phase; solid sodium sulphide ($Na_2S, 3.5H_2O$) loading = 30% (w/v); average particle size of solid sulphide = 9.25×10^{-4}m; speed of agitation = 16.67 rev s^{-1}; matching conversion = 20%.

Effect of temperature

Table 2 shows the rates of reactions of nitrotoluenes with solid sodium sulphide, in the presence of catalyst TBAB, determined in the temperature range of 40-80°C. The apparent activation energies were calculated from the linear regression analysis of the experimental data as 2.94×10^4 kJ mol^{-1} and 2.81×10^4 kJ mol^{-1} with ONT and PNT as organic substrates, respectively. With MNT as the organic reactant, the apparent activation energy obtained was 1.16×10^4 kJ mol^{-1}. These activation energy values indicate that the reactions of ONT and PNT with solid sodium sulphide is kinetically controlled whereas that of MNT is a mass transfer controlled one.

Table 3—Effect of added water on the reactions of nitrotoluenes with solid sodium sulphide[a]

Volume of added water × 10⁵, m³	Rate of reaction × 10⁵, mol m⁻³ s⁻¹ of		
	o-nitro-toluene	m-nitro-toluene	p-nitro-toluene
0	0.82	1.60	1.90
1.0	0.87	6.10	3.05
2.0	0.92	9.95	4.62
3.0	1.05	10.17	5.09

[a]Reaction conditions: Volume of organic phase = 5.0×10^{-5} m³; concentration of nitrotoluenes in the organic phase = 1.0 mol m⁻³; concentration of catalyst TBAB = 0.025 mol m⁻³ of organic phase; solid sodium sulphide ($Na_2S,3.5H_2O$) loading = 30% (w/v); average particle size of solid sulphide = 9.25×10^{-4}m; speed of agitation = 16.67 rev s⁻¹; temperature = 60°C; matching conversion = 20%.

Effect of added water (Ω Phase) on solid-liquid phase transfer catalysis

Different researchers have studied the effect of added water on solid-liquid phase transfer catalyzed reactions. Some studies have revealed that trace amount of water do not affect the course of reaction[9]. Some other authors maintain that a small amount of water can have a profound effect on the rate of reaction[10-16]. With complete absence of water, very little or no reaction occurs, but with increasing amounts of water, the rate goes through a maximum, decreases and finally becomes independent of the amount of water present[14-16].

In this work, the effect of Ω phase on the reactions of nitrotoluenes with solid sodium sulphide was studied by varying the amount of added water from 0 to 3.0×10^{-5} m³ and determining the rate of reaction at each stage. As the amount of water varies, the mode of operation changes from solid-liquid to solid-liquid-liquid (slurry) and finally to liquid-liquid. With ONT, added water has very limited effect as there was only a 28% increase in rate with 3.0×10^{-5} m³ added water (which forms saturated solution with the used solid sulphide) as shown in Table 3. The maximum effect was realized with MNT as the organic substrate with a six-fold enhancement in rate. With PNT as the substrate, a maximum three-fold enhancement in rate was observed with the same volume of added water. As the reaction of MNT with solid sulphide is mass transfer controlled, the maximum rate enhancement may be attributed to the facilitated mass transfer in presence of externally added water[15,17]. With ONT

and PNT, as the reactions are kinetically controlled, the added water has limited effect on the rate of reaction. It has been reported that maximum rate enhancement with added water is in the case of mass transfer controlled reactions of benzyl chloride/p-chlorobenzyl chloride with solid sodium sulphide[16].

Conclusion

The reactions of nitrotoluenes with sodium sulphide were studied in the presence of phase transfer catalyst tetrabutyl ammonium bromide (TBAB) and in both liquid-liquid and solid-liquid modes. The role of mass transfer was assessed in both the modes.

It was found that the liquid-liquid reactions of all the three nitrotoluenes were kinetically controlled. In solid-liquid mode, the reactions of ONT and PNT were found to be free from mass transfer resistance whereas that of MNT was found to be mass transfer controlled.

The effect of added water (Ω phase) was studied with all three substrates and a maximum six-fold rate enhancement was observed with mass transfer controlled reaction of MNT with solid sodium sulphide.

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