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Nitration of Benzene at High-Concentrations of Sulfuric Acid

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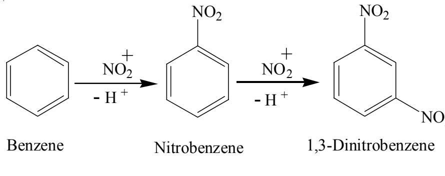
Nitration of benzene was carried out at high-concentrations of sulfuric acid (77-92 %) in a 1 L batch reactor with the objective to study the conversion of the reactants, yield and distribution of the products. A low speed of stirring (110 rpm) was employed in these studies to maintain the liquid-liquid interface flat, which facilitated the analysis. The conversion of reactants and the yield of products were good even at room temperature and at low stirring-speed. The conversion of nitric acid showed a steady increase with the increase in concentration of sulfuric acid. This increase was attributed to the increase in conversion of nitric acid to nitronium ion, whose equilibrium was shifted to the lower concentrations of H_2SO_4 in presence of the reactants. It was observed that a significant amount of 1,3-dinitrobenzene formed when the sulfuric acid concentration was greater than 85 %. The formation of 1,3-dinitrobenzene increased with the increase in concentration of sulfuric acid and increase in temperature. The conversion of benzene and the yield of nitrobenzene decreased accordingly.

Key Words: Aromatic nitration, Benzene, Conversion, Mixed acid, Nitrobenzene, Yield.

INTRODUCTION

Nitration of benzene is a very important reaction in organic process industries. The standard industrial procedure is to react benzene with a mixture of nitric and sulfuric acids (the so-called mixed-acid). Most of the reaction takes place in the aqueous phase[1]. Sulfuric acid constitutes the medium in which the reaction occurs. Its amount is usually much larger than the amounts of nitric acid and benzene. The nitronium ion (which acts as the electrophile) is generated by the reaction between sulfuric and nitric acids. The former acts as the catalyst in the reaction[2]. The benzene molecules diffuse across the interface into the aqueous phase and react with the nitronium ions present there. Two products are possible from this reaction *i.e.*, nitrobenzene and 1,3-dinitrobenzene. The latter forms by the nitration of nitrobenzene, as shown schematically below:

 (1)

The other isomers of dinitrobenzene do not form any significant amount. The products diffuse back to the organic phase depending upon their solubility in the aqueous phase.

The major use of nitrobenzene is in the production of aniline. It is also used in shoe and floor polishes, leather dressing, paint solvents and in the manufacture of perfumes. The major uses of 1,3-dinitrobenzene are in ammonia batteries, rubber processing and in the manufacture of dyes and drugs.

Nitration of benzene is a second-order reaction, first-order with respect to benzene as well as nitronium ion[3].

$$\text{rate} = k[\text{Benzene}][NO_2^+] \quad (2)$$

The generation of nitronium ion can be represented by the following reversible reaction[4].

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^- \quad (3)$$

Equation 3 represents the equilibrium between nitronium ion and nitric acid. The equilibrium constant is given by,

$$K = \frac{a_{NO_2^+} a_{H_2O}}{a_{HNO_3} a_{H^+}} = \frac{[NO_2^+]}{[HNO_3]} \frac{\gamma_{NO_2^+}}{\gamma_{HNO_3}} \frac{a_{H_2O}}{a_{H^+}} \quad (4)$$

where a and γ represent the activity and activity coefficient of the species, respectively. Therefore, the ratio of concentrations of nitronium ion and nitric acid is,

$$\frac{[NO_2^+]}{[HNO_3]} = \frac{K\gamma_{HNO_3} a_{H^+}}{\gamma_{NO_2^+} a_{H_2O}} \quad (5)$$

The right side of eqn. 5 is a constant at a particular temperature and at a fixed concentration of sulfuric acid. It has been reported in the literature that the value of $[NO_2^+]/[HNO_3]$ increases with the increase in concentration of sulfuric acid[4,5]. The increase is particularly rapid when the concentration of sulfuric acid is increased from 88 to 92 %[5].

Industrially, nitrobenzene is manufactured in batch as well as flow reactors[6]. The concentration of sulfuric acid used in commercial reactors is usually between 60 and 75 %. These reactors are operated at high temperatures (> 373 K) and at high speeds of agitation (> 1000 rpm). Most of the laboratory studies reported in literature on the nitration of benzene have been carried out at sulfuric acid concentrations below 80 %[7-9]. In these works, benzene was dissolved in sulfuric acid (sometimes with the help of acetic acid) and nitration was carried out in small cuvettes. The progress of reaction was monitored by UV-visible spectroscopy. Kobe and Mills[10] studied nitration of benzene at high-concentrations (70-95 %) of sulfuric acid in a batch reactor. However, they have not reported the second reaction (*i.e.*, nitration of nitrobenzene) and its effect on the conversion of benzene and yield of nitrobenzene.

From the foregoing discussion, it is evident that the experimental studies reported so far in the literature mostly consisted of the reactions carried out at low-concentrations of sulfuric acid in small cuvettes where the reaction mass was very small. The main difficulty of the spectroscopic method is that the absorbance curves of nitrobenzene and 1,3-dinitrobenzene overlap with each other in the mixture. The simultaneous nitration of nitrobenzene during the nitration of benzene has not been studied in any detail. The objective of the present work was to study the nitration of benzene at high-concentrations of sulfuric acid (between 77 and 92 %) in a 1 L batch reactor made of glass. The effects of concentration of sulfuric acid and temperature were studied. The conversion of benzene and nitric acid and the yields of nitrobenzene and 1,3-dintrobenzene were studied at 298, 310 and 317 K in this concentration range. The concentration profiles of the reactants and products have been developed. The difference between the nitration of benzene and nitrobenzene has also been pointed out.

EXPERIMENTAL

Benzene (99 % purity), sulfuric acid (98 % by wt.), nitric acid (70 % by wt.), sodium hydroxide (99 % purity), oxalic acid (99 % purity), phenolphthalein (99 % purity), acetone (HPLC grade), acetonitrile (HPLC grade) and methanol (HPLC grade) were procured from Merck (India). Standard samples of nitrobenzene (99 % purity), benzene sulfonic acid (99 % purity) and 1,3-dinitrobenzene (97 % purity) were procured from Alfa Aesar (India). The water used in this study was purified from a Millipore® water purification system. Its conductivity was $1 \times 10^{-7}\ \Omega^{-1}\ cm^{-1}$ and its surface tension was 72 mN/m (298 K). Sulfuric acid solutions of lower concentration were prepared by diluting the 98 % acid with water. The actual concentrations of the acids were measured by titration with a standard NaOH solution.

Conditions: The experiments were conducted at 298, 310 and 317 K. The temperature in the reactor was maintained within ± 1 K of the target temperature by a water-circulator, which had provisions for heating and cooling. The temperature of the reaction mass was measured with a thermometer.

Procedure: The nitration was carried out in a 1 L unbaffled glass reactor (diameter = 100 mm) placed in a water bath. The bath was connected to the water-circulator mentioned before. The glass agitator had two paddle-type impellers such that the upper paddle stirred the organic phase whereas the lower paddle stirred the aqueous phase. Both the paddle impellers had four vertical blades, which were fused to the agitator shaft at 90° to each other. The length of the blades was 25 mm and their height was 15 mm. The speed of the agitator was kept constant at 110 ± 5 rpm such that the interface remained flat during the experiments[11]. This procedure enabled us to collect the samples from the two phases intermittently during the course of reaction. At higher rotational speeds (> 150 rpm) sporadic dispersions of organic droplets in the aqueous phase developed, which induced inaccuracy in the collection of the samples. Therefore, for this study, the rotational speed was kept at

110 ± 5 rpm. Benzene and nitric acid were charged to the reactor in equimolar quantities in all experiments. Samples (*ca.* 1 g) from each of the phases were collected at *ca.* 5 and 10 min intervals, depending on the progress of the reaction. Two sets of samples were collected during every withdrawal. One set of samples was collected in 10 mL methanol, which was analyzed for the determination of the concentrations of benzene and nitrobenzene in the aqueous and organic phases. The other set was collected in 10 mL acetone, which was analyzed for determination of the concentration of 1,3-dinitrobenzene in the two phases. The reaction was quenched by dilution, followed by rapid chilling. Benzene and nitrobenzene were analyzed by HPLC (make: Perkin-Elmer; model: Series 200; detector: UV, λ = 254 nm) using C-18 column [make: Merck (Germany)]. The mobile phase was constituted of acetonitrile and water in 4:1 volumetric ratio. 1,3-Dinitrobenzene was analyzed by Janovsky's test[12] using UV-visible spectroscopy (make: Perkin-Elmer; model: Lambda 35). The detection was carried out at λ_{max} = 570 nm. This test is specific for 1,3-dinitrobenzene. Neither benzene nor nitrobenzene responds to this test.

It was found that benzene underwent spontaneous sulfonation in sulfuric acid in absence of nitric acid. The combined amount of free-benzene in the aqueous phase and benzene converted to its sulfonic acid derivative indicated that the solubility of benzene in the aqueous phase was low, which has been supported by Marziano *et al.*[9]. The degree of sulfonation increased with the increase in concentration of sulfuric acid. However, in presence of nitric acid, no sulfonation was detected until HNO_3 was exhausted.

RESULTS AND DISCUSSION

Conversion of nitric acid: The conversion of nitric acid increased with the increase in concentration of sulfuric acid as shown in Fig. 1. The conversion of nitric acid was less than 20 % when the concentration of sulfuric acid was below 80 %. However, the conversion increased rapidly when the concentration of sulfuric acid was increased beyond 83 %. The conversion of nitric acid was practically complete in 90 % sulfuric acid at 298 K. The conversion profile shown in Fig. 1 is similar to the profile reported in literature[5] representing the conversion of nitric acid to nitronium ion. However, the latter profile showed the rapid increase in the conversion of nitric acid at sulfuric acid concentrations above 87 %. The shift in the conversion of nitric acid in presence of benzene (and nitrobenzene) to the lower concentrations of sulfuric acid may be due to the consumption of the nitronium ions by reaction with these reactants so that the equilibrium for the reaction represented by eqn. 3 was shifted to the right side producing more nitronium ion. This caused more conversion of nitric acid at the lower concentrations of H_2SO_4. The conversion of nitric acid increased with the increase in temperature and 100 % conversion was achieved at lower concentrations of sulfuric acid. The sulfuric acid concentrations reported in Fig. 1 are the initial concentrations, *i.e.*, when the reactants were charged to the reactor. During the course of reaction, the concentration of sulfuric acid decreased by dilution with water generated by the reaction. Therefore, it can be concluded that the shift in the equilibrium for the conversion of nitric acid to nitronium ion was quite significant in presence of the reactants.

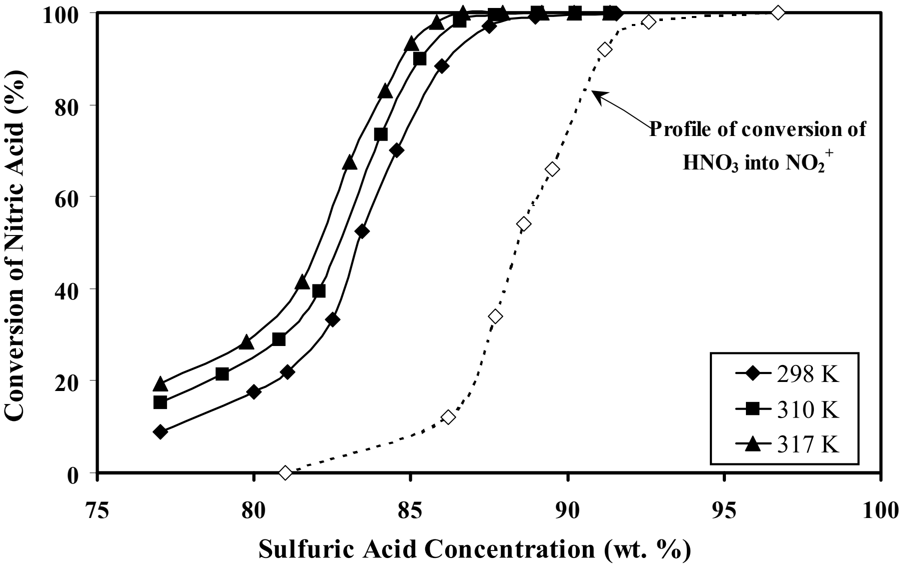


Fig. 1. Variation of conversion of nitric acid (measured after 1 h of reaction) with the concentration of sulfuric acid. The dotted line represents the conversion of nitric acid to nitronium ion reported [Ref. 5]

Conversion of benzene: The conversion profiles of benzene with increase in concentration of sulfuric acid are shown in Fig. 2. It can be observed from Fig. 2 that conversion increased with the increase in concentration of sulfuric acid. It reached a maximum around 87 % concentration of H_2SO_4, then decreased at the higher concentrations of the acid. Another important point observed from these figures is that the maximum conversion of benzene was about 80 %. Since the reactants, nitric acid and benzene, were charged to the reactor in equimolar quantities and the second reaction represented by eqn. 1 (*i.e.*, conversion of nitrobenzene to 1,3-dinitrobenzene) took place significantly, the conversion of nitric acid was completed well before the complete conversion of benzene. Therefore, a significant amount of benzene remained unreacted even though the conversion of nitric acid was completed. Nitric acid, therefore, was the limiting reactant for this reaction. It was consumed appreciably in the nitration of nitrobenzene. At sulfuric acid concentrations below 85 %, the conversion of benzene increased with the increase in temperature. However, at higher concentrations of H_2SO_4, the conversion decreased with increase in temperature since the extent of nitration of nitrobenzene increased with increase in temperature.

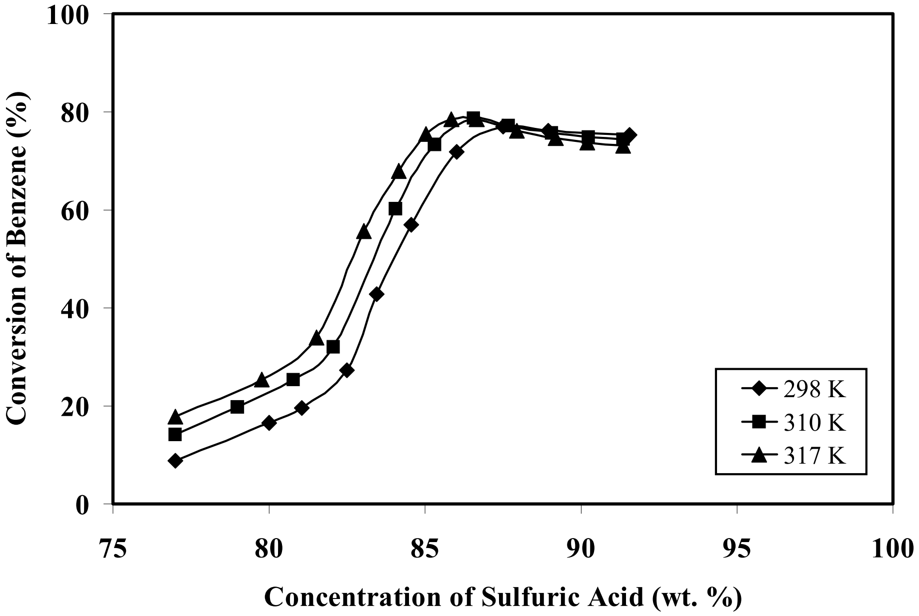


Fig. 2. Variation of conversion of benzene (measured after 1 h of reaction) with the concentration of sulfuric acid

Yield of nitrobenzene: The variation of yield of nitrobenzene (measured after 1 h of reaction) with the concentration of sulfuric acid is shown in Fig. 3. The yield decreased after *ca.* 87 % concentration of sulfuric acid. The reason for the decrease in yield is the higher rate of nitration of nitrobenzene at these concentrations of sulfuric acid. This reaction occurs at the lower concentrations of H_2SO_4 also, but the rate increases significantly at the higher concentrations of the acid. As mentioned in the 'Introduction' section, the nitration of organic compounds takes place in the aqueous phase. The solubility of benzene in sulfuric acid is much lower than the solubility of nitrobenzene. In fact, the solubility of nitrobenzene is quite high at sulfuric acid concentrations higher than 87 %[13]. A significant part of the nitrobenzene molecules remains in the aqueous phase after they are formed in the same phase. These molecules form very small droplets similar to the droplets of a microemulsion[13]. Therefore, at these concentrations of sulfuric acid, the nitronium ions encountered the nitrobenzene molecules in much greater numbers than the benzene molecules. In spite of the significantly lower rate of nitration of nitrobenzene as compared to benzene[2], its abundant availability in the aqueous phase rendered it a good competitor of benzene for reaction with the nitronium ions. Increase in temperature caused further conversion of nitrobenzene, which reduced its yield.

Yield of 1,3-dinitrobenzene: The variation of yield of 1,3-dinitrobenzene with the concentration of sulfuric acid is shown in Fig. 4. The yield was very small when the concentration of sulfuric acid was below 80 %. However, as the concentration

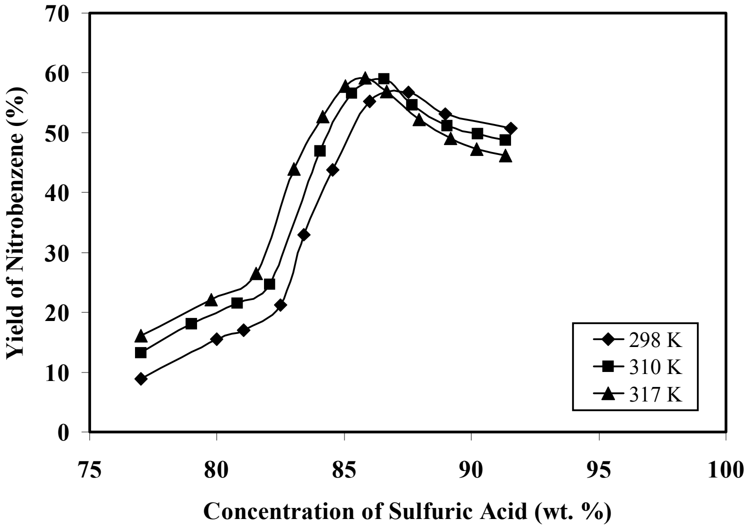


Fig. 3. Variation of yield of nitrobenzene (measured after 1 h of reaction) with the concentration of sulfuric acid

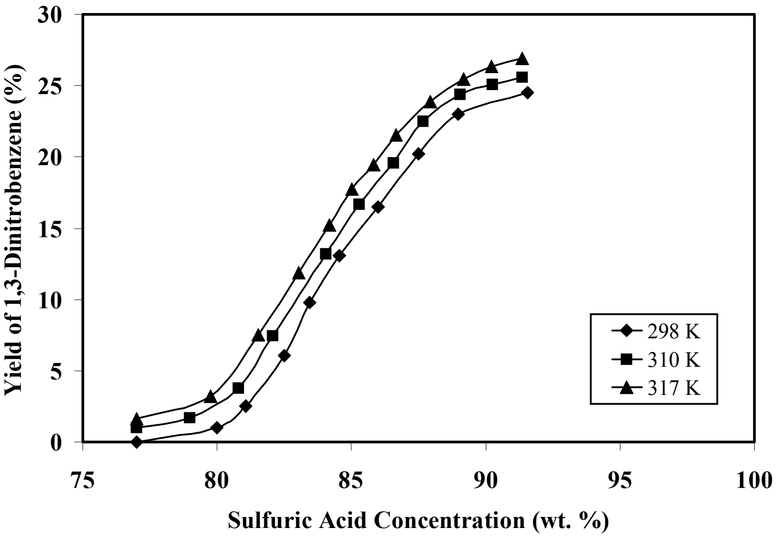


Fig. 4. Variation of yield of 1,3-dinitrobenzene (measured after 1 h of reaction) with the concentration of sulfuric acid

of sulfuric acid was increased, the yield steadily increased due to the reasons mentioned before. The formation of 1,3-dinitrobenzene also increased with the increase in temperature. The rate of increase in the yield of 1,3-dinitrobenzene with H_2SO_4 concentration became slower at acid concentrations > 90 % due to the near-complete conversion of HNO_3.

Concentration profiles in the reactor: The variation of concentrations of nitric acid, benzene, nitrobenzene and 1,3-dinitrobenzene with time are shown at three different concentrations of sulfuric acid at 298 K in Figs. 5-7. The concentration of benzene in the aqueous phase was practically zero during the experimental runs. Since the solubility of benzene in sulfuric acid is low and its reactivity is high, the small amount of benzene which diffused into the aqueous phase immediately reacted to form nitrobenzene. Fig. 5 shows the concentration profiles in 82.6 % H_2SO_4. It can be observed that the concentration of the reactants decreased and the same for the products increased very slowly with time. This happened due to the slow rate of reaction at this concentration of sulfuric acid. Therefore, the conversions and yields depicted in Figs. 1-4 were also low corresponding to this concentration. The concentration profiles in 86 % H_2SO_4 are shown in Fig. 6. At this concentration, however, the rate of reaction was very high. Therefore, the concentrations of the reactants decreased rapidly and the same for the products increased accordingly. These concentration profiles reflect the usual features of the series-parallel reactions. Similar concentration profiles were observed for 89 % H_2SO_4 (Fig. 7) as well. However, it can be observed from this figure that the concentration of nitric acid was virtually zero after 1 h of reaction. The concentration of nitrobenzene was lower than its concentration in 86 % H_2SO_4 after 1 h of reaction. The concentration of nitrobenzene reached maximum at 40 min, after which it decreased with time due to its conversion to 1,3-dinitrobenzene. The concentration profiles of 1,3-dinitrobenzene showed increase with time in all three systems presented in Figs. 5-7. However, its concentration was quite low for 82.6 % H_2SO_4.

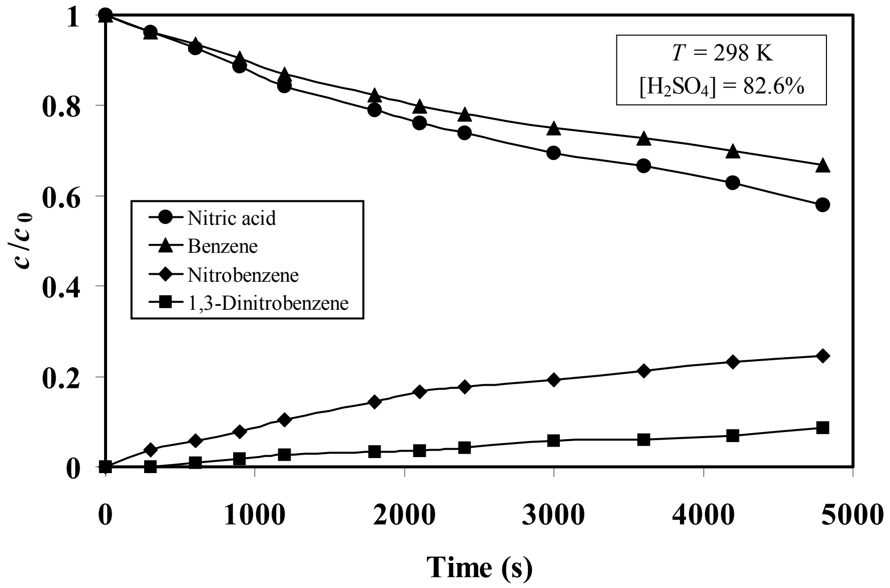


Fig. 5. Concentration profiles of the reactants and products in the reactor for 82.6 % H_2SO_4

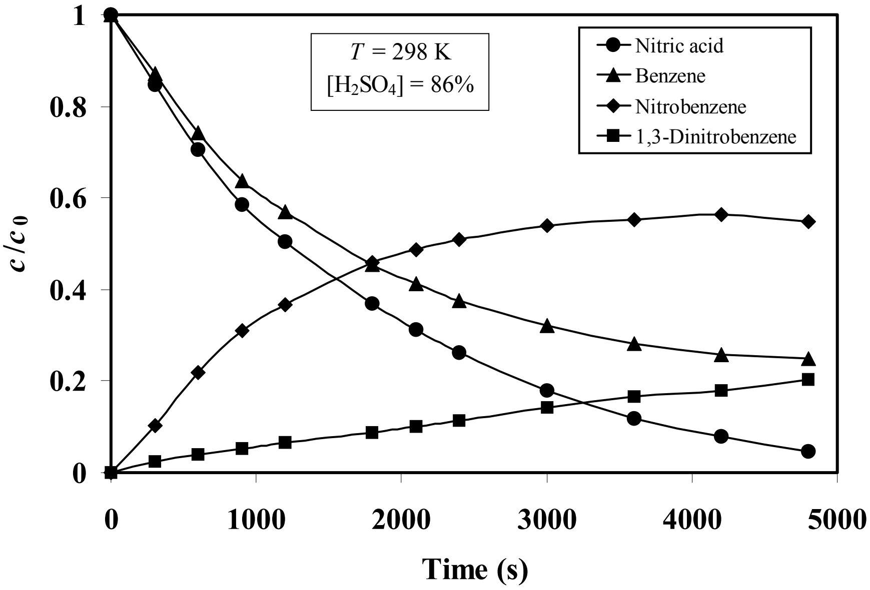


Fig. 6. Concentration profiles of the reactants and products in the reactor for 86 % H_2SO_4

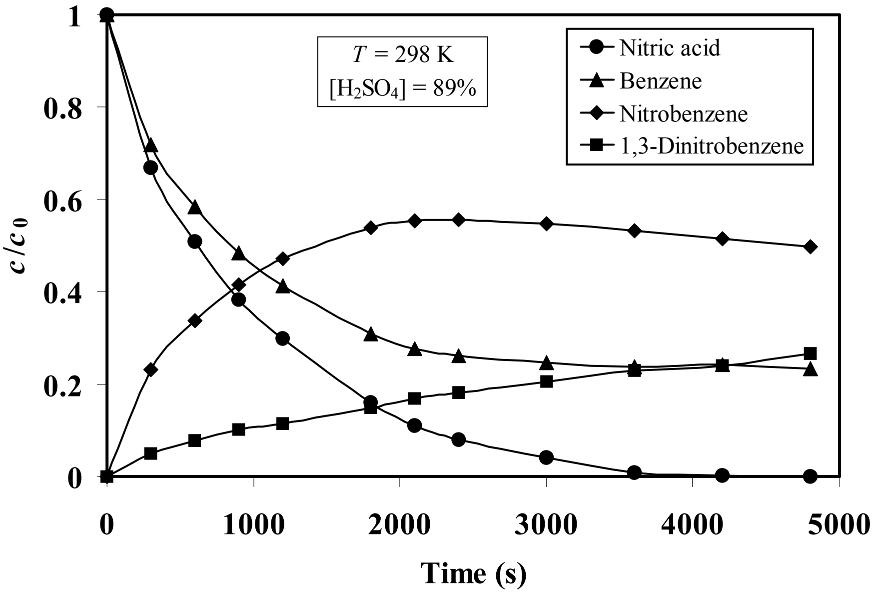


Fig. 7. Concentration profiles of the reactants and products in the reactor for 89 % H_2SO_4

Conclusion

This work has presented the details of the reactions occurring in the nitration of benzene in a batch reactor at high-concentrations of sulfuric acid. Good conversion of the reactants was achieved even at moderate temperatures and at low speed of stirring. Both nitrobenzene and 1,3-dinitrobenzene were produced in the reactor. The high conversion of nitric acid to nitronium ions facilitated the reactions. It was demonstrated that the $HNO_3 \rightleftharpoons NO_2^+$ equilibrium was shifted to the lower concentrations of sulfuric acid in presence of the reactants (*i.e.*, benzene and nitrobenzene). At high-concentrations of sulfuric acid, nitration of nitrobenzene was favoured by its high-concentration in the aqueous phase. The conversion of nitric acid was completed when the H_2SO_4-concentration was *ca*. 90 %, however, the conversion of benzene was not complete due to the consumption of nitric acid in the nitration of nitrobenzene. At sulfuric acid concentrations > 86 %, the conversion of benzene and yield of nitrobenzene decreased whereas the yield of 1,3-dinitrobenzene increased steadily. The yield of 1,3-dinitrobenzene was enhanced with the increase in temperature. The concentration profiles in the batch reactor showed the details of conversion of the reactants and the formation of the products with time, which resembled those of series-parallel reactions.

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