Nitration of Nitrobenzene at High-Concentrations of Sulfuric Acid: Mass Transfer and Kinetic Aspects

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This article reports studies on mass transfer and kinetics of nitration of nitrobenzene at high concentrations of sulfuric acid in a batch reactor at different temperatures. The effects of concentration of sulfuric acid, speed of stirring, and temperature on mass transfer coefficient were investigated. The kinetics of nitration under homogenized conditions was studied at different sulfuric acid concentrations at these temperatures. The reaction rate constants were determined. The variation of rate constant with sulfuric acid concentration was explained by the M_c *function. The activation energies of the reactions were determined from the Arrhenius plots. The regimes of the reactions were determined using the values of the mass transfer coefficients and the reaction rate constants. A model was developed for simultaneous mass transfer and chemical reaction in the aqueous phase. The yields of the three isomers of dinitrobenzene were determined, and the variation of isomer distribution with sulfuric acid concentration and temperature was analyzed. This work demonstrates that more than 90% conversion of nitrobenzene is possible at high-sulfuric acid concentrations resulting in high yield of the product even at moderate temperatures and at low speeds of stirring.*

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Keywords: activation energy, aromatic nitration, isomer distribution, mass transfer coefficient, mixed acid, rate constant, yield

Introduction

Aromatic nitration by mixed acid is one of the most ubiquitous reactions in the organic chemical industries. It is a heterogeneous liquid–liquid reaction, which occurs almost exclusively in the aqueous phase. The organic compound diffuses into the aqueous mixed-acid-phase and reacts with the nitronium ion generated by the reaction between concentrated sulfuric acid and nitric acid. In our previous study,[1] it was shown that the amount of nitrobenzene transported into the mixed-acid-phase is important for the yield of the product. Therefore, it is necessary to determine the mass transfer coefficient for transport of nitrobenzene into sulfuric acid to predict the rate of mass transfer and hence, the rate of reaction. The major parameters that influence the rate of mass transfer are the concentration of sulfuric acid, the temperature of reaction, and the speed of stirring. The first two parameters significantly affect the kinetics of the reaction. Kinetic studies of nitration of benzene,[2] toluene,[3] chlorobenzene,[4] and nitrobenzene[5–7] have been reported in the literature. However, only a few works have reported kinetic studies at high concentrations of sulfuric acid. Marziano and Sampoli[6] carried out the reactions in small cuvettes and the progress of reaction was studied spectrophotometrically. On the other hand, Westheimer and Kharasch[7] determined the rate constants by a calorimetric procedure. Very few works have reported mass transfer studies in aromatic nitration, possibly due to the high reactivity of the aromatic

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compounds toward sulfuric acid leading to the sulfonation of the reactants. Experimental studies on mass transfer of nitrobenzene in sulfuric acid have been carried out by Modak and Juvekar[5] with sulfuric acid concentrations between 14.0 and 15.6 kmol/m^3. They have employed a stirring speed ca. 2π rad/s and carried out the experiments at 300 K.

From the review of the literature on the nitration of aromatic compounds, it has been observed that a high temperature and a high speed of stirring are usually employed even when the aromatic ring is active, such as that in benzene. In our earlier work on the nitration of nitrobenzene[1] for which the aromatic ring is deactivated, it has been demonstrated that good yield of the product is achievable, even at room temperature and at a low stirring speed, if the concentration of sulfuric acid is high. This shows the prospect that high yield can be achieved if a moderately higher temperature is used in the reactor. So far, the mass transfer studies on the nitration of nitrobenzene have been restricted to sulfuric acid concentrations upto 15.6 kmol/m^3 and at room temperature. The reaction rate constants have been reported at the high-sulfuric acid concentrations at 298 and 313 K in cuvettes and in a calorimeter. The yield of reaction and the distribution of the product isomers at different sulfuric acid concentrations and at different temperatures have not been determined so far. The objective of this work is to determine the mass transfer coefficients and the reaction rate constants for the nitration of nitrobenzene at high concentrations of sulfuric acid at room temperature and at moderately higher temperatures. These parameters are very essential for the rational design of the nitration process. The mass transfer coefficients were determined following a procedure similar to that described by Modak and Juvekar.[5] The results have been described in the section entitled "Determination of mass transfer coefficient." A novel method was employed to determine the rate constants under homogenized conditions, which has been depicted in the section entitled "Determination of reaction rate constants." Using the values of mass transfer coefficients and the rate constants, the reaction regimes were determined, which has been illustrated in the section entitled "Determination of reaction regime." Finally, a model was developed for simultaneous mass transfer with chemical reaction in the aqueous phase using the values of the mass transfer coefficients and the rate constants. The details of this procedure have been discussed in the section entitled "Model for mass transfer with chemical reaction." The total yields of the dinitrobenzene isomers were determined at sulfuric acid concentrations between 14.1 and 17.1 kmol/m^3 at 313 and 323 K. The yield of 1.3-Dintrobenzene at 298 K was reported in our previous study.[1] The percentage of the three isomers of dinitrobenzene at these sulfuric acid concentrations and temperatures have also been determined. This has been described in the section entitled "Determination of yield and distribution of isomers of dinitrobenzene."

Experimental

Nitrobenzene (99% purity), sulfuric acid (18.3 kmol/m^3), and nitric acid (15.5 kmol/m^3) were procured from Merck (India). Standard organic samples, 1,2-Dinitrobenzene (99% purity), 1,3-Dinitrobenzene (97% purity), 1,4-Dinitrobenzene (98% purity), and 3-Nitrobenzenesulfonic acid (sodium salt, 98% purity) were procured from Alfa Aesar (India). HPLC-grade methanol, water, acetonitrile, pentane, dichloromethane, and 2-Propanol were procured from Merck (India). Sulfuric acid solutions of lower concentrations were prepared by diluting the concentrated acid (18.3 kmol/m^3) with water. The water used in this study was purified from a Millipore® water purification system. Its conductivity and surface tension were $1 \times 10^{-7}\ \Omega^{-1}\ \text{cm}^{-1}$ and 72 mN/m (at 298 K), respectively.

To determine the mass transfer coefficient of nitrobenzene in aqueous sulfuric acid, it is necessary to find out the equilibrium solubility of nitrobenzene in sulfuric acid. A heterogeneous mixture of nitrobenzene and sulfuric acid was prepared. The amount of nitrobenzene in the mixture was twice its amount that could be dissolved in sulfuric acid under equilibrium conditions. The mixture was stirred using a magnetic stirrer in a sealed glass vessel placed inside a water bath. The temperature of the bath was maintained by a thermostatic water circulator. The equilibrated mixture was allowed to separate into two phases for 1 day inside the bath. Samples from the aqueous phase were collected by inserting a pipette through the organic phase. About 1 g of sample from each phase was collected, dissolved in methanol, and then analyzed. The amount of nitrobenzene present in the sample was determined by UV-Visible spectrophotometry (make of the spectrophotometer: Perkin-Elmer, model: Lambda 35). The absorption of nitrobenzene was measured at $\lambda_{\text{max}} = 260$ nm. Samples from the organic phase were dissolved in water. The amount of sulfuric acid dissolved in the organic phase was determined by acid–base titration using aqueous NaOH that was standardized with oxalic acid. All these experiments were repeated thrice to check the reproducibility. The results were highly reproducible.

The possibility of formation of 3-Nitrobenzenesulfonic acid at temperatures higher than 298 K was investigated by HPLC [make: Perkin-Elmer, model: Series 200, column: Hibar-Purospher-STAR RP-18 (Merck), detector: UV, $\lambda = 254$ nm]. The mobile phase was constituted of acetonitrile and water in 3:2 volumetric ratio. Its flow rate was maintained at 16.67×10^{-3} cm^3/s.

The experiments to determine the mass transfer coefficient of nitrobenzene were carried out by the batch dynamic process. Nitrobenzene was contacted with sulfuric acid (without any nitric acid) of different concentrations in the glass reactor placed in a water bath. The reactor has been described in our previous study.[1] The transfer of nitrobenzene into the aqueous phase was measured as a function of time. For the determination of the amount of nitrobenzene in the aqueous phase, ca. 1 g of samples were collected at definite time intervals. The samples were dissolved in methanol. The amount of nitrobenzene present in the sample was determined by UV-Visible spectroscopy as described earlier. The mass transfer coefficients were determined at 298 and 313 K at sulfuric acid concentrations between 14.1 and 17.4 kmol/m^3 at the impeller speeds of 2π and 4π rad/s.

Kinetic studies of nitration were carried out in the batch reactor under homogenized condition. Experiments for the determination of rate constant were carried out between 14.1 and 17.2 kmol/m^3 sulfuric acid concentrations at 298, 313, and 323 K. Stock solutions of each sulfuric acid concentration were prepared for carrying out the reactions. Using the acid from the same stock solution, the nitration reactions were carried out at the three temperatures. The initial nitric acid/nitrobenzene mole ratio (M) was 1:2 for studying the second-order kinetics. It was experimentally established that the value of the second-order rate constant did not vary with M. The experimental procedure was as follows. A known amount of nitrobenzene was dissolved in sulfuric acid in the reactor placed in the water bath, and the mixture was stirred rapidly to attain homogeneity. The amount of nitrobenzene dissolved in sulfuric acid was 20–30% of its equilibrium solubility at the corresponding sulfuric acid concentration. Sulfonation of nitrobenzene did not occur under these conditions. After the dissolution of nitrobenzene was complete, nitric acid of required amount was added to the reactor, and the reaction mixture was stirred at the impeller speed of 2π rad/s. The samples were withdrawn from the reactor at certain time intervals. They were dissolved in methanol and chilled to quench the reaction. The concentrations of the reactant (i.e., nitrobenzene) and product (i.e., 1,3-Dinitrobenzene) were analyzed by HPLC (column: Hibar-Purospher-STAR RP-18 (Merck), detector: UV, $\lambda = 254$ nm). The mobile phase was constituted of acetonitrile and water in 3:2 volumetric ratio. Its flow rate was maintained at 16.67×10^{-3} cm^3/s. The advantage of the experimental procedure described earlier was that the effect of water produced in the reaction was insignificant to dilute the sulfuric acid medium, and the analysis could be performed by HPLC rather than by UV-Visible spectrophotometry in which both nitrobenzene and 1,3-Dinitrobenzene absorb at the same region of the spectrum.

Heterogeneous nitration of nitrobenzene was carried out in the reactor at 15.7 kmol/m^3 sulfuric acid concentration at 298 K. Nitric acid and nitrobenzene were charged to the reactor in 1:3 mole ratio to reduce the formation of solid dinitrobenzene isomers in the aqueous phase. The aqueous phase was prepared by mixing nitric acid, sulfuric acid, and water in the required proportion. The mixed acid was first charged into the reactor. A known amount of pure nitrobenzene was then poured carefully on top of the aqueous phase. Agitation of the two phases was then maintained at 2π rad/s under flat-interface condition. The samples from the aqueous as well as the organic phases were collected at ~5-min intervals. They were dissolved in methanol and chilled to quench the reaction. The concentrations of the reactant (i.e., nitrobenzene) in the aqueous phase and the product (i.e., the dinitrobenzene isomers) in both phases were analyzed by HPLC as described earlier.

The yield of 1,3-Dinitrobenzene at 298 K was reported in our previous study.[1] The yields at 313 and 323 K were determined by keeping the molar ratio of sulfuric acid:nitrobenzene:nitric acid constant at 4:1:1. The reaction was carried out for 1 h. The two phases were stirred at 2π rad/s. The solid product and the unreacted reactants were removed immediately from the reactor, diluted with water, and chilled with ice to quench any further reaction. The solid product was filtered out and repeatedly washed with water to remove the trace amounts of the reactants. Then, it was dried *in vacuo* and the amount of product was determined gravimetrically.

The amounts of the three isomers of dinitrobenzene were determined at different sulfuric acid concentrations at the three temperatures mentioned earlier. The solid product was thoroughly triturated in a mortar and the triturated mixture was ground in a ball mill to obtain a uniform mixture of the isomers. The isomer distribution was analyzed by HPLC by adapting the method given in literature.[8] The procedure was as follows. A small amount of the reaction product (after triturating and grinding) was dissolved in 2-Propanol and diluted with dichloromethane. The solution was then analyzed by HPLC (column: Brownlee Analytical Silica 5 μm (Perkin-Elmer), detector: UV, $\lambda = 254$ nm). The mobile phase was constituted of a mixture of pentane (99.5%) and 2-Propanol (0.5%), and dichloromethane in 4:1 volumetric ratio. Its flow rate was maintained at 11.67×10^{-3} cm^3/s.

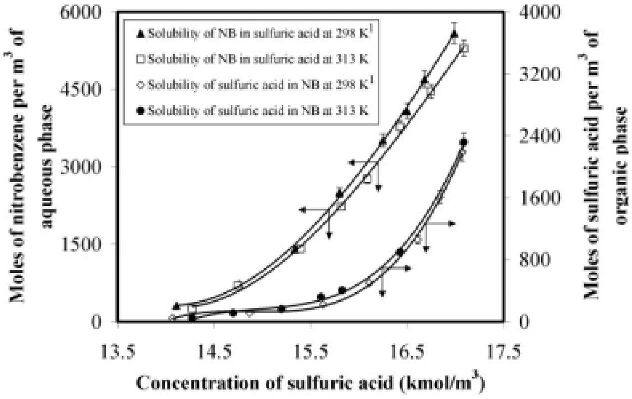

Figure 1. Variation of solubility of nitrobenzene in sulfuric acid (and vice versa) with the concentration of sulfuric acid at different temperatures ('NB' represents nitrobenzene).

Results and Discussion

Determination of mass transfer coefficient

The rate of change of concentration of nitrobenzene in the aqueous phase can be described by the following,

$$\frac{d}{dt}\left(V_{\mathrm{a}}C_{\mathrm{NB}}^{\mathrm{a}}\right) = \left(\frac{k_L A}{V_{\mathrm{a}}}\right)\left(V_{\infty}\overline{C}_{\mathrm{NB}} - V_{\mathrm{a}}C_{\mathrm{NB}}^{\mathrm{a}}\right) \tag{1}$$

where $C_{\mathrm{NB}}^{\mathrm{a}}$ is the concentration of nitrobenzene in the aqueous phase, $\overline{C}_{\mathrm{NB}}$ is the equilibrium concentration of nitrobenzene in the aqueous phase, k_L is the mass transfer coefficient, A is the interfacial area ($= \pi d^2/4$, where d is the diameter of the reactor), V_{∞} is the volume of the equilibrated mixture of nitrobenzene and sulfuric acid, and V_{a} is the volume of the aqueous phase at time t. Equation 1 takes into account the change in volume of the aqueous phase that occurs especially at the high concentrations of sulfuric acid. From Eq. 1, it can be observed that the value of equilibrium concentration of nitrobenzene in the aqueous phase ($\overline{C}_{\mathrm{NB}}$) is required to determine the mass transfer coefficient. The data on equilibrium solubility of nitrobenzene in sulfuric acid and vice versa at 313 K are shown in Figure 1. The data at 298 K from our previous study[1] are also shown in the figure for comparison. The solubility of nitrobenzene was found to increase with the increase in concentration of sulfuric acid. The increase in solubility of nitrobenzene was due to the formation of a dispersion of nitrobenzene into the sulfuric acid, which resembles a microemulsion.[1] It is likely that this dispersion is thermodynamically stable as the standard microemulsions.[9] It can be observed from Figure 1 that the solubility of nitrobenzene decreased slightly with increase in temperature, especially at the higher concentrations of sulfuric acid (i.e., between 15.5 and 17.2 kmol/m^3). The rupture of the hydrogen bonds at the higher temperature is believed to be the reason behind the decrease in solubility. The solubility of sulfuric acid in the organic phase increased with the concentration of sulfuric acid. However, the effect of temperature on the solubility of sulfuric acid in the organic phase was small. The experiments on solubility at temperatures higher than 313 K were not carried out due to the sulfonation of nitrobenzene. It was observed that a significant amount of 3-Nitrobenzenesulfonic acid was formed at 323 K.

Assuming that the change in volume of the aqueous phase occurs solely due to the transfer of nitrobenzene into the aqueous phase, and that the volume change of mixing is negligible, V_a can be expressed as follows:

$$V_{\mathrm{a}} = \frac{V_0}{\left(1 - C^{\mathrm{a}}_{\mathrm{NB}} M_{\mathrm{NB}}/\rho_{\mathrm{NB}}\right)} \tag{2}$$

where V_0 is the initial volume of the aqueous phase, M_{NB} is the molecular weight of nitrobenzene, and ρ_{NB} is its density. Inserting the values of V_a and $\frac{dV_a}{dt}$ in Eq. 1 we get,

$$\frac{dC^{\mathrm{a}}_{\mathrm{NB}}}{dt} = \left(\frac{k_L A}{V_0^2}\right)\left(1 - C^{\mathrm{a}}_{\mathrm{NB}} M_{\mathrm{NB}}/\rho_{\mathrm{NB}}\right)^2 \times \left[V_\infty \overline{C}_{\mathrm{NB}} - \left(V_\infty \overline{C}_{\mathrm{NB}} M_{\mathrm{NB}}/\rho_{\mathrm{NB}} + V_0\right) C^{\mathrm{a}}_{\mathrm{NB}}\right] \tag{3}$$

Equation 3 was numerically solved by the Runge-Kutta-Gill method using the initial condition: $C^{\mathrm{a}}_{\mathrm{NB}} = 0$ at $t = 0$. The mass transfer coefficient, k_L, was obtained by fitting the concentration profile obtained by solving Eq. 3 to the experimental data obtained in this work. The concentration profiles of nitrobenzene at different sulfuric acid concentrations at the impeller speeds of 2π and 4π rad/s at 298 K are shown in Figures 2a, b, respectively. It can be observed from these figures that the data were fitted well by the profiles at all sulfuric acid concentrations. It can be seen from Figures 2a, b that the mass transfer rates were quite high even at such low speeds of agitation. For the impeller speed of 2π rad/s, about 22% of the equilibrium solubility was reached after 3 *K*s for 14.1 kmol/m^3 concentration of sulfuric acid, whereas 78% of the equilibrium solubility was reached after the same time for 17 kmol/m^3 concentration of sulfuric acid. In general, the tendency to reach the equilibrium solubility increased as the concentration of sulfuric acid increased. The increase in k_L was spectacular beyond 16 kmol/m^3 concentration of sulfuric acid. The spontaneity observed in the dissolution of nitrobenzene in sulfuric acid is unique. It is likely that the stability achieved by the formation of microemulsion is the main driving force for the increase in mass transfer rate with the increase in sulfuric acid concentration. At 4π rad/s impeller speed, the rate of mass transfer was very fast, which can be observed from Figure 2b. It was observed that 95% of the equilibrium solubility was attained in just 720 s for 17.1 kmol/m^3 concentration of sulfuric acid. The increase in k_L with the increase in the speed of stirring agrees qualitatively with the results reported in the literature on agitated liquid–liquid systems.[2] The mass transfer coefficient increased by one order of magnitude at the high-sulfuric acid concentrations when the agitation speed was doubled.

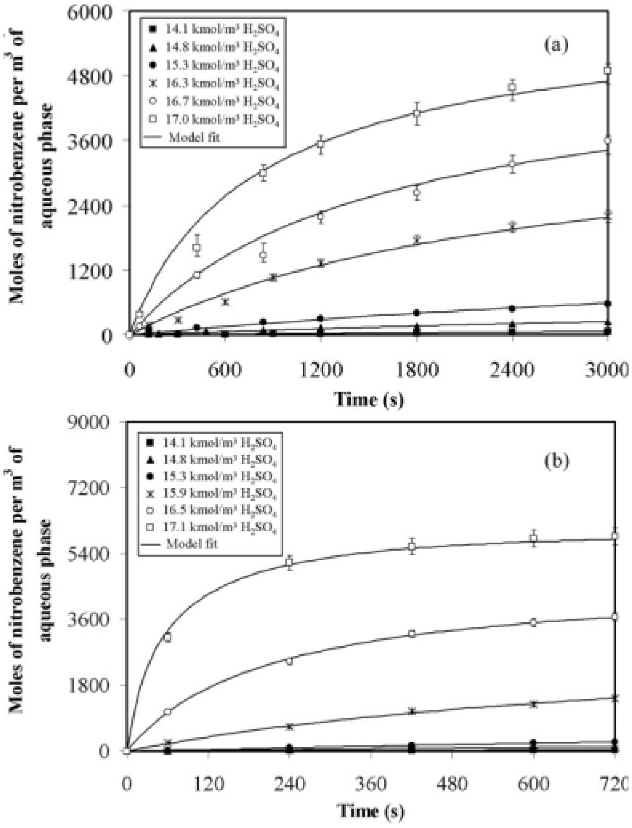

Figure 2. Determination of mass transfer coefficient of nitrobenzene at 298 K at different sulfuric acid concentrations at (a) 2π rad/s, and (b) 4π rad/s impeller speeds.

The concentration profiles of nitrobenzene at different sulfuric acid concentrations at 313 K with the impeller speeds of 2π and 4π rad/s are shown in Figures 3a, b, respectively. It can be observed from these figures that the rate of mass transfer increased significantly with increase in sulfuric acid concentration and impeller speed as observed in Figure 2. A comparison of k_L for 2π and 4π rad/s impeller speeds at 298 and 313 K is presented in Figure 4. Apart from the increase in the value of k_L with increase in sulfuric acid concentration and speed of stirring (which has been discussed before), it is evident from this figure that k_L increased with the increase in temperature, which is also in qualitative agreement with the results reported in the literature.[10] A comparison with the results reported by Modak and Juvekar[5] indicates that the values of mass transfer coefficient obtained in this study are somewhat lower than that reported by them. It may be due to the fact that the reactor used in this study had larger diameter than the reactor used by Modak and Juvekar,[5] whereas the diameter and height of the impellers were comparable. This probably caused lower values of the mass transfer coefficient in this study.

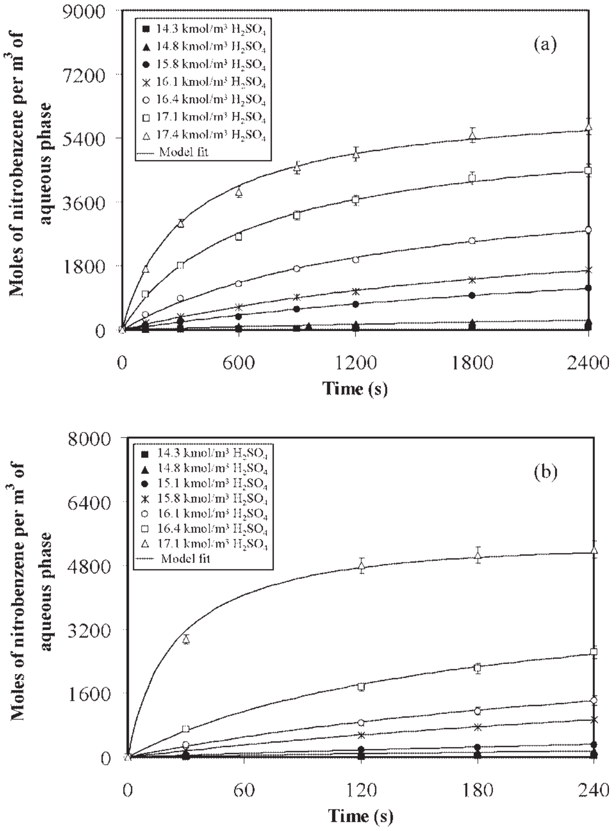

Figure 3. Determination of mass transfer coefficient of nitrobenzene at 313 K at different sulfuric acid concentrations at (a) 2π rad/s, and (b) 4π rad/s impeller speeds.

Determination of reaction rate constants

The generation of nitronium ion in mixed acid and the mechanism by which nitrobenzene reacts with the nitronium ion is depicted in Figure 5. The rate of nitration can be expressed in terms of the concentrations of the reactants as follows[2,4]:

$$r = k_{2,\mathrm{exp}} C_{\mathrm{NB}} C_{\mathrm{HNO_3}} \tag{4}$$

where $k_{2,\mathrm{exp}}$ is the observed (i.e., experimentally determined) second-order rate constant, and C_{NB} and $C_{\mathrm{HNO_3}}$ are the concentrations of nitrobenzene and nitric acid in the aqueous phase, respectively. The observed rate constant $k_{2,\mathrm{exp}}$ can be a strong function of sulfuric acid concentration.[6,7] The rate expressed by Eq. 4 can change by several orders of magnitude if the concentration of sulfuric acid changes.

In this study, the reactions were carried out in a single phase taking advantage of the high solubility of nitrobenzene in sulfuric acid as described in the "Experimental" section. Therefore, the reaction mixture was homogeneous and the reaction was free from any mass transfer effect. The rate of homogeneous reaction in the constant volume batch reactor can be described by the following rate equation.

$$r = C^0_{\mathrm{NB}} \frac{dX_{\mathrm{NB}}}{dt} = k_{2,\mathrm{exp}} \left(C^0_{\mathrm{NB}}\right)^2 (1 - X_{\mathrm{NB}})(M - X_{\mathrm{NB}}), M \neq 1 \tag{5}$$

where $M = C^0_{\mathrm{HNO_3}}/C^0_{\mathrm{NB}}$ and X_{NB} is the conversion of nitrobenzene. On integration of Eq. 5, we get,

$$\ln\left[\frac{M - X_{\mathrm{NB}}}{M(1 - X_{\mathrm{NB}})}\right] = k_{2,\mathrm{exp}}\left(C^0_{\mathrm{HNO_3}} - C^0_{\mathrm{NB}}\right)t \tag{6}$$

Therefore, a plot of $\ln\left[\frac{M-X_{\mathrm{NB}}}{M(1-X_{\mathrm{NB}})}\right]$ vs. time should be linear passing through the origin with slope equal to $k_{2,\mathrm{exp}}$ ($C^0_{\mathrm{HNO_3}} - C^0_{\mathrm{NB}}$). The observed rate constant, $k_{2,\mathrm{exp}}$, can be calculated from the slope. In this study, the initial mole ratio of nitric acid and nitrobenzene (M) was 0.48. The reactions were performed at 298, 313, and 323 K. The concentration profiles of nitrobenzene at 15 kmol/m^3 H_2SO_4 concentration are presented in Figure 6a at these three temperatures. The corresponding plots of $\ln\left[\frac{M-X_{\mathrm{NB}}}{M(1-X_{\mathrm{NB}})}\right]$ vs. time are shown in the Figure 6b. Similarly, the concentration profiles of nitrobenzene and the corresponding linear plots at 16.9 kmol/m^3 H_2SO_4 are shown in the Figures 7a, b, respectively. It can be observed from these figures that the data were fitted well by the straight lines given by Eq. 6. The observed rate constants calculated from the slopes of the plots are presented in Figure 8. It can be observed from this figure that the value of rate constant is maximum when the sulfuric acid concentration is ca. 16.7 kmol/m^3. The reason for this is explained later in this section. The rate constants obtained in this study

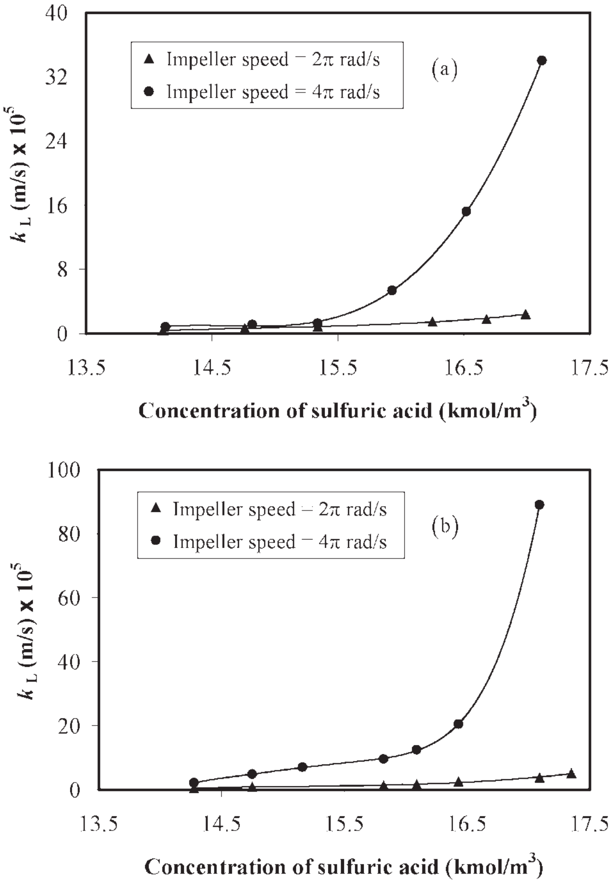

Figure 4. Comparison of the values of k_L obtained at different impeller speeds (a) at 298 K, and (b) at 313 K.

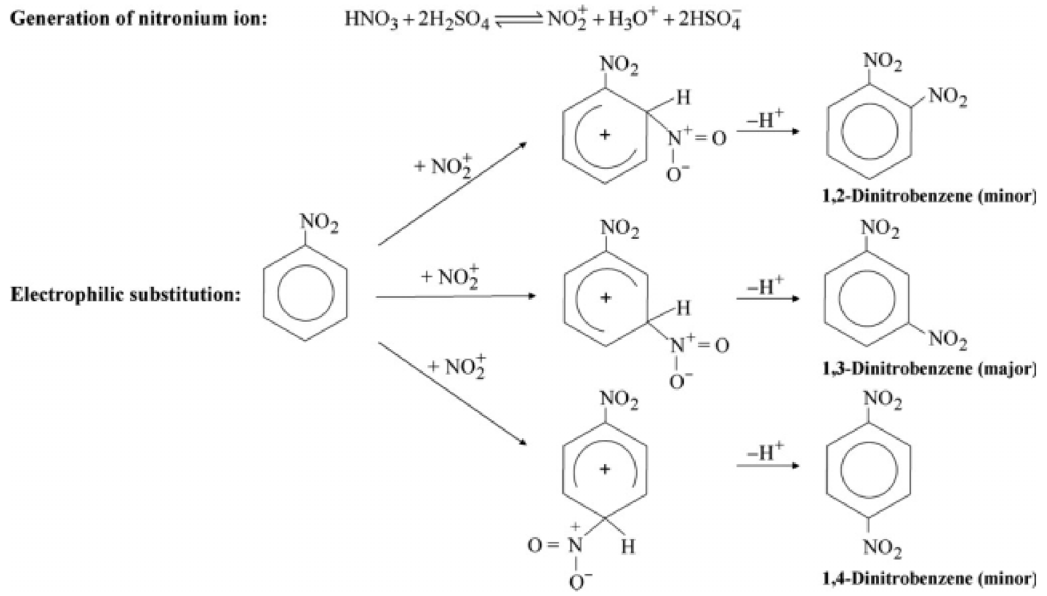

Figure 5. Reaction mechanism of nitration of nitrobenzene with mixed acid.

are compared with the values reported in the literature at 298,[6,7] 300,[5] and 313 K[7] in Figure 8. It can be observed that the rate constants obtained in this work compare well with the results reported in the literature.

The rate-determining step in homogeneous aromatic nitration in mixed acid is believed to be the attack of the nitronium ion NO_2^+ on the aromatic compound. The rate can be expressed in terms of the concentrations of nitrobenzene and nitronium ion as follows[2,4]:

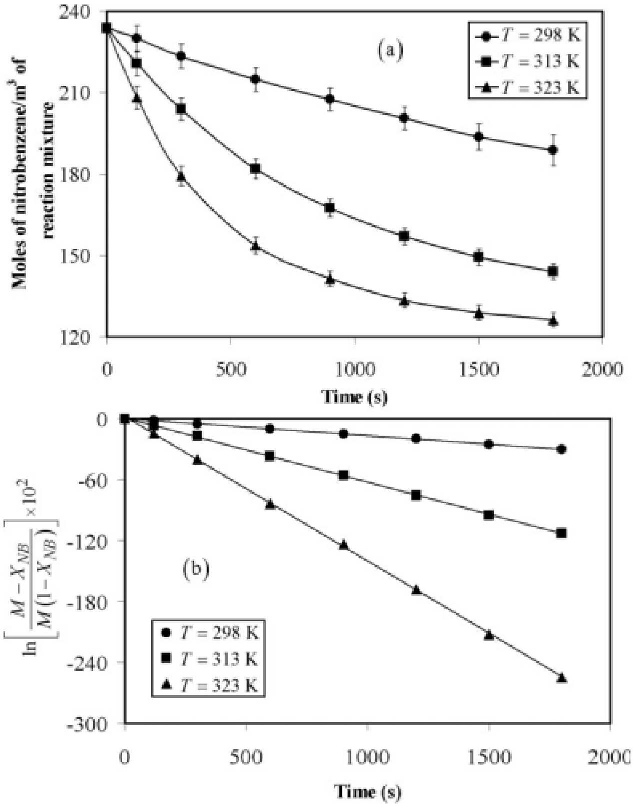

Figure 6. (a) Concentration profiles of nitrobenzene during nitration, and (b) determination of rate constants at 298, 313, and 323 K at 15 kmol/m^3 concentration of sulfuric acid.

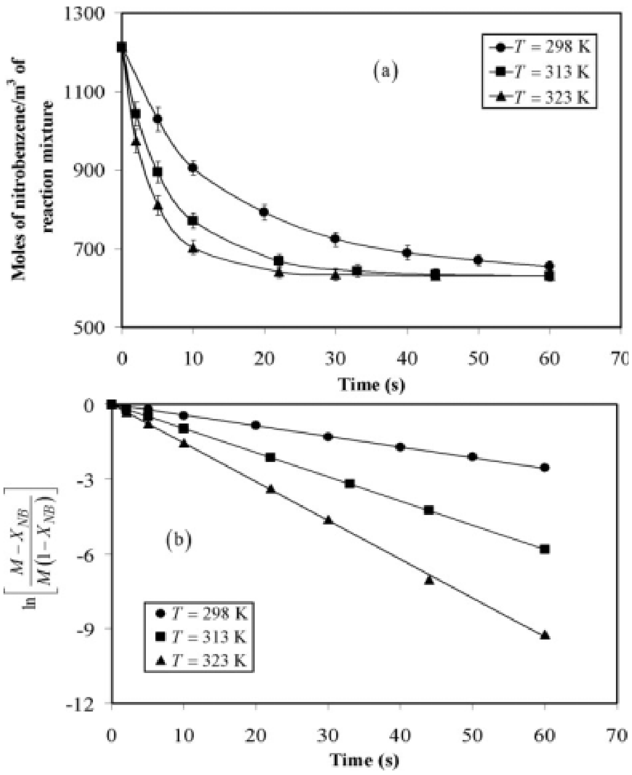

Figure 7. (a) Concentration profiles of nitrobenzene during nitration, and (b) determination of rate constants at 298, 313, and 323 K at 16.9 kmol/m^3 concentration of sulfuric acid.

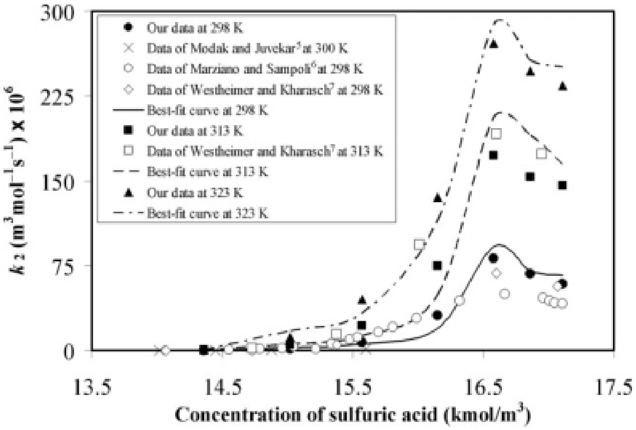

Figure 8. Variation of second-order rate constant with the concentration of sulfuric acid at 298, 313, and 323 K.

$$r = k^*_{2,\mathrm{exp}} C_{\mathrm{NB}} C_{\mathrm{NO}_2^+} \tag{7}$$

where $k^*_{2,\mathrm{exp}}$ is the observed rate constant and $C_{\mathrm{NO}_2^+}$ is the concentration of the nitronium ion in the acid phase. In addition, the reaction-rate in the acid phase can be written using a Brønsted-Bjerrum rate law (transition-state theory) as follows[11]:

$$r = k'_2 C_{\mathrm{NB}} C_{\mathrm{NO}_2^+} \frac{\gamma_{\mathrm{NB}} \gamma_{\mathrm{NO}_2^+}}{\gamma^{\#}} \tag{8}$$

where k'_2 is a thermodynamic parameter that depends on temperature γ_{NB} and $\gamma_{\mathrm{NO}_2^+}$ are the activity coefficients of nitrobenzene and nitronium ion, respectively, and $\gamma^{\#}$ is the activity coefficient of the transition-state intermediate. The parameter k'_2 is unique for each aromatic compound. Based on the rate expression given by Eq. 8, a rate equation has been proposed by Marziano and coauthors employing the M_c function of sulfuric acid as follows[6,12,13]:

$$r = k'_2 C_{\mathrm{NB}} C_{\mathrm{NO}_2^+} 10^{nM_c} \tag{9}$$

where n is another thermodynamic parameter, which is unique for each aromatic compound. The M_c function for sulfuric acid represents a general scale that depicts its acidity. The value of M_c depends only on the concentration of the acid at a given temperature. The quantity 10^{nM_c} describes the change in the ratio of the activity coefficients in Eq. 8 with change in sulfuric acid concentration and takes into account the effective concentrations of the reactants.

From Eqs. 4 and 7, the relation between $k^*_{2,\mathrm{exp}}$ and $k_{2,\mathrm{exp}}$ can be written as follows:

$$k^*_{2,\mathrm{exp}} = \frac{k_{2,\mathrm{exp}} C_{\mathrm{HNO}_3}}{C_{\mathrm{NO}_2^+}} \tag{10}$$

From Eqs. 4 and 9, the relation between k'_2 and $k_{2,\mathrm{exp}}$ can be written as follows:

$$k'_2 = \frac{k_{2,\mathrm{exp}} C_{\mathrm{HNO}_3}}{C_{\mathrm{NO}_2^+} 10^{nM_c}} \tag{11}$$

From Eq. 11, we can write,

$$\log k_{2,\mathrm{exp}} - \log(C_{\mathrm{NO}_2^+}/C_{\mathrm{HNO}_3}) = \log k'_2 + nM_c \tag{12}$$

Therefore, a plot between $[\log k_{2,\mathrm{exp}} - \log(C_{\mathrm{NO}_2^+}/C_{\mathrm{HNO}_3})]$ and M_c should produce a straight line with slope equal to n and intercept equal to $\log k'_2$. However, to determine the values of n and k'_2, it is necessary to determine M_c and $(C_{\mathrm{NO}_2^+}/C_{\mathrm{HNO}_3})$.

The M_c function: The M_c function at 298 K was developed in the form of a polynomial by using the data of Marziano et al.[13] In the sulfuric acid concentration range between 14.1 and 17.1 kmol/m^3, the polynomial is given by the following,

$$-M_c = 6.47 \times 10^{-4} C^5_{\mathrm{H_2SO_4}} - 39.8 \times 10^{-3} C^4_{\mathrm{H_2SO_4}} + 91.8 \times 10^{-2} C^3_{\mathrm{H_2SO_4}} - 9.39 C^2_{\mathrm{H_2SO_4}} + 36.6 C_{\mathrm{H_2SO_4}} \tag{13}$$

This polynomial was used in this study. The values of M_c at the higher temperatures were determined by the following equation given by Marziano et al.[14]

$$M_c(T) = M_c(298\mathrm{K}) \left[\frac{200}{T} + 0.3292 \right] \tag{14}$$

The $(C_{\mathrm{NO}_2^+}/C_{\mathrm{HNO}_3})$ ratio: Equilibria of nitric acid in aqueous sulfuric acid have been studied extensively at room temperature by different techniques such as Raman spectroscopy,[15–17] UV spectroscopy,[16,17] and NMR spectroscopy.[18] These works have identified the molecular and ionic species present in the solutions. Marziano et al.[14] have presented the experimental data on the ionization ratio at 313 and 333 K between 14.1 and 18.3 kmol/m^3 sulfuric acid concentrations. The amounts of $\mathrm{HNO_3}$ converted to $\mathrm{NO_2^+}$ in different sulfuric acid solutions are shown in Figure 9. At the high concentrations of sulfuric acid (>14.1 kmol/m^3), nitric acid is present as nitronium ion and molecular nitric acid (i.e., $C^0_{\mathrm{HNO}_3} = C_{\mathrm{NO}_2^+} + C_{\mathrm{HNO}_3}$). The values of $(C_{\mathrm{NO}_2^+}/C_{\mathrm{HNO}_3})$ at 298 and 313 K were determined from the ionization ratio $(C_{\mathrm{NO}_2^+}/C_{\mathrm{HNO}_3})$ presented in Figure 9. The values at 323 K

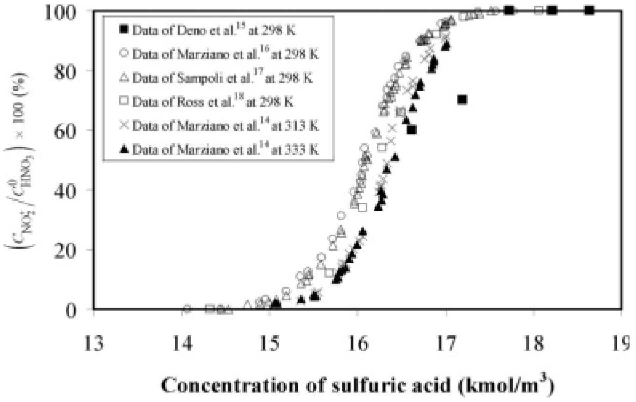

Figure 9. Percentage of $\mathrm{HNO_3}$ converted to $\mathrm{NO_2^+}$ in aqueous sulfuric acid at 298, 313, and 333 K.

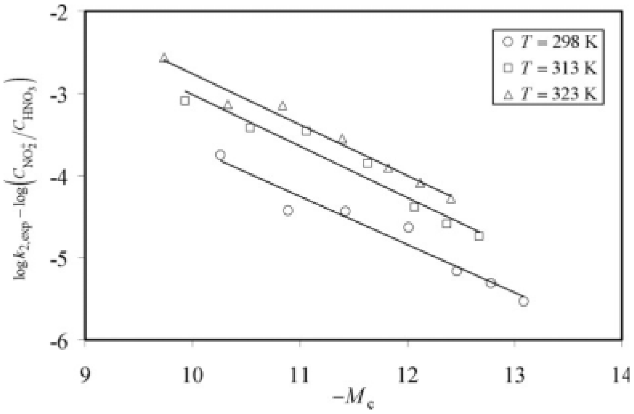

Figure 10. Determination of the thermodynamic parameters *n* and k'_2.

were obtained by interpolation of the data between 313 and 333 K.

Figure 10 shows the plots of $[\log k_{2,\exp} - \log(C_{NO_2^+}/C_{HNO_3})]$ vs. M_c at the different temperatures. It can be observed from this figure that the data were fitted well by straight lines in all cases. The values of n and $\log k'_2$ obtained at different temperatures are presented in Table 1. It is evident that the value of n was virtually constant over these temperatures, whereas the value of k'_2 increased with increase in temperature.

The best-fit curves corresponding to the values of n and k'_2 are shown in Figure 8. It can be seen from the figure that the fit to the experimental values of the second-order rate constant was good, and the profiles explained the increase and decrease of the rate constant well. The ratio $(C_{NO_2^+}/C_{HNO_3})$ in Eq. 11 increases, whereas the quantity 10^{nM_c} decreases with the increase in sulfuric acid concentration. The effect of the former quantity is stronger than the latter upto 16.7 kmol/m^3 sulfuric acid concentration. Beyond this concentration, the quantity 10^{nM_C} dominates over the $(C_{NO_2^+}/C_{HNO_3})$ ratio. Therefore, a decrease in rate constant is observed beyond this sulfuric acid concentration.

Using the fitted values of n and k'_2, we can calculate the value of k^*_2 by using the following relationship.

$$k^*_{2,\mathrm{cal}} = k'_2 10^{nM_C} \tag{15}$$

Figure 11 shows the comparison between the experimentally observed and calculated values of k^*_2 at different temperatures and at different concentrations of sulfuric acid. From the values of $k^*_{2,\mathrm{cal}}$ at different temperatures, the activation energy (E^*_2) for the electrophilic attack of nitronium ion on the nitrobenzene molecule can be determined. The relationship between $k^*_{2,\mathrm{cal}}$ and the reaction temperature (T) was described by the Arrhenius equation,

$$k^*_{2,\mathrm{cal}} = k^*_{2,0} \exp\left(-\frac{E^*_2}{RT}\right) \tag{16}$$

where $k^*_{2,0}$ is the frequency factor and R is the universal gas constant. The value of E^*_2 was found to be 91.3 kJ/mol.

Table 1. Values of *n* and $\log k'_2$ at Three Temperatures

Nitration Temperature (K)	n	$\log k'_2$
298	0.586	2.185
313	0.626	3.239
323	0.616	3.390

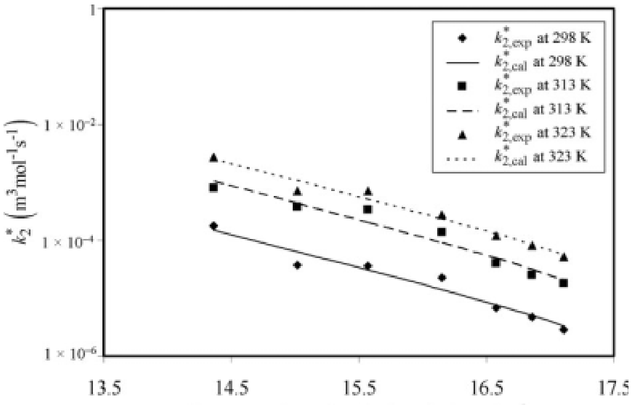

Figure 11. Variation of experimental and calculated values of k^*_2 with sulfuric acid concentration at different temperatures.

From the values of $k_{2,\exp}$ at different temperatures, the activation energy (E_2) of the reaction between nitrobenzene and nitric acid was calculated for each sulfuric acid concentration by the Arrhenius equation. The plots of ln $k_{2,\exp}$ vs. $1/T$ are shown in Figure 12. The data were fitted well by the straight lines. The slopes of these straight lines give the values of the activation energy E_2 at each sulfuric acid concentration. The relation between E_2 and E^*_2 is given by the following,

$$E_2 = E^*_2 + \Delta H \tag{17}$$

where ΔH is heat of the reaction for the reaction: $HNO_3 + H^+ \rightarrow NO_2^+ + H_2O$. The values of ΔH at each sulfuric acid concentration were determined and are presented

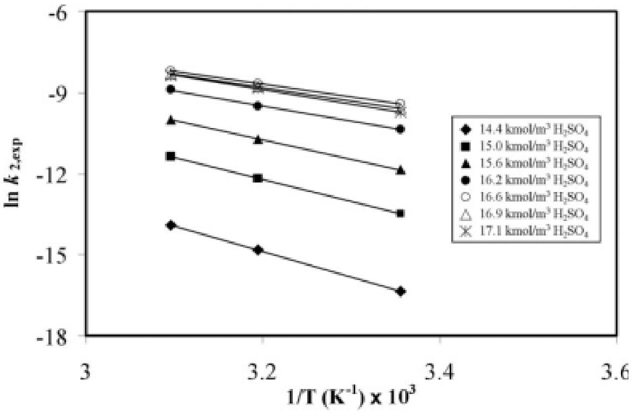

Figure 12. Arrhenius plots at different concentrations of sulfuric acid.

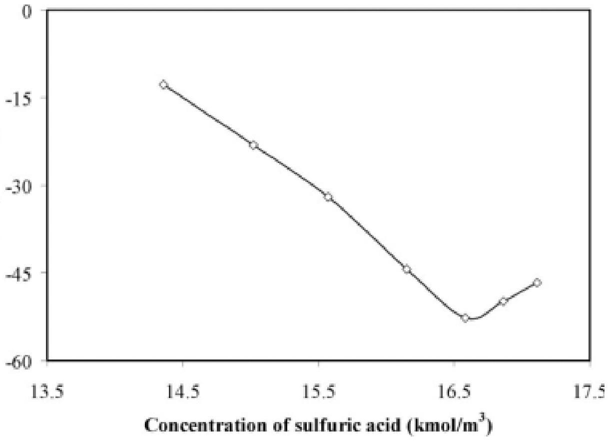

Figure 13. Variation of the heat of reaction with sulfuric acid concentration for the reaction: $HNO_3 + H^+ \rightarrow NO_2^+ + H_2O$.

in Figure 13. It is observed from the figure that the magnitude of ΔH decreased (i.e., the exothermicity of the reaction increased) with increase in sulfuric acid concentration. This agrees with the prediction of Cox and Strachan.[4] The value of ΔH passed through a minimum and then increased at the high concentrations of sulfuric acid. The values of ΔH agree well with the values reported in the literature.[19]

Determination of reaction regime

The diffusivity of nitrobenzene (D_{NB}) in sulfuric acid was calculated by using the modified Wilke-Chang equation proposed by Perkins and Geankoplis.[20]

$$D_{\mathrm{NB}} = \frac{7.4 \times 10^{-15} T \left(\bar{\phi}\bar{M}\right)^{1/2}}{\mu v_{\mathrm{m}}^{0.6}} \tag{18}$$

where μ is the viscosity of aqueous sulfuric acid, v_{m} is the molar volume of nitrobenzene at normal boiling point, and T is the temperature. The quantity $\bar{\phi}\bar{M}$ is defined as follows[3]:

$$\bar{\phi}\bar{M} = x_{\mathrm{w}}\phi_{\mathrm{w}}M_{\mathrm{w}} + x_{\mathrm{s}}\phi_{\mathrm{s}}M_{\mathrm{s}} \tag{19}$$

where x_{w} and x_{s} are the mole fractions, ϕ_{w} and ϕ_{s} are the association factors, and M_{w} and M_{s} are the molecular weights of water and sulfuric acid, respectively. The diffusivity of nitrobenzene at different sulfuric acid concentrations at 298 and 313 K are presented in Table 2. It can be observed from this table that the diffusivity decreased with increase in sulfuric acid concentration, passed through a minimum and then increased at the high-sulfuric acid concentrations. This happened because $\bar{\phi}\bar{M}$ increased with increase in sulfuric acid concentration, whereas the viscosity increased with sulfuric acid concentration upto 15.9 kmol/m³ and then decreased.

The Hatta number was calculated by the following expression,[21] using the values of $k_{2,\mathrm{exp}}$ and k_L reported in the previous sections.

$$\mathrm{Ha} = \frac{\sqrt{D_{\mathrm{NB}} k_{2,\mathrm{exp}} C^0_{\mathrm{HNO_3}}}}{k_L} \tag{20}$$

The Hatta number at different sulfuric acid concentrations at 298 and 313 K are presented in Table 2. The values of Hatta number indicate that the reactions took place in the slow regime.[21] The Hatta number increased with increase in sulfuric acid concentration, passed though a maximum and then decreased at the high-sulfuric acid concentrations. This can be explained as follows. The mass transfer coefficient (k_L) increased with increase in sulfuric acid concentration. The rate constant ($k_{2,\mathrm{exp}}$) increased with sulfuric acid concentration upto 16.7 kmol/m³ and then decreased. The diffusivity decreased with increase in sulfuric acid concentration, passed through a minimum, and then increased at the high sulfuric acid concentrations. However, the variation of diffusivity with sulfuric acid concentration was much less when compared with the variation of $k_{2,\mathrm{exp}}$ with sulfuric acid concentration. Therefore, the resulting effect was an increase in Hatta number followed by a decrease, as mentioned earlier. Hatta number was found to increase with the increase in temperature. The increase in Hatta number with increase in temperature can be attributed to the large increase in the reaction rate constant with temperature.

Model for mass transfer with chemical reaction

A model has been developed for the nitration process using mass balance in the aqueous phase by taking into account of the amount of nitrobenzene transferred through the interface, the amount of nitrobenzene reacted, and its accumulation. This model will be useful to predict the concentration profiles of the reactants and the products as well as the conversion profiles of the reactants in the aqueous phase during nitration. It was confirmed from the values of the Hatta number that the reaction takes place in the slow regime. This enables us to use the mass transfer coefficients obtained in absence of chemical reaction without a significant loss in accuracy. The model presented here is based on a few assumptions. The aqueous phase is assumed to be homogeneous. The mass transfer is assumed to occur from the organic phase to the aqueous phase, and the reverse is not significant. The change in volume of the aqueous phase occurs solely due to the transfer of nitrobenzene into the aqueous phase. The solid product present in the aqueous phase is assumed to have negligible effect on the volume

Table 2. Diffusivity of Nitrobenzene in Sulfuric Acid and Hatta Number

Reaction Temperature (K)	Sulfuric Acid Concentration (kmol/m³)	$D_{\mathrm{NB}} \times 10^{10}$ (m²/s)	Ha × 10^2
298	14.1	0.82	0.24
	14.8	0.72	1.19
	15.3	0.70	1.99
	16.3	0.74	6.68
	16.7	0.78	11.25
	17.0	0.81	7.51
313	14.3	1.32	0.85
	14.8	1.24	2.01
	15.8	1.20	5.41
	16.1	1.22	9.81
	16.4	1.26	13.87
	17.1	1.37	9.38
	17.4	1.40	7.05

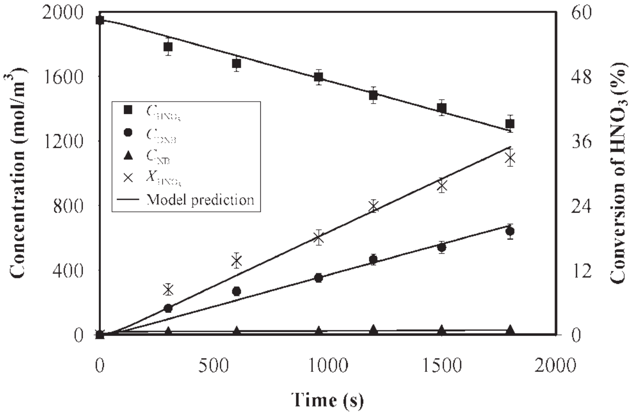

Figure 14. Concentration profiles of nitrobenzene, nitric acid and dinitrobenzene isomers, and the conversion profile of nitric acid in the aqueous phase at 15.7 kmol/m^3 concentration of sulfuric acid at 298 K. $C^0_{HNO_3}$ = 1946.88 mol/m^3.

change. The change in volume due to the formation of water and consumption of nitric acid is assumed to be negligible. It is further assumed that the volume change of mixing is negligible. The equilibrium concentration of nitrobenzene in the aqueous phase in absence of chemical reaction is assumed to remain the same in the reaction mixture. Therefore, it is apparent that this model can be expected to be sound upto moderately high sulfuric acid concentrations.

The material balance for nitrobenzene in the aqueous phase is given by the following,

$$\frac{d}{dt}(V_R C_{NB}) = \frac{k_L A}{V_R}\left(V_\infty \overline{C}_{NB} - V_R C_{NB}\right) - k_{2,\exp} C_{HNO_3} C_{NB} V_R \tag{21}$$

where V_R is the volume of the aqueous phase. Equation 21 can be rearranged as follows,

$$\frac{dC_{NB}}{dt} = k_L A \overline{C}_{NB}\left(\frac{V_\infty}{V_R^2}\right) - \left(\frac{k_L A}{V_R} + k_{2,\exp} C_{HNO_3}\right) C_{NB} - \frac{C_{NB}}{V_R}\frac{dV_R}{dt} \tag{22}$$

V_R can be expressed by the following equation (i.e., similar to Eq. 2).

$$V_R = \frac{V_0}{(1 - C_{NB} M_{NB}/\rho_{NB})} \tag{23}$$

The material balance for nitric acid in the aqueous phase is given by the following,

$$\frac{d}{dt}(V_R C_{HNO_3}) = -k_{2,\exp} C_{HNO_3} C_{NB} V_R \tag{24}$$

Equation 24 can be written as follows,

$$\frac{dC_{HNO_3}}{dt} = -k_{2,\exp} C_{HNO_3} C_{NB} - \frac{C_{HNO_3}}{V_R}\frac{dV_R}{dt} \tag{25}$$

The material balance for dinitrobenzene isomers in the aqueous phase is given by the following,

$$\frac{d}{dt}(V_R C_{DNB}) = k_{2,\exp} C_{HNO_3} C_{NB} V_R \tag{26}$$

Upon rearrangement Eq. 26 gives,

$$\frac{dC_{DNB}}{dt} = k_{2,\exp} C_{HNO_3} C_{NB} - \frac{C_{HNO_3}}{V_R}\frac{dV_R}{dt} \tag{27}$$

Equations 22, 25, and 27 were simultaneously solved by the Runge-Kutta-Gill method using the initial conditions: $C_{NB} = 0$, $C_{DNB} = 0$, and $C_{HNO_3} = C^0_{HNO_3}$ at $t = 0$. The values of $\overline{C}_{NB}$, $k_{2,\exp}$, and k_L reported in the preceding sections were used. The fractional conversion of nitric acid was calculated by the following equation.

$$X_{HNO_3} = 1 - \frac{V_R C_{HNO_3}}{V_0 C^0_{HNO_3}} \tag{28}$$

Figure 14 shows the comparison between the experimental and the theoretical concentration profiles of the reactants and the product isomers at 15.7 kmol/m^3 sulfuric acid concentration. The conversion profiles of nitric acid are also shown in this figure. The conversion of nitric acid was calculated from the amount of the main product (i.e., 1,3-Dinitrobenzene) formed, and its percentage in the mixture of the three isomers (see the next section). It is seen from the figure that the theoretical concentration and conversion profiles were in good agreement with the experimental data. The deviation of the experimental data from the profiles in the initial period is likely due to the turbulence created in the aqueous phase when the agitation was started.

Determination of yield and distribution of isomers of dinitrobenzene

The net yields of the three isomers of dinitrobenzene at different temperatures at various concentrations of sulfuric acid are presented in Figure 15. The yields were determined

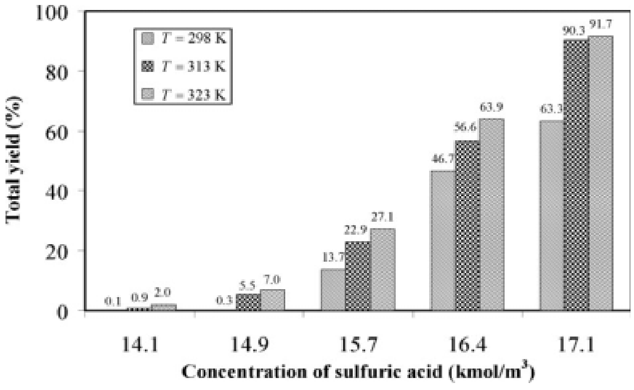

Figure 15. Variation of overall yields of the dinitrobenzene isomers with the concentration of sulfuric acid at three temperatures after 1 h of reaction.

The reactants were charged to the reactor in the molar ratio, HNO$_3$:Nitrobenzene:H$_2$SO$_4$ = 1:1:4.

Table 3. Distribution of Isomers of Dinitrobenzene in the Product

Concentration of Sulfuric Acid (kmol/m^3)	Isomers of DNB in the Product (mol %)								
	298 (K)			313 (K)			323 (K)		
	1,3-DNB	1,2-DNB	1,4-DNB	1,3-DNB	1,2-DNB	1,4-DNB	1,3-DNB	1,2-DNB	1,4-DNB
14.1	99.98	0.01	0.01	99.94	0.02	0.04	98.95	0.96	0.09
14.9	99.98	0.02	0.00	99.02	0.94	0.04	98.98	0.96	0.06
15.7	95.55	4.21	0.24	98.13	1.86	0.01	96.76	2.97	0.27
16.4	95.08	4.61	0.31	94.17	5.82	0.01	96.10	3.64	0.26
17.1	91.64	7.35	1.01	91.48	8.33	0.19	91.07	8.00	0.93

after 1 h of reaction. The yield increased with the increase in concentration of sulfuric acid. The highest yields obtained at 298, 313, and 323 K were 63.3, 90.3, and 91.7%, respectively, at 17.1 kmol/m^3 concentration of sulfuric acid. At the high conversions of nitrobenzene, a hard porous solid mass of the product was formed inside the reactor, which probably did not allow the reaction to proceed further and hence, did not allow the yield to be even higher. Although the rate constant decreased beyond 16.7 kmol/m^3 concentration of sulfuric acid, the yield increased due to the high concentrations of nitrobenzene and nitronium ion present in the aqueous phase.

The proportions of the dinitrobenzene (DNB) isomers (i.e., 1,2-Dinitrobenzene, 1,3-Dinitrobenzene, and 1,4-Dinitrobenzene) in the product are presented in Table 3. It is observed from the table that the percentage of 1,3-Dinitrobenzene in the product decreased with the increase in concentration of sulfuric acid, whereas the amounts of other isomers, especially 1,2-Dinitrobenzene, steadily increased. Also, the yield of 1,2-Dinitrobenzene was higher than the yield of 1,4-Dinitrobenzene. This is probably due to the stabilization of the transition state for the *ortho*-substitution by dipolar interaction between nitrobenzene and the electrophile NO_2^+.[22] The reason behind the stabilization is due to the existence of $-I$ and $-R$ effects in the nitrobenzene molecule, which results in nonuniform distribution of positive charge at the *ortho* and *para* positions in the resonating structures. The higher concentration of positive charge in the *para* position than that in the *ortho* position causes greater stabilization for the *ortho* substitution. Therefore, a higher amount of the *ortho* isomer is produced. It has been reported in the literature[23,24] that a solvent of high-dielectric constant facilitates the electrophilic substitution at the *ortho* position. With increase in sulfuric acid concentration, the dielectric constant of sulfuric acid increases (e.g., the dielectric constant of water is 78.5, whereas the dielectric constant of 18.6 kmol/m^3 sulfuric acid is 101).[25] Therefore, the high dielectric constant of concentrated-sulfuric acid favors the *ortho* product.

Conclusions

Some important kinetic and mass transfer aspects of the nitration of nitrobenzene in a batch reactor have been studied. Rate of transport of nitrobenzene from the organic phase to the aqueous phase was found to increase with the increase in sulfuric acid concentration, stirring speed, and temperature. The enhancement in solubility occurred due to microemulsification of nitrobenzene in the aqueous phase at the high concentrations of sulfuric acid. The rate constants of the reactions at 298, 313, and 323 K at different sulfuric acid concentrations were determined. The rate constant was highest at ca. 16.7 kmol/m^3 sulfuric acid concentration at all three temperatures. The rate constant decreased beyond this concentration due to the changes in the activity coefficients of the reactants. These phenomena were explained by the M_c function. Although the rate constant decreased at the high-sulfuric acid concentrations, yield of the products increased at these concentrations due to the high concentrations of nitrobenzene and nitronium ion in the aqueous phase. The increase in yield with temperature was due to the tremendous increase in rate constant with temperature. In this work, nitric acid and nitrobenzene were charged to the reactor in 1:1 molar ratio to determine the yield of reaction. The usual industrial practice is to use excess nitric acid. Therefore, it is expected that even higher yields may be obtained by charging excess amount of nitric acid to the reactor. Hatta numbers at these sulfuric acid concentrations were calculated using the values of mass transfer coefficient and the rate constant. The Hatta number was found to increase with increase in temperature, and the slow reaction regime prevailed at all conditions. The proportion of the dinitrobenzene isomers varied with sulfuric acid concentration as well as temperature. The percentage of 1,2-Dinitrobenzene increased, whereas the percentage of 1,3-Dinitrobenzene decreased with increase in sulfuric acid concentration. A model was developed for simultaneous mass transfer with chemical reaction. The experimental concentration and conversion profiles matched well with the prediction of the model.

Acknowledgments

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Notation

A = interfacial area (m^2)
C_{DNB} = concentration of the dinitrobenzene isomers in the reactor (mol/m^3)
C_{HNO_3} = concentration of nitric acid in the aqueous phase (mol/m^3)
$C_{H_2SO_4}$ = concentration of sulfuric acid (kmol/m^3)
C_{NB} = concentration of nitrobenzene in the aqueous phase (mol/m^3)
$\overline{C}_{NB}$ = equilibrium concentration of nitrobenzene in the aqueous phase (mol/m^3)
$C_{NO_2^+}$ = concentration of the nitronium ion in the aqueous phase (mol/m^3)
C_{NB}^0 = initial concentration of nitrobenzene in the aqueous phase (mol/m^3)

$C^0_{HNO_3}$ = initial concentration of nitric acid in the aqueous phase (mol/m^3)
C^a_{NB} = concentration of nitrobenzene in the aqueous phase (mol/m^3)
d = diameter of the reactor (m)
D_{NB} = diffusivity of nitrobenzene (m^2/s)
E_2 = activation energy of nitration of nitrobenzene (J/mol)
E^*_2 = activation energy for the attack of NO_2^+ on the nitrobenzene molecule (J/mol)
Ha = Hatta number
k_L = mass transfer coefficient (m/s)
$k_{2,exp}$ = observed second-order rate constant (m^3 mol^{-1} s^{-1})
k'_2 = thermodynamic parameter defined in Eq. 8
$k^*_{2,0}$ = frequency factor (m^3 mol^{-1} s^{-1})
$k^*_{2,cal}$ = calculated second-order rate constant with respect to the actual concentration of the nitrating agent, NO_2^+ (m^3 mol^{-1} s^{-1})
$k^*_{2,exp}$ = observed second-order rate constant with respect to actual concentration of the nitrating agent, NO_2^+ (m^3 mol^{-1} s^{-1})
M = initial molar ratio of nitric acid and nitrobenzene
$\overline{M}$ = molecular weight of aqueous sulfuric acid (kg/mol)
M_c = activity coefficient function
M_{NB} = molecular weight of nitrobenzene (kg/mol)
M_s = molecular weight of sulfuric acid (kg/mol)
M_w = molecular weight of water (kg/mol)
n = thermodynamic parameter defined in Eq. 9
r = rate of reaction (mol m^{-3} s^{-1})
R = universal gas constant (J mol^{-1} K^{-1})
t = time (s)
T = temperature (K)
V_0 = initial volume of aqueous phase (m^3)
V_∞ = volume of the aqueous phase constituted of nitrobenzene and sulfuric acid under equilibrium conditions (m^3)
V_a = volume of aqueous phase (m^3)
v_m = molar volume of nitrobenzene at its normal boiling point (m^3/kmol)
V_R = volume of aqueous phase during reaction (m^3)
x_s = mole fraction of sulfuric acid
x_w = mole fraction of water
X_{HNO_3} = conversion of nitric acid
X_{NB} = conversion of nitrobenzene

Greek letters

γ_{NB} = activity coefficient of nitrobenzene
$\gamma_{NO_2^+}$ = activity coefficient of nitronium ion
$\gamma^\#$ = activity coefficient of the transition-state intermediate
ΔH = enthalpy change, J/mol
λ_{max} = wavelength at which the maximum absorption occur (nm)
μ = viscosity of the aqueous sulfuric acid (Pa s)
ρ_{NB} = density of nitrobenzene (kg/m^3)
ϕ = association factor of aqueous sulfuric acid
ϕ_s = association factor of sulfuric acid
ϕ_w = association factor of water

Literature Cited

1. Rahaman M, Mandal BP, Ghosh P. Nitration of nitrobenzene at high-concentrations of sulfuric acid. *AIChE J*. 2007;53:2476–2480.
2. Quadros PA, Oliveira NMC, Baptista CMSG. Continuous adiabatic industrial benzene nitration with mixed acid at a pilot plant scale. *Chem Eng J*. 2005;108:1–11.
3. Cox PR, Strachan AN. Two-phase nitration of toluene. Part II. *Chem Eng J*. 1972;4:253–261.
4. Cox PR, Strachan AN. Two phase nitration of chlorobenzene. *Chem Eng Sci*. 1971;26:1013–1018.
5. Modak SY, Juvekar VA. Role of interfacial reaction in heterogeneous aromatic nitration. *Ind Eng Chem Res*. 1995;34:4297–4309.
6. Marziano NC, Sampoli M. A simple linear description of rate profiles for the nitration of aromatic compounds in the critical range 80–98 wt% sulphuric acid. *J Chem Soc Chem Commun*. 1983;9:523–524.
7. Westheimer FH, Kharasch MS. The kinetics of nitration of aromatic nitro compounds in sulfuric acid. *J Am Chem Soc*. 1946;68:1871–1876.
8. Raverkar SR, Rao NVR. High-performance liquid chromatographic analysis of dinitrobenzene isomers. *Chromatographia*. 1989;28:412–414.
9. Ruckenstein E. The origin of thermodynamic stability of microemulsions. *Chem Phys Lett*. 1978;57:517–521.
10. Cussler EL. *Diffusion: Mass Transfer in Fluid Systems*. Cambridge: Cambridge University Press, 1997.
11. Olah GA, Malhotra R, Narang SC. *Nitration: Methods and Mechanisms*. New York: Wiley-VCH, 1989.
12. Marziano NC, Cimino GM, Passerini RC. The M_c activity coefficient function for acid-base equilibria. Part 1. New methods for estimating pK_a values for weak bases. *J Chem Soc Perkin Trans 2*. 1973;1915–1922.
13. Marziano NC, Tomasin A, Traverso PG. The M_c activity coefficient function for acid-base equilibria. Part 5. The M_c activity coefficient for a reliable estimate of thermodynamic values. *J Chem Soc Perkin Trans 2*. 1981;1070–1075.
14. Marziano NC, Tomasin A, Tortato C, Zaldivar JM. Thermodynamic nitration rates of aromatic compounds. Part 4. Temperature dependence in sulfuric acid of $HNO_3 \rightarrow NO_2^+$ equilibrium, nitration rates and acidic properties of the solvent. *J Chem Soc Perkin Trans 2*. 1998;1973–1982.
15. Deno NC, Peterson HJ, Sacher E. Nitric acid equilibria in water-sulphuric acid. *J Phys Chem*. 1961;65:199–201.
16. Marziano NC, Traverso PG, De Santis A, Sampoli M. Determination of the basicity of nitric acid in concentrated sulphuric acid by Raman and ultraviolet spectroscopy. *J Chem Soc Chem Commun*. 1978;20:873–874.
17. Sampoli M, De Santis A, Marziano NC, Pinna F, Zingales A. Equilibria of nitric acid in sulfuric and perchloric acid at 25°C by Raman and UV spectroscopy. *J Phys Chem*. 1985;89:2864–2869.
18. Ross DS, Kuhlmann KF, Malhotra R. Studies in aromatic nitration 2. ^{14} N NMR study of the nitric acid/nitronium ion equilibrium in aqueous sulfuric acid. *J Am Chem Soc*. 1983;105:4299–4302.
19. Edwards HGM, Turner JMC, Fawcett V. Raman spectroscopic study of nitronium ion formation in mixtures of nitric acid, sulfuric acid and water. *J Chem Soc Faraday Trans*. 1995;91:1439–1443.
20. Perkins LR, Geankoplis CJ. Molecular diffusion in a ternary liquid system with the diffusing component dilute. *Chem Eng Sci*. 1969;24:1035–1042.
21. Doraiswamy LK, Sharma MM. *Heterogeneous Reactions: Analysis, Examples and Reactor Design*, vol. 2. New York: Wiley, 1984.
22. Norman ROC, Radda GK. The *ortho:para*-ratio in aromatic substitution. Part III. A general discussion. *J Chem Soc*. 1961;3610–3616.
23. Paul MA. *Ortho-para* directive effects for aromatic nitration in acetic anhydride. *J Am Chem Soc*. 1958;80:5332–5333.
24. Xiao H, Chen L, Ju X, Ji G. A theoretical study on nitration mechanism of benzene and solvent effects. *Sci China B*. 2003;46:453–464.
25. Gillespie RJ, Cole RH. Dielectric constant of sulfuric acid. *Trans Faraday Soc*. 1956;52:1325–1331.

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