Nitration of Nitrobenzene at High-Concentrations of Sulfuric Acid

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Introduction

Aromatic nitration is one of the most widely used reactions in organic process industry. It is carried out by reacting the organic compound with mixed acid (a mixture of concentrated nitric and sulfuric acids). Aromatic nitro compounds find wide use in the manufacture of dyes and explosives. The reaction is carried out in batch, as well as continuously stirred-tank reactors. Reports of experimental studies on nitration of benzene,[1–3] toluene,[3–9] o-xylene,[10] chlorobenzene,[3,11] and nitrobenzene[12] are available in the literature. Most of these works have performed kinetic studies at low-concentrations of sulfuric acid (<15 kmol/m^3). Some of these works have employed high-speeds of stirring.[5,6,11]

The nitration reaction is believed to take place in the aqueous phase, where the mixed acid produces nitronium ion (NO_2^+). The organic molecules diffuse into the aqueous phase, and the electrophilic substitution takes place thereafter. In reaction media containing low-concentrations of sulfuric acid (below ~10 kmol/m^3), the reaction is first-order with respect to both nitric acid and the organic compound (overall second-order).[13] This reaction proceeds in the *slow regime*. When the sulfuric acid concentration is high, the rate of reaction depends on interfacial area and mass-transfer coefficient, and the reaction proceeds in the *fast regime*.[13]

Some of the major parameters identified to be crucial in this heterogeneous reaction with respect to yield and selectivity are, concentration of sulfuric acid, temperature of reaction, and the speed of stirring. The rate of transfer of the organic compound into the aqueous phase mainly depends on the concentration of the acid phase and the speed of stirring. The latter parameter varies between 1,000 and 5,000 revolutions per min in the industrial reactors. High-speed stirring generates a dispersion of the organic phase into the aqueous phase. The speed of stirring determines the diameter of the droplets, and, hence, the interfacial area.

The objective of this work was to study the nitration of nitrobenzene in reaction media constituted with sulfuric acid at high-concentrations. The effect of concentration of sulfuric acid on the solubility of the organic compound in the acid phase was studied. The interfacial phenomena involving spontaneous microemulsification occurring during the solubilization of the organic compound into sulfuric acid were investigated. The conversion of the reactant was studied in a batch reactor, and the yield of the major product (1,3-Dinitrobenzene) was determined at various concentrations of sulfuric acid between 14.1 and 17.1 kmol/m^3.

Experimental

Nitrobenzene (99% purity), sulfuric acid (18.3 kmol/m^3) and nitric acid (15.5 kmol/m^3) were procured from Merck (India). "Fuming" nitric acid (24.1 kmol/m^3) was procured from Merck (Germany). 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). Acetone and methanol of HPLC grade were procured from Merck (India). The water used in this study was purified from a Millipore® water purification system. Its conductivity was 1×10^{-5} S/m and its surface tension was 72 mN/m (298 K). Sulfuric acid solutions of lower concentration were prepared by diluting the concentrated acid (18.3 kmol/m^3) with water.

The nitration reactions were carried out in an unbaffled glass reactor (dia. = 10 cm; capacity = 1,000 cm^3) placed in a water bath. The reactor had provisions for sample withdrawal through two Teflon-coated septa placed on the walls of the reactor. The glass agitator had two paddle-type impellers mounted on its shaft, 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,

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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 60 revolutions per minute. The molar ratio of sulfuric acid, nitrobenzene and nitric acid was kept at 37:13.2:1. The samples ($\sim$1 g) from the aqueous, as well as the organic phases were collected at approximately five-min intervals. The reaction was quenched by diluting the collected sample into a large volume of acetone followed by rapid chilling. The samples were analyzed by Janovsky's test[12,14] using a UV–visible spectrophotometer (make: PerkinElmer, model: Lambda 35). The detection of the 1,3-Dinitrobenzene was carried out at $\lambda_{\max}$ = 570 nm. Nitrobenzene, 1,2-Dinitrobenzene and 1,4-Dinitrobenzene do not respond to this test. During the reactions, samples ($\sim$1 g) were collected at 10-min intervals for determination of unreacted nitrobenzene in the aqueous phase. These samples were dissolved in methanol. The amount of nitrobenzene present in the sample was determined by UV spectroscopy from its absorption at $\lambda_{\max}$ = 260 nm.

To determine the yield of 1,3-Dinitrobenzene at different concentrations of sulfuric acid the molar ratio of sulfuric acid, nitrobenzene and nitric acid was kept at 4:1:1. The product and the unreacted reactants were removed from the reactor, diluted with water, chilled, and the solid product was filtered out with repeated washing. It was dried *in vacuo*, and the amount of 1,3-Dinitrobenzene was determined by Janovsky's test.[12,14] The amount of 1,3-Dinitrobenzene present in the organic phase was determined by the same test. From these data, the yield of 1,3-Dinitrobenzene was calculated. The trace amount of unreacted nitrobenzene present in the product was determined by HPLC (make: PerkinElmer, model: Series 200, column: C18, detector: UV, $\lambda = 254$ nm). The mobile phase was constituted of acetonitrile and water in 3:2 volumetric ratio.

For determining the solubility of nitrobenzene in the aqueous phase an excess amount of nitrobenzene was added to the sulfuric acid solution, and the mixture was agitated for about 4 h in a sealed glass vessel (placed inside a water bath) under magnetic stirring. The equilibrated mixture was allowed to separate in two phases for one day. Samples from the aqueous phase ($\sim$1 g) were collected and dissolved in methanol. The amount of nitrobenzene present in the sample was determined by UV spectroscopy ($\lambda_{\max}$ = 260 nm). The amount of sulfuric acid dissolved in the organic phase was determined by acid-base titration using standardized NaOH.

The possibility of formation of the sulfonic acid derivatives of nitrobenzene in the aqueous phase (in the absence of any nitric acid) was investigated by HPLC (column: C18, detector: UV, $\lambda = 254$ nm). The mobile phase was constituted of methanol and water in 4:1 volumetric ratio. The possibility of formation of the sulfonic acid derivative was also investigated by NMR spectroscopy. The organic extract of the aqueous phase was analyzed by NMR spectrometer (make: Varian, model: Mercury Plus 400). The organic compounds present in the aqueous phase were extracted with ethyl acetate. The ethyl acetate was evaporated *in vacuo* in a rotary evaporator. The sample collected from the residue was dissolved in $CDCl_3$ and its ^{1}H-NMR was measured at 400 MHz.

The interfacial tension between the aqueous and organic phases was measured by a digital tensiometer (make: Krüss, model: K9). The du Noüy ring method was used to measure the interfacial tension. The heavier aqueous phase (collected after equilibration) was placed in the sample vessel and the platinum-iridium ring was dipped inside it. Then the lighter organic phase was poured very carefully on top of the aqueous phase. The system was allowed to stabilize for 1 h. The ring was pulled at a very slow speed ($\sim$200 μm/s) until it pierced through the aqueous-organic interface.

The droplet-size distribution of nitrobenzene in the aqueous phase was measured using a dynamic light scattering nanoparticle analyzer (make: Horiba, model: LB-550).

All experiments were conducted at room-temperature (298 K).

Results and Discussion

The nitration reaction takes place by the electrophilic substitution of the nitronium ion on the aromatic ring. Since the reaction mainly takes place in the aqueous phase, the rate of reaction depends on the concentration of nitrobenzene in the aqueous phase. Therefore, it is important to study the solubility of nitrobenzene in the acid phase. Solubility of nitrobenzene was found to depend strongly on the concentration of sulfuric acid. As the concentration of acid was increased, the solubility increased tremendously (Figure 1). A sharp increase in solubility was observed around 16.6 kmol/m^3 concentration of the acid. The solubility of sulfuric acid in the nitrobenzene phase also increased in a similar manner, which is depicted in Figure 1. The data reported by Modak and Juvekar[12] are shown in Figure 1 for comparison. To understand the phenomena behind this significant increase in solubility, the aqueous phase was analyzed by dynamic light scattering. These experiments showed that a fine dispersion of the nitrobenzene droplets was developed in the aqueous phase, which resembled microemulsion. Some of the droplet-size distributions are shown in Figure 2. These distributions were obtained after equilibrating the aqueous and organic phases for one day. The droplet-size distributions were of

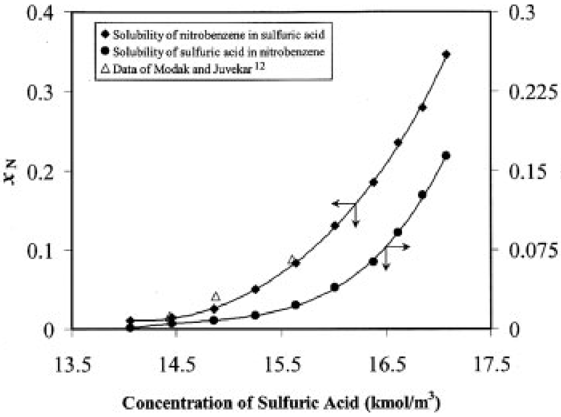

Figure 1. Variation of solubility of nitrobenzene in sulfuric acid (and vice versa) with the concentration of sulfuric acid.

x_N and x_S denote the mole fractions of nitrobenzene and sulfuric acid, respectively.

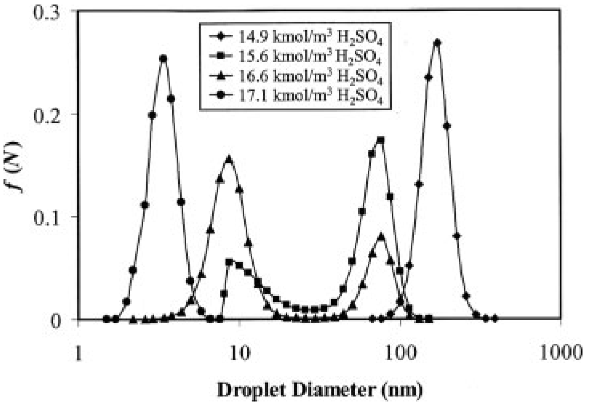

Figure 2. Droplet-size distributions of nitrobenzene at different concentrations of sulfuric acid.

f(*N*) represents the number fraction of the nitrobenzene droplets having size within a small interval.

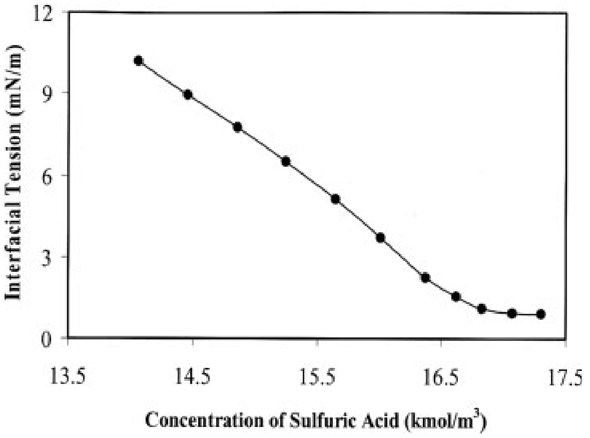

Figure 3. Variation of interfacial tension between nitrobenzene and sulfuric acid with the concentration of sulfuric acid.

unimodal and bimodal types as shown in Figure 2. As the concentration of sulfuric acid was increased, the size of the droplets reduced. At 14.9 kmol/m^3 concentration of sulfuric acid, a large fraction of the droplets had a diameter of a few hundred nanometers, whereas at 17.1 kmol/m^3 concentration, the droplets were very small (<10 nm). This reduction in size occurred due to the decrease in the interfacial tension between nitrobenzene and sulfuric acid. The variation of interfacial tension with increase in the concentration of sulfuric acid is shown in Figure 3. The interfacial tension, however, did not reach the near-zero values usually observed in the surfactant-stabilized microemulsions. The minimum of the interfacial tension curve was attained when the acid concentration was 17.1 kmol/m^3. The size of the droplets increased with time due to the coalescence between the droplets. In the bimodal distributions shown in Figure 2, the larger droplets (50–100 nm) were formed by the coalescence of the smaller droplets. It is likely that a hydrogen-bonded network developed between the sulfuric acid and nitrobenzene molecules, which stabilized the microemulsion for days and even weeks. Nonetheless, the nitrobenzene molecules were chemically free to participate in the nitration reaction as we will discuss later. The size of the droplets and the number of droplets (which depends on the amount of the organic compound dissolved in the aqueous phase) present in the aqueous phase determine the total interfacial area.

To check whether any significant sulfonation reaction took place in the concentrated sulfuric acid medium, the aqueous phase was analyzed by high-performance liquid chromatography (HPLC) and ^{1}H-NMR spectroscopy, as explained in the previous section. There was no peak due to the 3-Nitrobenzenesulfonic acid in the chromatogram. The ^{1}H-NMR spectrum exhibited the presence of signals at $\delta = 7.53$ (*t*, J = 7.2 Hz, 2H, ArH), 7.68 (*t*, J = 7.2 Hz, 1H, ArH), 8.21 (*d*, J = 7.6 Hz, 2H, ArH). These signals are quite similar to the spectrum of nitrobenzene reported in the literature.[15] There was no additional peak anticipated for 3-Nitrobenzenesulfonic acid. This is expected since it is well-known that sulfonation of nitrobenzene proceeds extremely slowly due to the presence of the deactivating nitro group in the benzene ring. At these concentrations of sulfuric acid, however, sulfonation is significant in more active aromatic compounds, such as toluene or benzene.

Since the solubility of 1,3-Dinitrobenzene in sulfuric acid is low even at high-concentrations of the acid, it may be expected that most of the product formed by the reaction would be transported back to the organic phase. At 14.1 kmol/m^3 concentration of sulfuric acid, the amount of 1,3-Dinitrobenzene formed was small, and there was hardly any trace of it in the aqueous phase. The entire product transported back to the organic phase. However, at higher concentrations of sulfuric acid, it was observed that a significant amount of 1,3-Dinitrobenzene remained in the aqueous phase. The concentration profiles of 1,3-Dinitrobenzene in the aqueous phase are shown in Figure 4. 1,3-Dinitrobenzene has significant solubility in nitrobenzene (0.45 moles dissolve in 1 mole of nitrobenzene at 298 K). Therefore, it is likely that 1,3-Dinitrobenzene was solubilized by the nitrobenzene present in the aqueous phase. The concentration profiles of nitrobenzene in the aqueous phase are shown in Figure 5. It is apparent from Figures 4 and 5 that the amount of nitroben-

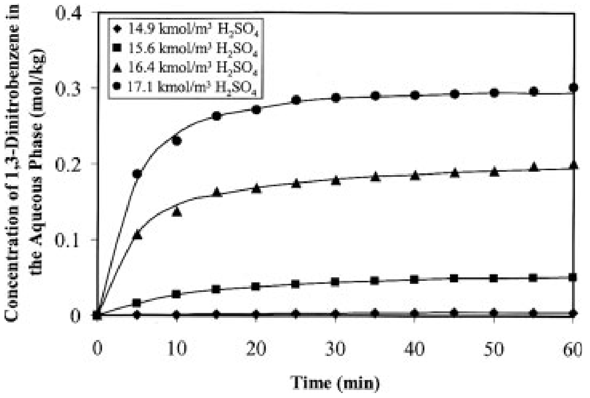

Figure 4. Concentration profiles of 1,3-Dinitrobenzene in the aqueous phase at different concentrations of sulfuric acid.

Reactants were charged to the reactor in the molar ratio, HNO_3 : Nitrobenzene : H_2SO_4 = 1:13.2:37.

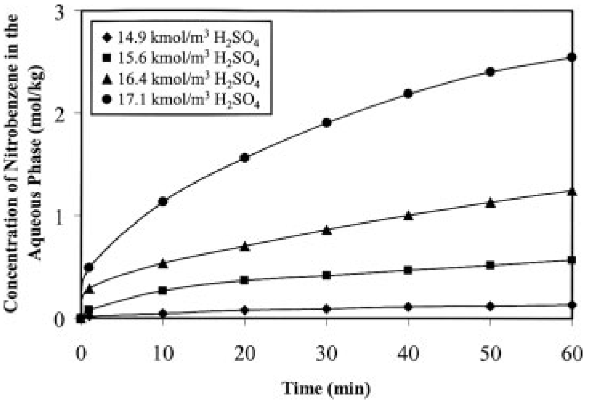

Figure 5. Concentration profiles of nitrobenzene in the aqueous phase during the reaction.

Reactants were charged to the reactor in the molar ratio, HNO_3: Nitrobenzene : H_2SO_4 = 1:13.2:37.

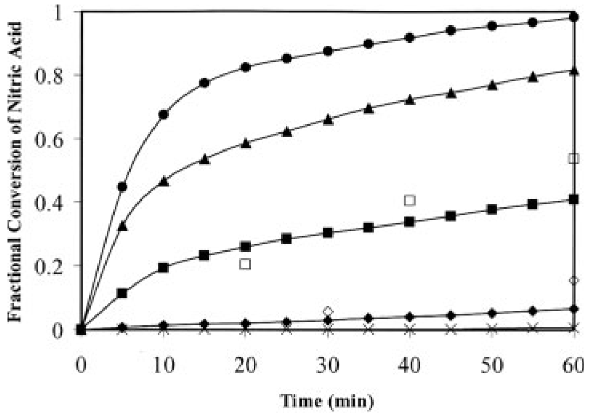

Figure 6. Conversion profiles of nitric acid at 14.1 kmol/m^3 (×), 14.9 kmol/m^3 (◆), 15.6 kmol/m^3 (■), 16.4 kmol/m^3 (▲) and 17.1 kmol/m^3 (●) concentrations of sulfuric acid.

Reactants were charged to the reactor in the molar ratio, HNO_3 : Nitrobenzene : H_2SO_4 = 1:13.2:37. The data of Modak and Juvekar[12] at 14.9 kmol/m^3 (HNO_3 : Nitrobenzene : H_2SO_4 = 1:33:48) (◇), and 15.6 kmol/m^3 (HNO_3 : Nitrobenzene : H_2SO_4 = 1:33:51) (□) concentrations are also shown in the figure for comparison.

zene in the aqueous phase was sufficient to solubilize the 1,3-Dinitrobenzene formed by the reaction in the aqueous phase. The concentration of nitrobenzene in the aqueous phase initially increased rapidly with time. Transfer of nitrobenzene from the organic to the aqueous phase, and its reaction with nitric acid took place simultaneously. Since nitric acid was the limiting reactant, the rate of reaction slowed down after some time, and the concentration of nitrobenzene slowly increased toward its solubility limit. It was observed that after 1 h of reaction, the concentration of nitrobenzene in the aqueous phase was between 25% (for 14.1 kmol/m^3 H_2SO_4), and 70% (for 17.1 kmol/m^3 H_2SO_4) of its equilibrium solubility. Therefore, the aqueous phase was not saturated with nitrobenzene. This is due to the slow stirring, simultaneous reaction, and the long time required for attaining the equilibrium solubility.

The conversion of nitric acid during the reaction is shown in Figure 6. The conversion was calculated by the procedure given by Modak and Juvekar.[12] From Figure 6, it is evident that the conversion increased with the increase in concentration of sulfuric acid. This is due to the increase in the concentration of nitrobenzene in the aqueous phase and the interfacial area. In this reaction, the ratio of nitric acid and nitrobenzene charged to the reactor was 1:13.2. However, the concentrations of nitric acid and nitrobenzene in the aqueous phase (where the nitration reaction took place) were comparable, especially in the lower acid concentrations. Therefore, the rate of reaction depended on the concentrations of both nitric acid and nitrobenzene. The data of Modak and Juvekar[12] are also presented in Figure 6 for comparison in the reactivity. The slightly higher conversions reported by Modak and Juvekar[12] are possibly due to the lower concentration of nitric acid (consequently a higher ratio of nitrobenzene to nitric acid) in the aqueous phase used in their work.

The yield of 1,3-Dinitrobenzene at different concentrations of sulfuric acid are presented in Table 1. In these studies, nitric acid and nitrobenzene were charged to the reactor in their stoichiometric ratio (i.e., 1:1) to ensure maximum conversion of nitrobenzene. It can be observed from the results presented in Table 1 that the amount of product formed at 14.1 kmol/m^3 and 14.9 kmol/m^3 sulfuric acid concentrations was very small. However, the yield of 1,3-Dinitrobenzene increased with the increase in the concentration of sulfuric acid. The high-concentration of nitrobenzene in the acid phase and large interfacial area are believed to be the main factors behind this significant increase in the yield of the product, apart from the high-concentration of the nitronium ion in concentrated sulfuric acid. The highest yield obtained at the room-temperature was 58% (at 17.1 kmol/m^3 concentration of sulfuric acid). The nitration reaction produces water, which dilutes the acid. This factor, along with the low-reactivity of nitrobenzene (as compared to benzene or toluene) is responsible for the low-yield. At high-concentrations of the acid, a major portion of the product turned into a hard porous mass inside the reactor. A significant amount of nitrobenzene was trapped inside the pores. The mixing was not sufficient in this three-phase system. This also caused low-yield. The 1,3-isomer constituted about 93% of the product, which agrees well with the results reported in the literature.[16] The composition of the product did not change with the variation in the concentration of sulfuric acid. Also, the yield did not increase at higher concentrations of sulfuric acid.

Table 1. Yield of 1,3-Dinitrobenzene at Various Concentrations of Sulfuric Acid after 1 h of Reaction

Concentration of Sulfuric Acid (kmol/m^3)	Yield (Moles of 1,3-Dinitrobenzene Formed per 100 moles of Nitrobenzene Charged to the Reactor)
14.1	0.1
14.9	0.3
15.6	13.1
16.4	44.4
17.1	58.0

Reactants were charged to the reactor in the molar ratio, HNO_3: Nitrobenzene : H_2SO_4 = 1:1:4.

Conclusions

This work presents some important physicochemical phenomena associated with the nitration of nitrobenzene in concentrated sulfuric acid. A very rare spontaneous microemulsification phenomenon resulting in the dispersion of fine droplets of nitrobenzene in the aqueous sulfuric acid phase was observed. The nitrobenzene molecules were not involved in any chemical reaction with sulfuric acid. This microemulsification phenomenon is believed to be responsible for the high-solubility of nitrobenzene in the acid phase. It also generated a large amount of interfacial area. This caused a significant increase in the yield of the product (1,3-Dinitrobenzene), with an increase in the concentration of sulfuric acid. The product is soluble in nitrobenzene only. However, it distributed between the organic and the aqueous phases. The presence of the product in the aqueous phase was attributed to the large amount of nitrobenzene in the aqueous phase. The conversion of nitric acid increased rapidly with the increase in the concentration of sulfuric acid. The maximum yield of 1,3-Dinitrobenzene was 58% at 298 K. Reaction carried out at a higher temperature at this concentration of sulfuric acid should increase the yield of the product. Vigorous stirring is required, which can prevent the solid product from forming a hard porous cake inside the reactor.

Acknowledgments

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