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Nitration of toluene in a microreactor

Raghunath Halder [a,*], Adeniyi Lawal [a], Reddy Damavarapu [b]

[a] *New Jersey Center for Microchemical Systems, Department of Chemical, Biomedical and Materials Engineering,*
Stevens Institute of Technology, Castle Point, Hoboken, NJ 07030, United States
[b] *Energetics and Warheads Division, Armament Research, Development and Engineering Center, U.S. Army - Picatinny Arsenal, NJ, United States*

Abstract

Highly exothermic reactions such as aromatic nitration can be carried out in a highly efficient manner in microreactors due to the high heat and mass transfer rates in such reactors. In this study, nitration of toluene was conducted in a microreactor immersed in a constant temperature bath using concentrated nitric acid as the nitrating agent. The effects of residence time, reaction temperature, and acid concentration, etc., on the reactor performance were studied. The results indicate that in the microreactor the nitration reaction proceeds rapidly, even without sulfuric acid, probably by self-protonation of nitric acid. Also, no by-products were detected. The isomeric distribution of the product nitrotoluenes was found to be identical to that generally found in the mixed-acid nitration. The results were compared with the data obtained from a batch reactor, and the microreactor reaction rates were found to be much higher than the batch reactor rates.

Keywords: Nitration; Microreactor; Nitric acid; Nitrotoluene

1. Introduction

Nitration of aromatics is an industrially important reaction for formation of intermediates of many compounds including pharmaceuticals, dyes, explosives, pesticides, etc. These nitration reactions are generally fast and highly exothermic, for example, the heat of reaction for toluene mononitration is 125 kJ/mol [1]. For these reasons, the nitration process can result in temperature runaway in a conventional reactor if not controlled properly. Also, the less efficient mixing and temperature control in the conventional reactors can lead to the formation of undesirable products, such as aromatic acids and aldehydes. Due to its industrial importance, several papers, e.g., [2,3] and patents [4–6] have been published on nitration of toluene.

Industrially nitration is mainly carried out by a mixed-acid process. In this process a mixture of concentrated nitric acid and sulfuric acid is used to nitrate toluene. The purpose of sulfuric acid is to donate a proton to nitric acid, thus forming a nitronium ion which then reacts with toluene to form the three isomers of nitrotuluene in the mononitration process. Sulfuric acid also acts as a water binder which enables this reaction to proceed towards completion. The drawback of this process is that a large amount of sulfuric acid is needed and the spent acid has to be regenerated because a simple neutralization is inconceivable nowadays for environmental and economic reasons.

Liquid phase nitration of toluene is a two phase liquid–liquid reaction in which toluene diffuses to the aqueous acid phase and the reaction takes place in the acid phase [7]. Microreactors have been shown to have very high heat transfer rate due to the high surface area to volume ratio, which enables the microreactors to control highly exothermic reactions very efficiently. Also, due to high mass transfer rates in the microreactors compared to conventional reactors, the reactor productivity or reaction rate can be increased greatly in a microreactor over the conventional reactors for a multiphase reaction in which the reaction is limited by mass transfer. The enhanced mass transfer rate in a microreactor is due to circulation of small alternating slugs of the two liquids at very high speed as shown by Burns and Ramshaw [8] and Dummann et al. [9]. The efficient heat and mass transfer characteristics of a microreactor also enable the suppression of the formation of undesirable by-products. Burns and Ramshaw identified mass

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[*] Corresponding author. Tel.: +1 201 216 8578; fax: +1 201 216 8306.
E-mail address: rhalder@stevens.edu (R. Halder).

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transfer controlled and kinetically controlled regimes for the nitration with mixed acid. The mass transfer rate in the microreactor can be high enough that the reaction can be controlled by intrinsic kinetics only. In this study, the liquid–liquid nitration of toluene is conducted with nitric acid alone in a microreactor in order to demonstrate that reaction rate in a microreactor is superior to that in conventional reactors for this reaction. Originally, we planned to study the effect of different 'solid acid' catalysts, including ZSM-5, on the isomeric distribution in the nitration of toluene by concentrated nitric acid in a packed bed microreactor. The ZSM and other zeolite catalysts have been shown to increase the selectivity of *p*-nitrotoluene in a conventional reactor over the usual distribution of the three nitrotoluenes found in a mixed-acid nitration as shown by Kowk et al. [10], Esakkidurai et al. [11], Vassena et al. [12] and Bernasconi et al. [13]. However, we found that the isomeric distribution using different solid acids packed in the microreactor was very similar to the mixed-acid nitration. It was also found that in the microreactor, concentrated nitric acid reacted very rapidly even at ambient temperature without any sulfuric acid or solid acid catalysts.

2. Experimental set-up and procedure

Fig. 1 shows a sketch of the experimental set-up used to test the performance of different solid acid catalysts for the nitration of toluene. Toluene and concentrated nitric acid were pumped by two HPLC pumps and mixed in a 1/16 in. SS316L T-mixer. After mixing the two reactants in the T-mixer at room temperature, the reaction mixture was passed through a tubular microreactor packed with different solid acid catalysts. The reactor was made of SS316L stainless steel having an inner diameter of 775 μm. The total length of the packed reactor was 8.5 cm of which 6.0 cm was packed with the catalyst. Downstream of the catalyst bed, the remaining reactor length was filled with inert glass beads. The particulate catalyst size was in the range of 75–150 μm. The glass beads were spherical and were in the size range of 63–75 μm. The glass beads were used to prevent any fine catalyst particles from clogging the filter placed at the ends of the reactor. In each of the experiments reported here with solid catalysts, 13 mg of solid acid catalyst, and about 20 mg of glass beads were used. The reactor was connected to the rest of the experimental set-up with PTFE fittings. The reactor was then immersed in a constant temperature water bath to obtain uniform reaction temperature. The tube connecting the reactor with the T-mixer had an inner diameter of 775 μm. From the constant temperature bath the mixture flowed to a product receiver where the product was collected in sodium carbonate solution to stop any further reaction. The tube used to connect the product receiver, and the reactor had also an inner diameter of 775 μm. The total length of the flow path after the T-Mixer was 220 cm and mainly consists of 775 μm inner diameter SS316L tube.

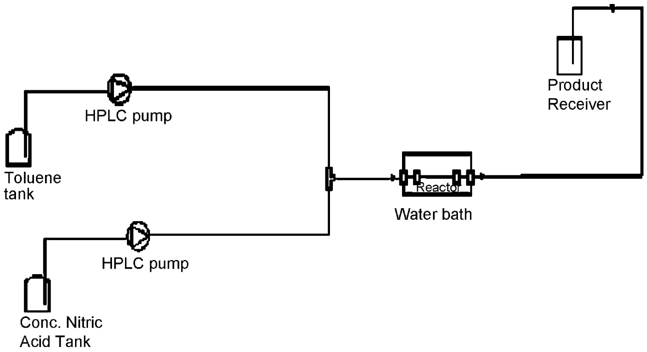


Fig. 1. Set-up for toluene nitration.

2.1. Analytical procedure

After attaining steady state during a run, the sample was collected in the product receiver containing sodium carbonate solution to neutralize the unreacted nitric acid and thus to prevent further reaction. The organic phase was then separated from the aqueous phase. A fraction of the organic phase was diluted using excess toluene, and then the diluted sample was analyzed in a Shimadzu model GC-14B gas chromatograph using an Agilent DB5 column and a thermal conductivity detector with helium as the carrier gas. An internal standardization method was used following the procedure given by Grob [14]. The concentration of the unreacted toluene was calculated from the concentrations of the three nitrotoluenes since no other products or by-products were found to form in the process. Nitric acid was used as the limiting reactant in all the runs, and since the mass flow rates of the aqueous and organic phases changed due to the reaction, the conversion of the limiting reactant nitric acid was calculated from a mass balance which is as follows:

$$w = \frac{\mathrm{MW_{NT}} \times C}{\mathrm{MW_{NT}} \times C + (R - C) \times \mathrm{MW_T}},$$

which when solved for the conversion gives,

$$C = \frac{\mathrm{MW_T} \times w \times R}{\mathrm{MW_{NT}} - (\mathrm{MW_{NT}} - \mathrm{MW_T}) \times w} \qquad (1)$$

where C is the conversion in fraction, $\mathrm{MW_{NT}}$ the molecular weight of nitrotoluene (137), $\mathrm{MW_T}$ the molecular weight of toluene (92), w the weight fraction of total nitrotoluenes (i.e., *o*-, *m*- and *p*-nitrotoluenes) in the product organic phase and R (≥ 1) is the molar feed ratio of toluene to nitric acid. Determination of conversion by measurement of the nitric acid concentration in the aqueous phase was not done because we observed brown fumes, probably of nitrogen dioxide formed during the process, accumulating in the product receiver on top of the liquid phase.

3. Results and discussions

3.1. Effect of solid catalysts on isomeric distribution

Fig. 2 shows the results obtained with the reactor packed with different solid catalysts, and Table 1 shows the isomeric distribution of the three nitrotoluenes obtained. Zeolite-based

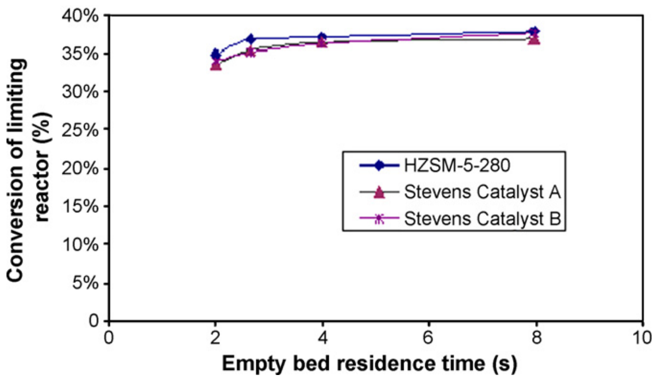


Fig. 2. Effect of residence time on conversion (reactor at 90 °C, HNO_3 conc. = 90% (w/w), toluene/HNO_3 molar ratio = 1.3, 13 mg of catalyst).

Stevens catalysts A and B were prepared at Stevens Institute of Technology with different SiO_2 to Al_2O_3 ratio by sol–gel method. ZSM-5-280 in the hydrogen form (with a SiO_2/Al_2O_3 mole ratio of 280) was commercially obtained. It appears from the data that the conversion does not change much with residence time suggesting that the conversion is close to an equilibrium value. The conversion and the isomeric distribution appear to be very similar for all the three solid acids studied and the isomeric distribution is very similar to the isomeric distribution generally obtained in a mixed-acid toluene nitration.

The low conversion obtained in the experiments may be explained as follows.

Nitronium ion is responsible for the nitration of toluene with nitric acid. Marziano et al. [15] found that the concentration of nitronium ion is highly dependent on the nitric acid concentration. As the reaction progresses the acid is diluted due to the formation of water in the reaction, and nitronium ion concentration decreases. In fact, it has been observed that nitronium ion is nonexistent below certain concentration of nitric acid [16]. The catalyst bed length was very small compared to the total length of the microchannel after contacting the reactants. Thus, it appeared that in the microreactor set-up, most of the conversion took place outside the solid catalyst bed, and thus the effect of the solid catalysts on the isomeric distribution and conversion could not be established.

To prove that most of the conversion took place outside the solid acid catalyst bed, we conducted experiments in an empty tube of 775 μm inner diameter and 120 cm long (after the T-mixer) in which the whole length of the tube from the T-mixer, except 5 cm at the exit portion for sample collection, was immersed in the constant temperature bath. All the following data in the microreactor were taken from this reactor of length 120 cm, practically all of which was immersed in the constant temperature bath.

Table 1
Isomeric distribution with different 'solid acid' catalysts

	Catalyst		
	HZSM-5-280	Stevens catalyst A	Stevens catalyst B
o-Nitrotoluene (%)	55.82	55.57	54.94
p-Nitrotoluene (%)	39.58	40.10	40.23
m-Nitrotoluene (%)	4.60	4.33	4.82
o-/*p*-Ratio	1.41	1.39	1.37

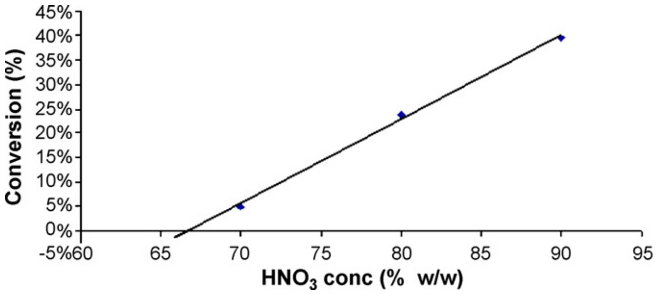


Fig. 3. Effect of nitric acid concentration on conversion.

3.2. Effect of feed nitric acid concentration on conversion

The effect of initial nitric acid concentration on the conversion in the empty tube is shown in Fig. 3. The data show that initial nitric acid concentration has a strong effect on the conversion, and this is due to the effect of water on nitronium ion concentration as mentioned above. Extrapolation of the experimental data shows that below a nitric acid concentration of 66% (w/w) or 14 mol/l the nitronium ion concentration becomes zero. Thus, the nitronium ion concentration can be written as,

$$[NO_2{}^+] = k([[HNO_3] - 14]) \qquad (2)$$

where k is the proportionality constant.

3.3. Effect of reaction temperature on conversion

The effect of temperature on conversion is shown in Fig. 4. The flow rates were sufficiently low that final conversion was attained at the end of the reactor. It appears from these results that with decrease in temperature the conversion slightly increases. This may be due to increase in nitronium ion concentration with decrease in temperature as reported by Edwards and Fawcett [16].

We also conducted experiments by immersing the reactor in the water bath at 22 °C to find out the extent of the conversion

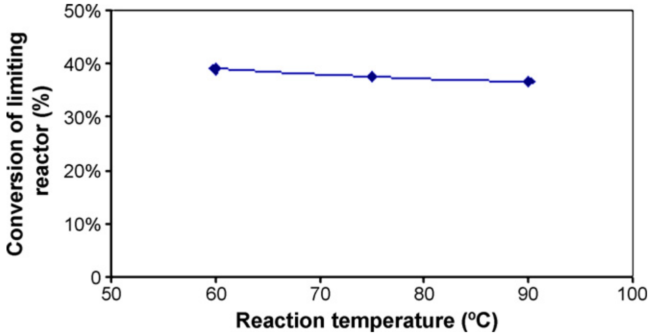


Fig. 4. Effect of reaction temperature on final conversion (toluene to nitric acid molar flow ratio = 1.3, 0.15 ml/min of toluene, 0.05 ml/min of 90 wt.% HNO_3).

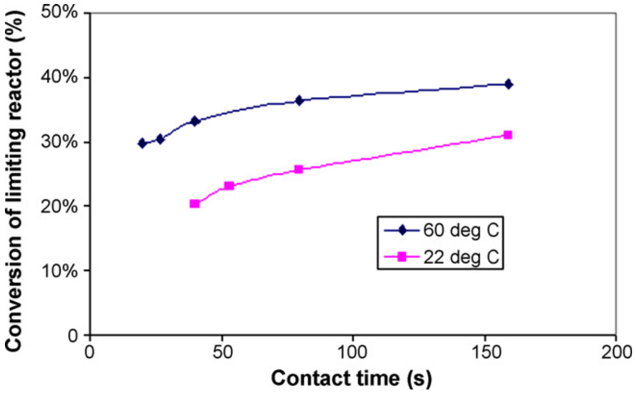


Fig. 5. Conversion in empty tube with residence time (HNO_3 conc. = 90% (w/w), toluene/HNO_3 molar ratio = 1.3, 120 cm reactor length).

taking place at ambient temperature without any solid acid. As mentioned above, 115 cm length of the reactor was immersed in the water bath keeping 5 cm out of the bath to collect samples. Fig. 5 shows the conversion near ambient temperature (room temperature was 20 °C during the runs). In each of the runs, the water bath temperature did not deviate by more than 0.5 °C from 22 °C. It appears from these data that the nitration of toluene with 90 wt.% nitric acid proceeds rapidly even at ambient temperature and without any other catalyst. This is due to nitric acid acting as a self-catalyst in which one molecule of nitric acid protonates another leading to the formation of the nitronium ion according to the following reaction [17]:

$$2HNO_3 \leftrightarrow NO_2^+ + NO_3^- + H_2O$$

For a comparison of this conversion with the conversion at the higher temperature of 60 °C, the 60 °C data are also included in Fig. 5. Although the data at 60 °C suggest that final conversion was attained at 160 s residence time, data for the 22 °C run show that conversion was still increasing with residence time and if the trend of Fig. 4 continues, the final conversion would probably have been more than that of 60 °C. These data might explain the reason why we were not obtaining our desired increase in the selectivity of *p*-nitrotoluene with solid acids, particularly with ZSM-5-280 catalyst. The data suggest that most of the conversion was taking place outside the solid acid catalyst bed.

4. Experimentation in a batch reactor

To compare the reaction rates of the microreactor and a batch reactor, we conducted the nitration reaction in a batch reactor made by PARR Instrument Company, model 5511 having a volume of 25 ml. It is made of stainless steel 316 and equipped with a magnetic drive stirrer. It has an electrical heating system and also a jacketed heating/cooling system. The reactor comes with, among other devices, a controller which can control the stirrer speed and reactor temperature, a pressure transducer and a sampling valve. For a batch run, initially 5 ml of 90 wt.% nitric acid was charged to the reactor. From a constant temperature water bath, water was circulated through the jacket at a temperature which would give the desired reactor temperature. After the reactor attained the desired temperature, 15 ml of toluene was introduced into the reactor by a syringe through the sampling port. The total volume of the reactants was thus 20 ml. After adding the toluene, the temperature of the reactor was found to rise immediately, however very quickly it came back to the desired reactor temperature due to the cooling by the jacket. The reactor temperature was maintained constant by circulating water from the constant temperature bath through the jacket. The stirrer speed was kept constant at 400 rpm. Although this is a liquid–liquid reaction, during a run the pressure of the reactor was found to increase with time even in a run made at 22 °C. We found some brown fumes to be present in the reactor after the completion of the run. This is possibly due to the formation of some nitrogen dioxide which increased the reactor pressure. Under this gas pressure, samples were collected at different times through the sampling port. The conversion and isomeric distribution were determined in a gas chromatograph as mentioned before.

4.1. Comparison of the batch reactor and microreactor data

Figs. 6–9 show the comparison of the conversion and the average reaction rates for the batch reactor and the microreactor at two temperatures of 60 °C and 22 °C. The average reaction rates reported in these figures are based on whole reactor volume and not on the acid phase only. Based on the acid phase volume

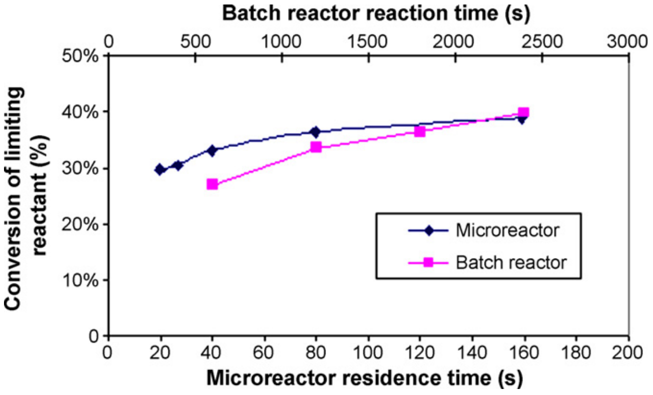


Fig. 6. Conversion with time in microreactor and batch reactor at 60 °C (toluene:HNO_3 molar feed conc. ratio = 1.3).

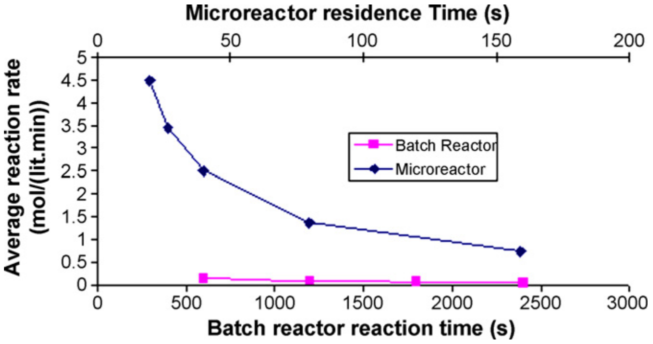


Fig. 7. Average reaction rate in microreactor and batch reactor at 60 °C.

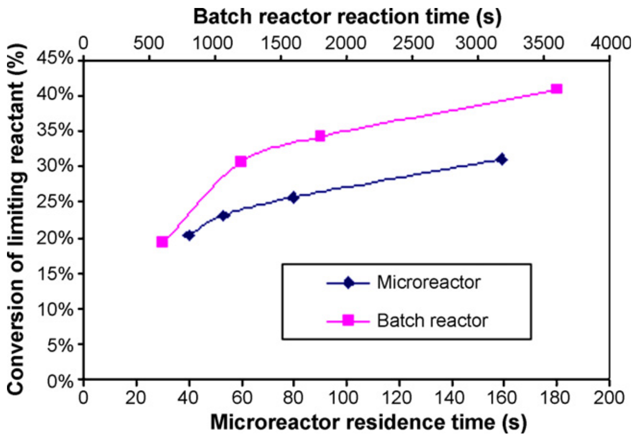


Fig. 8. Conversion with time in microreactor and batch reactor at 22 °C (toluene:HNO_3 molar feed conc. ratio = 1.3).

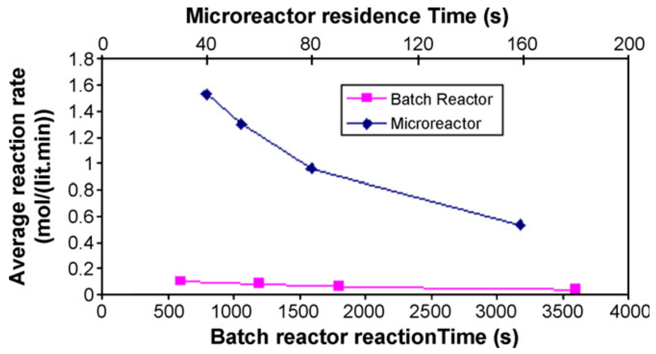


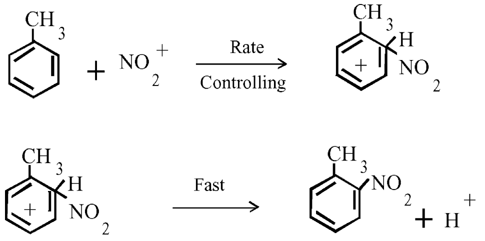
Fig. 9. Average reaction rate in microreactor and batch reactor at 22 °C.

the rates would be 4 times higher than the rates reported in the figures. The microreactor data were obtained in a 120 cm long 775 μm inner diameter empty microreactor as mentioned before. The values of the ratio of the reaction rates of the two reactors at 60 °C and 22 °C as shown in Figs. 7 and 9 are approximately 30 and 15, respectively. This suggests that mass transfer rates influence the rate in the batch reactor. The higher ratio of the reaction rates at higher temperature is probably due to intrinsic kinetic rate rising much more rapidly than the mass transfer rate with the rise in temperature resulting in the influence of mass transfer resistance becoming more predominant at higher temperature. As mentioned later in this work, in the microreactor intrinsic kinetics probably influences the reaction rate under our operating conditions, while both mass transfer and intrinsic kinetics probably influence the rate in the batch reactor, particularly at low temperature. While appreciable amount of by-products were found in the microreactor, no appreciable by-products were found in the microreactor.

Burns and Ramshaw [8] conducted the nitration reaction of toluene in a microreactor with mixed acid and found that the mass transfer coefficient is much higher in the microreactor compared to a conventional reactor.

5. Kinetic studies from microreactor data

In the nitration of toluene, the nitronium ion reacts with toluene to form the transition complex which then gives nitrotoluene and hydrogen ion. The reaction takes place in the acid phase where toluene diffuses from the organic phase [7].



The reaction rate is given by,

$$\mathrm{Rate} = k_2[\mathrm{Tol}][\mathrm{NO_2}^+] \tag{3a}$$

where [Tol] is the toluene concentration and $[\mathrm{NO_2}^+]$ is the nitronium concentration in the acid phase.

The rate equation of nitration of aromatics using mixed acid as given by [18] is,

$$\mathrm{Rate} = k_2[\mathrm{HNO_3}][\mathrm{Aromatic}] \tag{3b}$$

This indicates that the nitronium ion concentration is proportional to the nitric acid concentration in mixed acid. As mentioned previously, nitronium ion in nitric acid is formed by the protonation of one molecule of nitric acid by another. Although the concentration of nitronium ion is a function of nitric acid concentration, as shown in Fig. 3 it is not a true thermodynamic equilibrium.

A simple pseudo-first order rate for this reaction in the microreactor is assumed based on the following assumptions:

1. The concentration of toluene in the acid phase is very small compared to the organic phase. For a slow intrinsic kinetics rate compared to the mass transfer rate, the concentration of toluene in the acid phase is assumed to be constant and equal to its saturation concentration.
2. The variation of saturation concentration of toluene in nitric acid is independent on the temperature in the range of reaction temperatures studied.

Based on the assumptions and substituting the value of $[\mathrm{NO_2}^+]$ from Eq. (2) into Eq. (3a) rate Eq. (3b) becomes,

$$\mathrm{Rate} = k_1[[\mathrm{HNO_3}] - 14] \tag{4}$$

where $[[\mathrm{HNO_3}] - 14]$ is a reduced nitric acid concentration and k_1 is the pseudo-first order rate constant.

Experiments have been conducted at high flow velocity and low temperature ranges where the mass transfer resistance is assumed to be negligible. Experiments were conducted using 120 cm long reactor with inner diameter of 775 μm. Reactants flow rates were 3.0 ml/min of toluene and 1.0 ml/min of 90% (w/w) HNO_3. The reaction temperatures were 22, 29 and 35 °C. The conversions of the limiting reactant, nitric acid, at these three temperatures were found to be 7.13, 8.97 and 12.3%, respectively. Correspondingly the conversions based on reduced nitric acid concentration were 20.32, 25.56 and 35.04%.

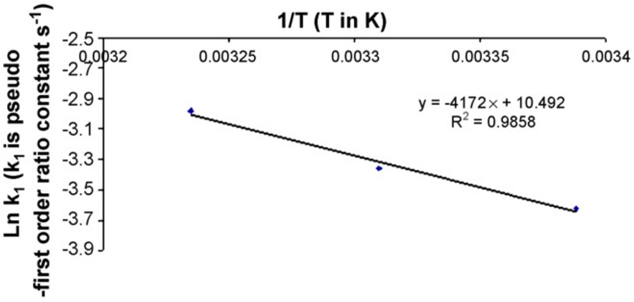


Fig. 10. Arrhenius plot of pseudo-first order rate constant.

For a first order reaction in a plug flow reactor, the fractional conversion can be written as:

$$X = 1 - e^{-k_1 \tau} \tag{5}$$

where X is the fractional conversion based on reduced concentration of nitric acid and τ is the residence time.

Fig. 10 shows the Arrhenius plot of the logarithm of pseudo-first rate constant obtained using Eq. (5) against $1/T$, where T is the absolute temperature in K.

The value of activation energy is found to be 8290 cal/mol from the plot, and the pseudo-first order reaction rate equation is,

$$\begin{aligned} \text{Rate} &= -\left(\frac{[\text{dHNO}_3]}{\text{d}t}\right) \\ &= 3.60261 \times 10^4 \exp\left(\frac{-4172}{T}\right)([[\text{HNO}_3] - 14]), \end{aligned} \tag{6}$$

where the first order rate constant, $3.60261 \times 10^4 \exp(-4172/T)$, is in s^{-1}.

The nitric acid concentrations represented in these equations are based on acid phase and hence the rate as represented by Eq. (6) is based on the acid phase volume only. The activation energy obtained in this work is close to the 8400 cal/mol as reported by Marziano et al. [15] for mixed-acid nitration where nitronium ion is also the nitrating species. Thus, under the conditions experiments were conducted in these three runs, the reaction is limited by intrinsic kinetics, since effect of mass transfer limitation on the rate would have decreased the value of activation energy significantly since the effect of temperature on mass transfer coefficient is small compared to its effect on reaction rate constant.

5.1. Prediction of the experimentally obtained conversions in the microreactor

The predicted conversions based on kinetically controlled rates given by Eq. (6) at different residence times at two temperatures of 22 °C and 60 °C are compared in Figs. 11 and 12 against the experimentally obtained conversions reported in Figs. 6 and 8. The predicted conversions based on reduced nitric acid concentration are converted to the conversion based on actual nitric acid concentration, which are shown in these figures. The experimental and predicted conversions are close enough to conclude that the reaction is kinetically controlled in our experimental conditions, since had mass transfer affected the reaction rates, the actual conversions would have been much lower than conversions predicted by kinetics. The differences between the experimental and predicted conversions could be due to several assumptions made in developing the rate equation which might not be very accurate. In the batch reactor at 22 °C kinetics might have more influence on the rate than at 60 °C, which made the ratio of the rate in microreactor and batch reactor higher at 60 °C. The rate in the batch reactor at 60 °C might either be fully controlled by mass transfer or kinetics might have some influence on the rate.

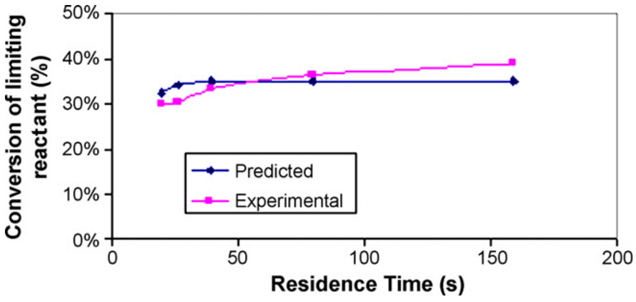


Fig. 11. Comparison of experimental and predicted conversion in microreactor at 60 °C.

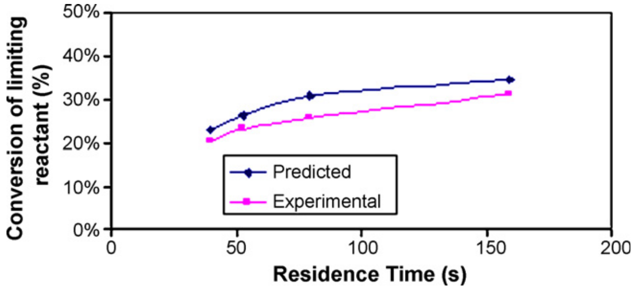


Fig. 12. Comparison of experimental and predicted conversion in microreactor at 22 °C.

The enhanced mass transfer rate in a microreactor is due to circulation of small alternating slugs of the two liquids at very high speed inside the reactor as stated by Burns and Ramshaw [8]. These alternate slugs were also observed in our work when a transparent tube was installed at the outlet of the stainless tube reactor.

6. Conclusions

The results obtained in this work suggest that in the multiphase liquid–liquid nitration of toluene with 90 wt.% nitric acid, in a microreactor intrinsic kinetics probably controls the reaction rate under all the conditions studied in this work. From the comparison of the results of the microreactor with those of the batch reactor, both mass transfer and intrinsic kinetics rates influence the reaction rate at low temperature while mass transfer rate has more influence on the reaction rate at high temperatures. Thus, for this reaction much higher reaction rate, in orders of magnitude, could be obtained in a microreactor than in the conventional reactors while at the same time preventing any temperature runaway due to its superior heat and mass transfer coefficients. By-products were also eliminated in the microreactor. However, with nitric acid alone as the nitrating agent, the yield of the nitrotoluenes is low due to the adverse dependency of water formed in the reaction on the nitronium ion concentration.

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