

AROMATIC NITRATION STUDIES IN HIGHER STRENGTH OF SULFURIC ACID: NITRATION OF NITROBENZENE

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Summary

Nitration reactions, conducted using mixed acid, are extremely exothermic, and tend to be explosive. It is necessary to study the reaction kinetics in detail to identify the window of operating parameters which offers safe operation yet desired performance. During our studies on nitration of nitroaromatics, the data suggests that nitroaromatics exist in the form of microemulsion at ambient temperatures. The microemulsion is found to play a major role in the kinetics of polynitration. The reaction of nitro compound (nitrobenzene) and nitric acid occurs at the interface between the organic microphase and acid phase.

Keywords: *Reaction path analysis, Multiscale analysis, Multiphase and particulate reactors.*

Introduction

Nitration reactions are extremely exothermic, and tend to be explosive. Nitration is, therefore, considered as one of the most hazardous industrial processes.^{1,2} From safety consideration, most polynitration reactions are conducted in a battery of small reactors operated in batch mode. These reactors are kept inside enclosures and operated by remote control. The origin of the explosive nature of nitration reaction lies in the peculiar behavior of the reaction and this work is an attempt to bring out some of these aspects of the reaction.

During our studies on nitration of nitroaromatics, we observed that the nitroaromatics exist in concentrated sulfuric acid (> 80% w/w) in the form of microemulsion³. The microemulsion is found to play a major role in the kinetics of polynitration. The major part of the reaction between the nitro compound and nitric acid occurs at the interface between the organic microphase and the acid phase. The microphase thus shields the aromatic species and reduces the contact with the acid present in the bulk. Thus it provides a natural control on the rate of nitration. The microemulsion is very stable over a certain range of temperature. At a critical temperature called inversion temperature, microemulsion phase vanishes and a homogeneous solution results. At this point, the reaction between nitroaromatic species and nitric acid becomes homogeneous. The rate of reaction can increase to a catastrophic level at this temperature. For better control of the polynitration reactions, it is necessary to understand their behavior in the vicinity of the critical point.

The aim of our studies is to understand the kinetics of polynitration with interfacial phenomenon as well as to collect the evidences for existence of microemulsions in reaction mixture. Also, the various effects on kinetics of nitration such as the presence of mole ratio of nitrobenzene (NB) to nitric acid as well as dinitrobenzene (DNB) to nitrobenzene have been studied. It is observed that the presence of dinitrobenzene strongly influences the reaction kinetics by inhibiting the rate.

Experimental Section

Nitrobenzene is used as the model reactant for mixed acid nitration. Reactions are conducted, under isothermal condition, in a batch reactor (100mL agitated reactor with a water cooled jacket). Batch reactor is used at relatively lower concentration of sulfuric acid (81-87 % w/w).

In the batch mode, the reaction mass is sampled at regular intervals of time. The sample is quenched with chilled methanol-water mixture and analyzed for conversion of nitrobenzene and the product distribution using HPLC. The parameters under study are strength of sulfuric acid, concentration of nitric acid, mole ratio of nitrobenzene and nitric acid. Some reactions are also conducted using mixture of nitrobenzene and dinitrobenzene as the feed stream.

Few phase equilibrium experiments were also performed under nonreacting conditions (i.e. in the absence of nitric acid) to identify formation of three distinct phases supporting the hypothesis of formation of microemulsions.

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Results and Discussion

Effect of Acid Strength - The reactions with equimolar feed were carried with varying strength of sulfuric acid (81-87%). The effect of loading as well as the strength is studied. As the sulfuric acid strength increases the time required for completion of reaction was reduced. In lower strength, i.e. 81%, the time required for the complete conversion is almost 8-9 days, while in case of higher strength, 88%, it is of the order of few hours (2-3 hrs). The data fits second order kinetics which is as shown in Fig. 1.

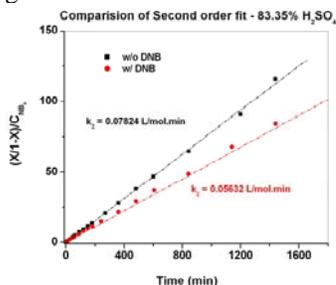


Figure 1: Effect of DNB on rate of nitration

Effect of Dinitrobenzene - Fig. 2 shows the kinetics in presence and absence of dinitrobenzene. The presence of dinitrobenzene inhibits the reaction which may result in the lesser conversion of nitrobenzene as compared to normal equimolar reaction. When DNB is added initially along with nitrobenzene, though the absolute interfacial area increases, the area per unit volume is expected to reduce which results in a drop in rate.

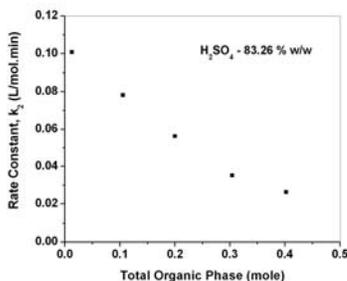


Figure 2: Rate constant dependence on organic phase

Microemulsions - Rahman et al.⁵ had shown the existence of particles in nitrobenzene - sulfuric acid system. The size of particles varies with strength of sulfuric acid. There size of particles varies over a range 10 - 500 nm. In this study the particles are observed as the middle phase in case of three phase formation, as like the Winsor - III phases.

Effect of Loading of NB - As the loading of NB increases, the interfacial area also increases but area per unit volume decreases leading to drop in rate of reaction. The plot for rate constant vs loading of total organic phase, for 83 % sulfuric acid, is shown in Fig. 3. From the plot of rate constant vs NB loading, one can get an idea of how interfacial area varies with rate. So if

the rate vs NB loading varies with square relation, then particles may be spherical one. Else, it can be of either bicontinuous layer or lamellar layer.

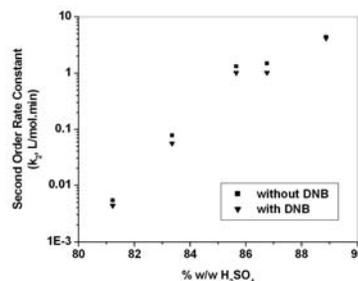


Figure 3: Effect of H₂SO₄ acid strength on 2nd order rate constant (Equimolar reaction for HNO₃, NB and DNB)

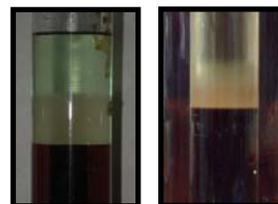


Figure 4: 3-phase formation in NB-H₂SO₄ system

Table 1: Three phase composition (at 26 °C, 1 atm)

| Components | Initial Composition (% w/w) | Final Composition (% w/w) | | |
|---------------|-----------------------------|---------------------------|--------------|--------------|
| | | Top Phase | Middle Phase | Bottom Phase |
| Sulfuric acid | 84.93 | 1.0 | 61.94 | 78.27 |
| Water | 15.07 | 0.1 | 0.05 | 21.72 |
| Nitrobenzene | 100.00 | 98.9 | 38.01 | 0.01 |

Conclusions

This work provides an insight into the nitration reaction kinetics at high strength of sulfuric acid. The reaction does not follow the expected elementary kinetics. The conversion profiles and rate obtained show the inhibition of reaction due to formation of product as well as initial loading of dinitrobenzene. The existence of three distinct phases is observed which indicates the formation of microemulsions. Further studies in the direction of understanding the details of inhibition are under consideration and progress.

References

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