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Study of the reaction paths for cleaner production of nitrochlorobenzenes using microwave irradiation

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ABSTRACT

2,4-Dinitrochlorobenzene (2,4-DNCB) is produced using microwave (MW) assisted nitration of monochlorobenzene (MCB). This offers the advantage of energy transformation and volumetric heating throughout in a shorter reaction time and controls the excess solvent usage. The present study investigates the conversion and selectivity for the production of nitro-chlorobenzene compounds by series nitration of chlorobenzene under microwave irradiation. Operating parameters such as reaction time, feed composition, microwave energy and reaction temperature were systematically investigated for the nitration of MCB. Advantages like reduction in reaction time, minimization of waste acid production, enhanced yield and selectivity for the desired products were important observations. The nitration kinetics of MCB and intermediate compounds like *para*-nitrochlorobenzene (PNCB) and *ortho*-nitrochlorobenzene (ONCB) have been further investigated. The kinetic batch reactor modeling was anticipated for the nitration as a forward reaction.

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1. Introduction

Electrophilic aromatic substitution reactions are of considerable importance in production of fine chemicals. However, traditional processes suffer a number of disadvantages, such as poor selectivity towards desired product and requirement for large quantities of mineral or Lewis acids as activators. In turn these acids are responsible for corrosion problems within the plant and the generation of large volumes of spent reagents, which, given the current environmentally conscious climate, are increasingly unacceptable. Major efforts are therefore being made towards developing processes that can reduce the volumes of spent liquids produced. Inorganic solid catalysts can offer significant benefits including enhanced selectivity. Additionally they can be easily removed from reaction mixtures and in some cases recycling is possible (Smith et al., 2000).

Among all electrophilic substitutions, nitration of aromatic substrates is a widely studied reaction of great industrial significance as many nitro-aromatics are extensively utilized as chemical feedstock

for a wide range of useful materials such as dyes, pharmaceuticals, etc. However, earlier technologies involve the excess use of corrosive liquid phase nitric acid–sulphuric acid mixture, responsible for the generation of large amounts of wastes, which are expensive to treat. Other associated problems are over-nitration, oxidation of by-products and poor selectivity. This necessitates the need for new, novel and simpler methods for nitration which can overcome these problems (Esakkidurai et al., 2003).

Use of microwave activation in organic syntheses has become standard tool for organic chemists because of enhancement in reaction rate, higher yield and improved selectivity. Further microwave assisted reactions are clean and safe (Deodher et al., 2010; Surati et al., 2012; Chandra Shekara et al., 2011). Microwave is a convenient way toward the goal of green/sustainable chemistry, and is strongly recommended to use in organic preparations (Surati et al., 2012).

The microwave (MW) assisted nitration reactions are much friendlier to the environment than their conventional counterparts. The effects usually observed with microwave activation in organic reac-

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tions are cleaner reaction with easier workup, and reduced effluent load (Umrigar et al., 2007). The MW dielectric heating effect uses the ability of some liquids and solids to transform electromagnetic energy into heat and thereby drive chemical reactions. Various examples of organic synthesis using microwave radiation, e.g., the Heck reaction, the Ullmann condensation reaction, and transition metal catalyzed carbonylation reactions, were cited (Kappe, 2004). Despite such an abundance of literature, to the best of our knowledge there is hardly any reported work on microwave (MW) assisted mono and di-nitration of chlorobenzene.

Thus, in light of the literature reported, in the present work it is proposed to study mono and di-nitration of chlorobenzene using minimum quantity of mixed acids ($\text{HNO}_3:\text{H}_2\text{SO}_4 = 1:1$) and varying reaction parameters like temperature, power, concentration of sulfuric acid (catalyst), without/with intermediate cooling in MW to study selectivity, conversion and kinetics of the reaction. Further to correlate the results, we have exposed proper kinetic model equation to signify the observed reaction paths.

We have studied reaction mixing in stoichiometric amounts of mixed acids (conventionally it is 5 times more) with monochlorobenzene (MCB) using microwave irradiation, which eliminates the production of spent acid. Several separation steps have been carried out to get pure form of nitrochlorobenzenes (NCBs). Upon further reaction of NCBs with mixed acids, *para*-NCB (PNCB) and *ortho*-NCB (ONCB) finally produce dinitro compounds: 2,4-dinitrochlorobenzene (2,4-DNCB) as a major and 2,6-dinitrochlorobenzene (2,6-DNCB) as a minor product.

Extraction of products and their analysis were carried using Thin Layer Chromatography (TLC), Gas Chromatography–Mass Spectrometry (GCMS) to calculate conversion, selectivity and to study the reaction kinetics. Main objective of the reaction was to utilize nitric acid and sulfuric acid in stoichiometry requirement to minimize their waste and separation cost. Use of microwave energy decreases reaction time, minimizes waste acid production, and enhances the yield and selectivity for the desired products.

2. Materials, methods and mechanism

2.1. Materials

MCB, concentrated nitric acid, sulfuric acid with a quoted purity 99%, 63% and 98%, respectively, PNCB, ONCB (both of 99%) were procured from Merck, India. All analytical reagents like diethylether and sodium bicarbonate for separation and neutralization of products mixture, *n*-octanol and ammonia for TLC, paraffin for melting point analysis and acetone for gas chromatography were also purchased from Merck, India.

2.2. Method

Reactions were carried out (using $\text{MCB}:\text{HNO}_3:\text{H}_2\text{SO}_4$, i.e., Cl:N:S:1:1:1) in a thermo-stated microwave assisted glass reactor equipped with a magnetic stirrer. An advanced microwave synthesis labstation (MILESTONE, India) operating at 2.45 GHz frequency was used in this study. For each run, sulfuric acid and nitric acid in desired proportion were mixed to prepare homogeneous mixture by maintaining the temperature 0–5 °C. Reaction was carried out at different temperatures and powers. Samples of about 10 mL were withdrawn from the reactor at different intervals of time and analyzed.

Batch round bottom flask reactor was used using heating mantle with condenser unit conventionally. And in microwave reactions, batch reactor with continuous stirring without any reflux system.

2.3. Reaction-mechanism of nitration

Acid-catalyzed nitration of aromatic compounds occurs according to the electrophilic aromatic substitution mechanism as proposed by Ingold and Hughes (Barnasconi, 2003). The accepted mechanism consists of four steps:



The first two steps involve the acid-catalyzed transformation of the nitric acid into the nitronium ion (NO_2^+), which is the actual active agent in the nitration reaction. Aromatic molecules of modest reactivity exhibit second-order kinetics in mixtures of nitric acid with a strong acid (sulfuric acid). Under these conditions, NO_2^+ ion is formed in a rapid pre-equilibrium and the third step of the nitration mechanism is the rate-determining step - 3.

In this step, NO_2^+ ion attacks the aromatic ring to form the intermediate. In case of reactive akylaromatic compounds, the original Ingold mechanism had to be modified by invoking two separate intermediates:



2.4. Analysis of reaction mass

Intermediate and final products were separated from excess acid mixtures and washed with acetone for further purification of the solid mass. Purity of products was measured with TLC (0.25 mm thickness) silica gel G coated Al plates (Merck) and the spots were visualized by exposing the dry plates in iodine vapor chamber using *n*-octanol:ammonia (7:3 v/v, upper layer) as a solvent for the analysis of NCBs as a primary detection of the product. It gives direct visualization (preliminary confirmation) of the yellow colored nitro-chloro products. Purity of monochloronitro compounds was determined using GC (GC 14-B-Shimadzu-SY-2, Japan). Product crystals were dissolved in sodium bicarbonate solution for neutralizing the sample to maintain the pH 7.0.

For analysis of dinitrochloro compounds GC–MS analysis was carried out using Agilent 5975 GC/MSD with 7890A GC system having HP-5 capillary column of 60 m length and 250 μm diameter with a programmed oven temperature from 50 to 280 °C, at 1 mL/min flow rate of He as carrier gas and ion source at 230 °C.

For further confirmation of the products, crystals were dissolved in sodium bicarbonate solution for neutralization of the sample and to maintain the pH 7.0 and analysed by FTIR-8400S with DRS system (Schimadzu make).

3. Results and discussion

Most of the conventional nitration methods are ecologically unfriendly as they involve reagents such as concentrated sulfuric acid, phosphoric acid, trifluoroacetic anhydride, etc. as catalysts in excess amounts. Use of excess quantities of acids

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