Catalysis Science & Technology

Accepted Manuscript

Catalysis Science & Technology

ARTICLE

Zeolite Y assisted Nitration of Aromatic and Heterocyclic Compounds and Decarboxylative nitration of α, β- Unsaturated Acids under Nonconventional conditions

V. Sudhakar Chary[a], K. C. Rajanna*[a], G. Krishnaiah[a], P. Srinivas[a]

Abstract: Zeolite Ywas found as an efficient catalyst for a facile nitration of aromatic compounds in acetonitrile as solvent in presence of small amounts of HNO_3 at room temperature. The reactions afforded mono nitro derivatives of aromatic compounds in about three hrs under stirred conditions with high yields and regioselectivity. Reaction times drastically reduced to about 20 min under sonication and to about 20sec under microwave irradiation. Zeolite is recovered after completion of the reaction and recycled for three to four times without any problem. The approach is particularly appropriate for the conversion of unsaturated cinnamic acids into nitrostyrenes.

1. Introduction

Nitration of aromatic substrates is one of the most widely studied reactions among all electrophilic substitution reactions, owing to a great industrial significance of many nitro aromatics, which are extensively utilized as chemical feedstock for the synthesis[1] of several useful materials, such as dyes, pharmaceuticals etc . However, a large number of earlier technologies involved the use of corrosive nitric acid–sulphuric acid mixture as main ingredient to trigger nitration. This led to large amount of acid waste sent to the industrial/ laboratory drains which are expensive to treat. In addition, over nitration, oxidation of by products and poor selectivity are other associated problems in this methodology[2]. Traditionally, the chemical industry has used homogeneous catalysts in the selective production of flavors, fragrances, agricultural products, food, and pharmaceuticals. But the homogeneous catalysts tend to generate large quantities of waste, including wash water streams, salts, and heavy metals. Mostly the regeneration and reusability of the catalyst is not possible[3-5]. Due to these reasons there has been ever green interest in the use and exploration of heterogeneous catalysts [6-9]. In several cases, inorganic solids could offer significant benefits by providing effective catalysis as well as enhanced selectivity. Zeolites are micro porous crystalline alumina silicates comprising a uniform pore structure associated with ion-exchange properties[8, 9]. Vast majorities of zeolites are synthetic materials even though they are naturally occurring minerals. Zeolites containing cages and channels find extensive applications[9-11] in organic reactions, either as active participants or as inert supports. Zeolite-based solid acids are potentially attractive due to the easy removability of substrate/product, catalyst recycling and possible regioselectivity due to their constraining environment. Zeolites have been extensively as heterogeneous catalysts because they can be recovered and recycled with greater ease and lower expense. The use of zeolite catalysts provides several advantages such as improved selectivity, high activity, and reduced corrosion. Recently, Smith and co-workers utilized zeolites as efficient green catalysts to enhance the para selectivity in chlorination, bromination, acylation and methanesulfonylation of simple aromatic substrates[12,13]. A perusal of literature revealed few reports on nitration of aromatic substitution reactions using Nitrogen dioxide and dinitrogen oxides in presence of different zeolites as catalysts[14-20]. In our earlier publication we have used Zeolite Y as an efficient catalyst for thiocyanation reactions of aromatic compounds[21]. Enthused by the outstanding performance of zeolites as green catalysts in different protocols[14-24], we have taken up the present work using Zeolite Y as a catalyst for effective decarboxylative nitration of α, β – unsaturated acids and nitration of aromatic compounds. The nitronium ion generated by using small amounts of HNO_3 in presence of Zeolite Y in acetonitrile medium. In addition, Zeolite solids are easily removed from reaction mixtures and recycled. Therefore, study of the use of inorganic solids as catalysts for electrophilic aromatic substitution reactions can make an important contribution to green chemistry. The study has been taken up under sonication and the assistance of microwave radiation encouraged by their

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utility in rate accelerations and yield enhancements.

2. Experimental procedure:

The Zeolite used is a Faujasite - Zeolite Y, procured from Zeolyst (International) in the form of Zeolite H-SDUSY Powder with a trade name (CBV- 720). The manufacturer reports the composition (molar ratio) of the $[(SiO_2)_x / (Al_2O_3)_y]$ in CVB-720 zeolite as 30 comprising 0.03 (Weight %) of Na_2O, surface area of 780 m_2/g, and a unit cell of 24.28 Å. All the other chemicals were reagent grade and obtained from either SD (Fine) chemicals (India) or Avra (India).

2.1. Conventional heating method: The typical procedure of nitration of phenols includes a clean round bottomed (RB) flask containing the phenol (10 mmol) in acetonitrile (15 mL). About 0.5 mL was added to the contents of RB flask followed by a catalytic amount of Zeolite. The reaction mixture was stirred at room temperature. After completion of the reaction, as was monitored by TLC, the reaction mixture was treated with $NaHCO_3$ solution. Organic compound extracted with ethyl acetate. The polarity is maintained by using ethyl acetate and petroleum ether mixtures. Contents of the reaction mixture were finally washed with Na_2SO_4 the compound is separated in china dish and preserved. Evaporation of ethyl acetate afforded crude product, which was subjected to column chromatography (silica gel, 100–200 mesh) using ethyl acetate-hexane as eluent to obtain the pure products.

To optimize the conditions in our study, the reaction was carried out with different molar ratios of aromatic compound (0.01 mol), HNO3 (0.01 mol), Zeolite Y (catalytic amounts) in a wide range of solvents such as DEM, DCE, THF, and acetonitrile. The reactions were too slow with low yields of products in DCE, DCM and THF media. However, the reactions underwent smoothly when 1:1:0.1 aromatic compound (0.01 mol), HNO_3 (0.01 mol) and CBV720 zeolite (0.001 mol/catalytic amount) are used in acetonitrile medium (Table 1). Therefore, the entire study is taken up in acetonitrile medium under the above optimized conditions.

2.2. Ultra Sound assisted Reaction:

The same ratio of substrate, reagent and zeolite is maintained in sonication procedure where it is used in conventional method. The reaction mixture which is taken in conical flask is placed in sonication chamber and the progress of the reaction is monitored by thin layer chromatography. The compound is washed with $NaHCO_3$ and Na_2SO_4 the compound is separated in china dish and preserved.

2.3. Microwave irradiation Reaction:

This method is useful that carries bulk activation of molecules in a short period of time and yields of the reaction mixture is better than

conventional method. The reactants involved in this technique are same as used in the previous procedures *i.e.* conventional and sonication techniques. The final product of the compound is collected under appropriate condition and is characterized by ^{1}H NMR, and Mass spectroscopic methods.

3. Reuse of the catalyst

After completion of the reaction the zeolite was recovered by filtration and washed several times with ethyl acetate and then ether and dried for further reuse. Catalyst (**Zeolite Y)** could be recycled safely up to three to four cycles.

Table -2: Recyclisation of Zeolite Y in Nitration reactions

Cycle	Phenol		Thiophene		Cinnamic acid	
	R.T (hr)	Yield (%)	R.T (hr)	Yield (%)	R.T (hr)	Yield (%)
First	3	65	6	73	5	72
Second	3	65	6	73	5	72
Third	3	65	6	73	5	72
Fourth	3	60	6	68	5	65

4. Results and Discussion

The present study has been found interesting due to a wide variety application of nitro derivative compounds in pharmaceutical, dyes, pesticides and industrial area. Mild and eco-friendly approaches with desktop chemicals and the reactions are studied under conventional; ultra sound assisted and microwave assisted conditions (Scheme-1).
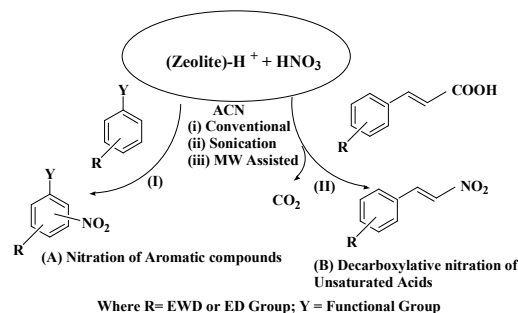
Scheme 1: Zeolite Y mediated Nitration and Nitro decarboxylation

Nitration of aromatic compounds and nitro decarboxylation of α, β-Unsaturated Acids underwent smoothly with Zeolite Y/HNO_3 under conventional and non-conventional conditions in acetonitrile medium. A wide range of aromatic compounds such as phenols, naphthols, toluene, halo benzenes, aniline, acetanilide, heteroaromatic compounds such as furan, thiophene and several others. The reaction times for most of the studied reactions are in the range of 3 to 6 hours, depending on the structure of the substrate. However, under sonication, "Reaction Times" reduced amazingly to 25 to 60 minutes at room temperature.

Table -1: Effects of Solvent and [Catalyst] in Zeolite Y catalysed Nitration reactions

Solvent	(Zeolite Y) mol	Phenol		Thiophene		Cinnamic acid	
		R.T (hr)	Yield (%)	R.T (hr)	Yield (%)	R.T (hr)	Yield (%)
ACN	0.001	3	65	6	73	5	72
ACN	0.005	3	70	6	78	5	75
ACN	0.010	3	70	6	78	5	72
DCM	0.010	12	35	12	30	12	28
DCE	0.010	12	40	12	35	12	30
THF	0.010	15	35	15	30	15	28

In microwave assisted reactions, the reaction times reduced to only few seconds (20 to 140sec). Rate of the reaction is faster with the electron releasing groups, while deactivated aromatic compounds were comparatively slow. This observation can be attributed to the availability of the electron density in the aromatic ring. As the electron density in the ring increases it was more readily attacked by the electrophilic nitronium ion, which is the key step in rate determining of the reaction. Interestingly, decarboxylative nitration of α, β unsaturated carboxylic acids also underwent smoothly under conventional and non-conventional conditions and afforded nitro alkenes. Cinnamic acids afforded β –nitrostyrenes as shown in Table -2. The reaction times for most of the studied reactions are in the range of 4 to 6 hours, depending on the structure of the substrate. However, under sonication, "Reaction Times" reduced amazingly to 60 to 100 minutes at room temperature. In microwave assisted reactions, the reaction times reduced to few seconds (100 to 180sec). However, in the case of acrylic and crotonic acids the reactions were slower than cinnamic acids. Spectroscopic data of isolated products are in agreement with earlier literature reports[25].

Mechanism of Nitration and Nitro decarboxylation:

Zeolite materials are microporous aluminosilicates with various uses, including acting as important catalysts in many processes. This reaction is known to be associated with Brønsted acid sites in the zeolite, formed when Si is substituted by Al in the framework, with an associated H^{+} ions being bound nearby to maintain charge neutrality[23]. Acidic zeolites are special type of heterogeneous catalysts and are of greatest practical importance. They can interact with water to absorb or release ions through ion exchange mechanism. They can selectively absorb ions that fit the cavities in their structures and thus function as a kind of molecular sieves. On the other hand zeolites being aluminosilicates contain a lattice structure bearing one- negative charge for each aluminium atom in the framework.

This lattice charge is counterbalanced by cations, which are mostly located within the zeolite pores, where most of the surface area is found. When the cation is a proton, the zeolite surface is acidic. The acid strength depends on both the lattice structure (arrangement of atoms with respect to each other in the lattice) and the (Si/Al) ratio. An increase in the (Si/Al) ratio increases acid strength and fewer acid sites[24]. This point coupled with the earlier works of Smith's research group and others on zeolite catalysed nitration[7] support our contention that the zeolite Y(Zeolite H-SDUSY Powder), being an acidic in nature, acts as a conjugate acid, while nitric acid is a Brønsted acid. Mechanism of nitration appears to follow "sorption mechanism". Nitric acid binds to the active sites of zeolite and captures a proton from the acidic zeolite through a weak noncovalent interaction (hydrogen bonding) and releases "nitronium ion" followed by water molecule (H_2O). Nitronium (NO_2^+) ions, in turn react with aromatic compounds to form nitro aromatics through electrophilic substitution mechanism.

Where R= EWD or ED Group; Y = Functional Group
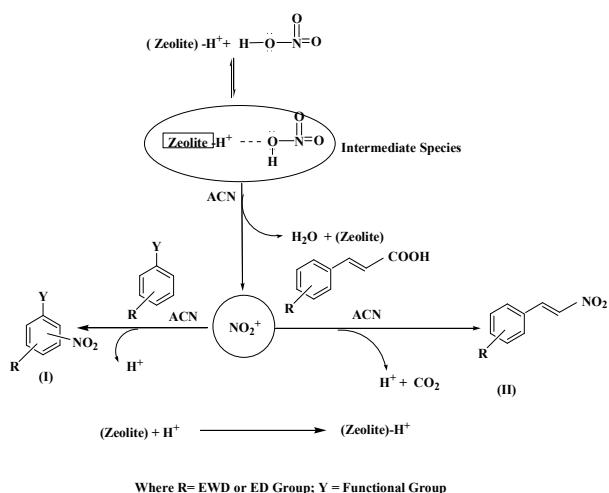
Scheme.2: Mechanism of Nitration and Nitro decarboxylation

However, in the case of α, β unsaturated carboxylic acids decarboxylative nitration takes place through electrophilic

interaction at olefinic carboxyl moiety. Detailed mechanistic path is **shown in Scheme-2.** Nitration of aromatic compounds and decarboxylative nitration of α, β unsaturated carboxylic acids underwent smoothly under present experimental conditions which can be seen from the data presented in table-4. Protons released in the final steps of mechanism might help to regenerate of the catalyst ready for recyclisation.

The pioneering work of Mason, Suslick and others[26-28] on ultrasonics has emerged as boon to chemists to use ultrasonics as green reaction tool to achieve organic synthesis. The reaction times under sonication "Reaction Times" reduced amazingly from 4 to 6 hours under conventional methods to 60 to 140 minutes. Such dramatic sonocatalysis could be attributed to cavitation phenomenon as explained in earlier by Mason, Suslick and other pioneers[26-28]. Trapped within a microbubble, the reactants are exposed to a high pressure and temperature upon implosion, and the molecules are fractured, forming highly reactive species with a great tendency to react with the surrounding molecules. When one of the phases is a solid such as Zeolite, the ultrasonic irradiation has several additional enhancement effects, and this is especially useful when the solid acts as a catalyst. The bubble collapse in the case of solid causes a sharp increase in the mass transfer at solid-liquid interface. The cavitation effects form microjects of solvent, which bombard the solid surface. This fact causes the exposition of unreacted surfaces of solid, increasing the interphase surface able to react. In general, the sonication presents beneficial effects on the chemical reactivity, such as to accelerate the reaction, to reduce the induction period, and to enhance the catalyst efficiency[26-28].

In microwave assisted reactions, the reaction times further reduced to only few seconds (100 to 180sec). Excitation with microwave radiation results in the molecules aligning their dipoles within the external field. Strong agitation, provided by the reorientation of molecules, in phase with the electrical field excitation, causes an intense internal heating, causing bulk activation molecules leading to high rate accelerations[29, 30].

5. Conclusions

In conclusion, the nitration of a variety of organic compounds good to excellent yields has been achieved using zeolite. Phenol substituted with electron-donating group enhances the reactivity and yields are high whereas, phenol substituted with electron-withdrawing group does not enhance the reactivity and the yields are low. These methods are mild, exceedingly efficient and highly selective as wide range of functional groups is well tolerated under the reaction conditions. The approach is particularly appropriate for the conversion of unsaturated cinnamic acids into nitrostyrenes.

Spectroscopic Data of certain β-Nitro Styrenes:

β - Nitro styrene: [1] HNMR (300MHz, CDCl$_3$): δ 6.40-6.44 (d, 1H, H-8, J=18Hz), 7.62-7.65 (m, 3H, H-3, H-4, H-5), 7.80 (d, 1H, H-7, J=18 Hz), 7.48 (d, 2H, H-2, and H-6, J=7.95 Hz); ^{13}C NMR δ 129.1, 129.4, 130.0, 139.0, 132.1, 137.1; m/z = 149.

2-Chloro β - Nitro styrene: [1] HNMR (300MHz, CDCl$_3$): δ 6.68 (d, 1H, H-8, J = 18.5 Hz), 7.28 (dd, 1H, H-4, J=9.0 Hz, J=7.5 Hz), 7.60 (dd, 1H, H-5, J=10 Hz, J = 8.0 Hz), 7.64 (d, 1H, H-3, J = 8.5 Hz), 7.75 (d, 1H, H-6, J=8.0 Hz), 8.32 (d, 1H, H-7, J = 18.5 Hz); ^{13}C NMR δ 127.7, 128.6, 128.7, 130.9, 133.0, 135.2, 136.2, 138.9; m/z = 183.

2- Methyl β - Nitro styrene: [1] HNMR (300MHz, CDCl$_3$): δ 2.95 (s, 3H, Me), 6.78 (d, 1H, H-8, J=18.5 Hz), 7.18 (dd, 1H, H-4, J=10 Hz, J = 8.5 Hz), 7.35 (dd, 1H, H-5, J = 9.5 Hz, J = 8.5 Hz), 7.54 (d, 1H, H-3, J=8.0 Hz), 7.78 (d, 1H, H-6, J = 9.5Hz), 8.28 (d, 1H, H-7, J=18.5 Hz); ^{13}C NMR δ 20.1, 126.9, 127.5, 129.1, 131.6, 132.1, 136.9, 137.8, 139.4; m/z = 163.

4- Chloro β - Nitro styrene [1] HNMR (300MHz, CDCl$_3$): δ 6.68 (d, 1H, H-8, J=18.0 Hz), 7.24 (d, 2H, H-2 and H-6, J=8.0 Hz), 7.68 (d, 2H, H-3 and H-5, J=8.5Hz) 8.28 (d, 1H, H-7, J=18.0 Hz); ^{13}C NMR δ 128.4, 129.6, 130.1, 137.3, 137.5, 138.2; m/z = 184.

4- Nitro β - Nitro styrene: [1] HNMR (300MHz, CDCl$_3$): δ 6.62 (d, 1H, H-8, J=18 Hz), 7.42 (d, 2H, H-2 and H-6, J=9.0 Hz); δ 7.78 (d, 2H, H-3 and H-5, J=9.5 Hz), 8.18 (d, 1H, H-7, J=18.0 Hz); ^{13}C NMR δ 124.2, 129.6, 135.9, 136.0, 139.7, 149.3; m/z = 194.

4- Methyl β - Nitro Styrene: [1] HNMR (300MHz, CDCl$_3$): δ 3.02 (s, 3H, CH$_3$), 6.68 (d, 1H, H-8, J=18 Hz); 7.44 (d, 2H, H-2 and H-6, J=8.0 Hz), 7.65 (d, 2H, H-3 and H-5, J=8.0 Hz), 7.85 (H-7, d,1H, J=18.0 Hz); ^{13}C NMR δ21.8, 127.4, 129.4, 130.3, 136.4, 139.4, 143.3; m/z = 163.

4- Methoxy β - Nitro Styrene: [1] HNMR (300MHz, CDCl$_3$): δ 3.82 (s, 3H, CH3); 6.45 (d, 1H, H-8, J=18.0 Hz); 7.48 (d, 2H, H-3 and H-5, J=8.5 Hz),7.75 (d, 2H, H-2 and H-6, J=8.0 Hz), 7.88 (d, 1H,H-7, J=18.0 Hz); ^{13}C NMR δ 55.4, 114.8, 122.4, 131.1, 134.8, 138.9, 162.8; m/z = 179.

2- OMe β - Nitro styrene: ^{1}H NMR δ 3.95(s, 3H, Me), 6.98 (m, 2H), 7.45 (m, 2H), 7.88 (d, 1H, J = 18.5 Hz), 8.12 (d, 1H, J = 18.5 Hz); ^{13}C NMR δ 55.8, 111.5, 119.2, 121.3, 132.6, 133.6, 135.7, 138.4, 159.7; m/z = 179

1–Nitro Ethene: [1] HNMR (300MHz, CDCl$_3$): δ 5.92 (dd, 1H, H$_b$, J=11.3 Hz, J = 1.5Hz), 6.65 (dd, 1H, Ha, J=15.5 Hz, J=11.3 Hz), 7.25 (dd, 1H, Hc, J=15.5Hz, J=1.5 Hz); m/z = 73.

1–Nitro Propene: [1] HNMR (300MHz, CDCl$_3$): δ 2.12 (d, 3H, CH$_3$, J = 6.9 Hz), 7.00 (d, 1H, H$_a$, J=16.5Hz,), 7 .18 (m 1H, H$_b$) m/z = 87.

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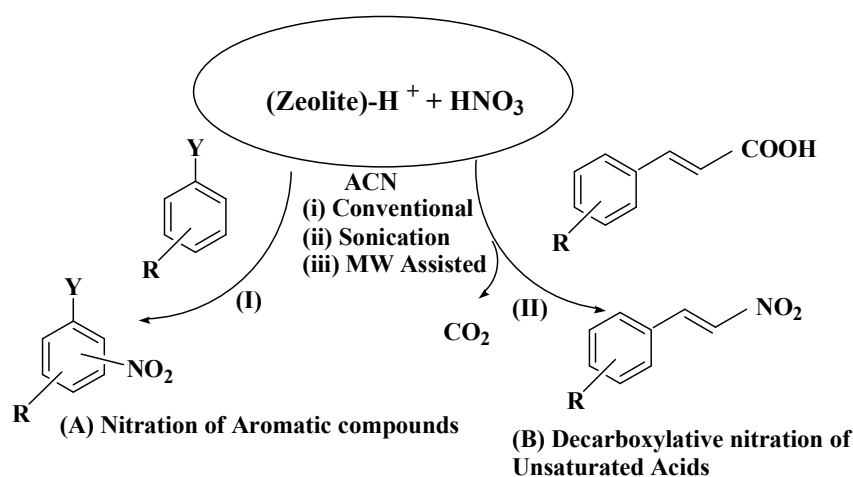**Table-3: Decarboxylative nitration of α, β- Unsaturated Acids by using Zeolite Y in Acetonitrile medium**

S.N	Substrate	Isolated Products	Conventional		Sonication		Microwave	
			R. T (hr)	Yield (%)	R. T (min)	Yield (%)	R. T (sec)	Yield (%)
1	CA	β- Nitrostyrene	5	72	60	75	90	78
2	2-Cl CA	2-Cl β- Nitrostyrene	5.5	68	80	70	120	70
3	4-Cl CA	4- Cl β- Nitrostyrene	5	72	70	70	100	75
4	4-OH CA	4- OH β- Nitrostyrene	4	80	50	85	80	88
5	4-NO$_2$ CA	4- NO$_2$ β- Nitrostyrene	6	70	90	74	200	75
6	4-OMe CA	4-OMe β- Nitrostyrene	4	75	50	76	100	75
7	AA	1- Nitro ethene	5.5	62	100	65	180	66
8	CRA	1- Nitro propene	6	65	90	66	150	70
9	2-Me CA	2- Me β- Nitrostyrene	6	66	85	65	180	70
10	4-Me CA	4-Me β- Nitrostyrene	4.5	74	75	76	90	80

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GRAPHICAL ABSTRACT

Zeolite Y assisted Nitration of Aromatic and Heterocyclic Compounds and Decarboxylative nitration of α, β- Unsaturated Acids under Nonconventional conditions

V. Sudhakar Chary[a], K. C. Rajanna*[a], G. Krishnaiah[a], P. Srinivas[a]

Abstract: Zeolite Ywas found as an efficient catalyst for a facile nitration of aromatic compounds in acetonitrile as solvent in presence of small amounts of HNO_3 at room temperature. The reactions afforded mono nitro derivatives of aromatic compounds in about three hrs under stirred conditions with high yields and regioselectivity. Reaction times drastically reduced to about 20 min under sonication and to about 20sec under microwave irradiation. Zeolite is recovered after completion of the reaction and recycled for three to four times without any problem. The approach is particularly appropriate for the conversion of unsaturated cinnamic acids into nitrostyrenes.

Where R= EWD or ED Group; Y = Functional Group

Scheme 1: Zeolite Y mediated Nitration and Nitro decarboxylation