

Nitration of Aromatic Compounds with Nitric Acid Catalyzed by Ionic Liquids

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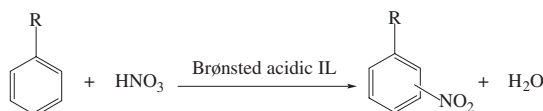
Nitration of simple aromatic compounds with 62% nitric acid is successfully carried out under solvent-free condition in a biphasic mode in the presence of the Brønsted acidic ionic liquids; the only by-product is water and ionic liquids are capable of being reused without any separation.

The nitration reaction of aromatic compounds with nitric acid is an important process in chemical industry with long history.^{1a-c} The nitroaromatic compounds so produced are widely used as raw materials for manufacturing a large range of chemical products such as dyes, pharmaceuticals, perfumes, and plastics. Traditionally, this reaction is carried out in the presence of mixtures of concentrated or fuming nitric acid with sulfuric acid or stoichiometric quantities of strong Lewis acids such as boron trifluoride, which inevitably leads to yielding a mass of acid waste and causing serious environment problem. Developing this important reaction in a catalytic and green way has been strongly desired and a host of nitrating systems has been reported.^{2a-c}

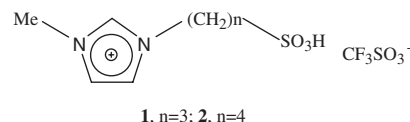
From either an industrial or environmental standpoint, however, the ideal nitration agent is aqueous nitric acid, which is inexpensive and generates only water as waste product. Unfortunately, few catalytic systems that involved using aqueous nitric acid as nitration agent are reported up to now. Waller et al. have demonstrated a few years ago that rare earth metal triflates are effective catalysts for nitration of aromatic compounds with 69% nitric acid.³ But in this case, a time- and energy-consuming process of separating and drying catalysts is indispensable in order to ensure the reusability of the catalysts. Furthermore, dichloromethane, an environmental and safety harmful volatile organic solvent, is also used as reaction medium.

Meanwhile, room temperature ionic liquids (RTILs) have gained more and more recognition as green and promising solvents for synthetic chemistry.^{4a-e} A few examples of application of ionic liquids as reaction medium for nitration reaction are reported.^{5a,b} Nevertheless, example of direct using ionic liquid as catalyst for nitration of aromatic compounds is absent of the literatures.

In this paper, we report what we believe to be the first example of nitration of aromatic compounds catalyzed by ionic liquids. Brønsted acidic ionic liquids, i.e. 3-methyl-1-(4-sulfobutyl)imidazolium trifluoromethanesulfonate and 3-methyl-1-(3-sulfopropyl)imidazolium trifluoromethanesulfonate, are demonstrated to be the effective catalysts for nitration of simple aromatic compounds with 62% nitric acid under solvent-free condition. Water is the only by-product. The reaction is carried out in a biphasic mode, so the nitroaromatic product can be very easily separated by decantation after reaction and the remaining ionic liquid is capable of being reused without any separation.



Ionic liquids:



The Brønsted acidic ionic liquids are prepared according to Ref. 6. In a typical experiment, ionic liquid (5–15% mol of aromatic compound), aromatic compounds (20 mmol) and 62% nitric acid (20–60 mmol) are charged successively into a 50 mL-round flask with magnetic stirrer. Then the reaction is allowed to proceed at 80 °C for 12–22 h. After reaction, the organic layer is separated by an extraction funnel and components in which are analyzed by a gas chromatograph equipped with a FID detector (Shimadzu GC-14A, ULBON HR-52 capillary column 25 m × 0.32 mm).

Results of nitration of some simple aromatic compounds with 62% nitric acid in the presence of Brønsted ionic liquids are listed in Table 1. No dinitrated products are detected in any case. As can be seen from the table, ionic liquid **1** and **2** have shown similar catalytic activity for the nitration of benzene with 62% nitric acid (Entries 1 and 2). In both cases, medium conversions of benzene are achieved. Both increasing the mole ratio of nitric acid to benzene (Entries 1, 3, and 4) and prolonging the re-

Table 1. Nitration of aromatics with catalytic quantities of ionic liquids^a

Entry	R	Ionic liquid	Conv. /%	Product distribution		
				<i>ortho</i>	<i>meta</i>	<i>para</i>
1	H	1 (5%)	70.1		n/a ^e	
2	H	2 (5%)	76.5		n/a	
3	H	1 (5%)	60.2 ^b		n/a	
4	H	1 (5%)	83.7 ^c		n/a	
5	H	1 (5%)	86.7 ^d		n/a	
6	H	1 (10%)	68.7		n/a	
7	H	1 (15%)	64.3		n/a	
8	Me	1 (5%)	93.2	43.6	4.9	52.5
9	Cl	1 (5%)	42.5	41.6	2.2	56.2
10	Br	1 (5%)	56.3	44	trace	56
11	NO ₂	1 (5%)	<1		n/a	

^a Reaction temperature: 80 °C, Reaction time: 12 h, Mole ratio of aromatic compounds/ nitric acid: 1:2.

^b Benzene/ nitric acid: 1:1, ^c Benzene/ nitric acid: 1:3.

^d Reaction time: 22 h.

^e Only one product formed without isomers.

action time (Entry 5) can remarkably enhance the conversion of benzene. It is very interesting, however, to observe a slight decreasing of the conversion of benzene when the amount of ionic liquid is raised (Entries 1, 6, and 7).

Then ionic liquid **1** is employed as catalyst for nitration of some other aromatic compounds, including toluene, chlorobenzene, and bromobenzene with 62% nitric acid under unoptimized reaction conditions (Entries 8–10), in all of these cases, medium to high conversions of aromatic compounds are also achieved. When nitrobenzene is used as substrate, no reaction is observed, which is in accord with the above results (Entry 11).

Once the reaction is over, our attention is paid to the issues of product separation and recycling of the Brønsted ionic liquids. This nitrating system is carried out in a biphasic mode, so it is very easy to perform the product separation by decantation or using an extraction funnel after reaction.

From the point of manufacturing view, a continuous reaction process without catalyst separation is very attractive in industry in the case of nitration of aromatic compounds with nitric acid. Then we examine the reusability of the remaining aqueous phase, consisted of nitric acid and ionic liquid, in a way that directly employed it as catalyst for next run, just replenishing a certain amount of 62% nitric acid to the aqueous phase. Results of recycling of nitration of benzene with nitric acid, under the same reaction condition as Entry 2 of table 1, are listed in Table 2. During the whole process, the mole ratio of benzene to nitric acid is kept at 1:2. It should be noted out, however, the concentration of nitric acid decreased steadily with the reaction goes on owing to the accumulating of water, which is formed as waste product and not separated from the system. As can be seen from the table, with the decreasing of the concentration of nitric acid, conversion of benzene decreased simultaneously, but it can still kept at 25.6% after 5 times recycle and the concentration of nitric acid decreased even to about 36%, which suggesting the Brønsted ionic liquid might has a great possibility to be applied in large scale as the concentration of ni-

tric acid could be easily kept at a suitable level when high concentrated or fuming nitric acid is employed to replenish the consumed nitric acid.

The nature of the Brønsted ionic liquids catalyzed nitration of aromatic compounds is not clear at this stage. The classical reaction mechanism of nitration of benzene in the presence of mixture acid of nitric acid and sulfuric acid is well established,¹ which involved the formation of NO_2^+ as nitrifier at first and then followed by electrophilic addition of NO_2^+ with benzene. Because the Brønsted ionic liquids have the sulfuric acid-like group $-\text{SO}_3\text{H}$ in their molecular structure, we are inclined to believe that the traditional reaction mechanism also functions here.

In conclusion, it is demonstrated that the Brønsted ionic liquids are a kind of novel and reusable catalysts for nitration of simple aromatic compounds with aqueous nitric acid. The reaction is carried out under solvent-free condition in a biphasic mode. In comparison with other nitrating system, it is a more green process with promising prospect for practical application.

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Table 2. Recycling of ionic liquid 2 for nitration of benzene^a

Run	Benzene/ nitric acid	Concentration of nitric acid/%	Conversion /%
1	1:2	62	76.5
2	1:2	51	65.2
3	1:2	45	52.1
4	1:2	40	37.5
5	1:2	36	25.6

^a The reaction condition is same as Entry 2 of Table 1.