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Xiufang Qi [a] , Guangbin Cheng [a] , Chunxu Lu [a] & Desheng Qian [a]

[a] School of Chemical Engineering, Nanjing University of Science and Technology , Nanjing, China

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Nitration of Simple Aromatics with NO_2 under Air Atmosphere in the Presence of Novel Brønsted Acidic Ionic Liquids

Xiufang Qi, Guangbin Cheng, Chunxu Lu, and Desheng Qian

School of Chemical Engineering, Nanjing University of Science and
Technology, Nanjing, China

Abstract: Aromatics nitrate with NO_2/air catalyzed by novel Brønsted acidic ionic liquids (ILs) without any volatile chlorinated organic solvent under mild conditions. The ILs employed were caprolactam based, [Caprolactam]X ($X^- = pTSO^-$, BSO^-, BF_4^-, NO_3^-), which are of relatively lower cost and lower toxicity than traditional imidazolium-based ILs. The nitration reactions were carried out at −15 to −0°C first, then at room temperature for a longer time with a little excessive NO_2 (ca. 1.4 eqv.) for moderate yield (for toluene). The IL could be reused four times.

Keywords: aromatics, nitration, NO_2/air, novel Brønsted acidic ionic liquids

Nitration of aromatics is a fundamental reaction of great industrial importance that provides key organic intermediates or energetic materials. Unfortunately, the usual commercial process of nitration of aromatics, which uses nitric and sulfuric acids, is not environmentally benign, resulting in disposal problems and regeneration of used acids, and often providing poor selectivity for the desired products. Therefore, various nitration approaches have been explored to avoid the problems of the traditional mixed-acid method.[1] Much success has been achieved, but some problems still exist, such as the volatile chlorinated solvents required in some processes.

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Address correspondence to Guangbin Cheng, School of Chemical Engineering, Nanjing University of Science and Technology, Xiao Ling Wei 200, Nanjing 210094, China. E-mail: gcheng@mail.njust.edu.cn

Because ionic liquids (ILs) have strong polarity, negligible vapor pressure, wide solubility to organics and inorganics, and variable Lewis/Brønsted acidity, they have been used in a series of reactions[2] as catalysts and/or solvents (instead of volatile organic solvents). That also drew our attention, and we desired to develop an environmentally benign nitration process using ILs as catalysts and solvents.

Because imidazolium-based ILs have relatively higher cost and toxicity[3] in general chemical applications, we made efforts to seek new Brønsted acidic ILs with lower cost and lower toxicity. Lactam-based Brønsted acidic ILs are relatively cheaper, easily available in large amounts from industry, and more environmentally friendly than imidazolium-based ILs.[4] The additional carbonyl groups in the lactam might lead to specific functions when these lactam-based ILs are used as media or solvents. Therefore, we chose [caprolactam]BF_4 and [caprolactam]NO_3, whose Brønsted acidities are relatively stronger, and applied them to nitration of simple aromatics. Considering that addition of large aromatic groups to the molecular of ILs may increase the solubility of ILs to aromatics, we synthesized two new caprolactam-based Brønsted acidic ILs, [caprolactam]pTSO and [caprolactam]BSO, with p-toluenesulfonic acid and benzenesulfonic acid as conjugated acid, respectively. Then the ILs were characterized by spectrometry, and their activity as catalysts for the nitration of toluene, chlorobenzene, and benzene were investigated. There are several reports on aromatics nitration with HNO_3 (67%)[5] or HNO_3/Ac_2O[6] in the presence of ILs. However, there has been no report on the nitration of aromatics with NO_2 using ILs as solvents and/or catalysts so far. NO_2 has potential applicable ability for nitration. In this article, we report for the first time the results of the nitration of simple aromatics with NO_2 under air atmosphere using Brønsted acidic ILs as catalysts.

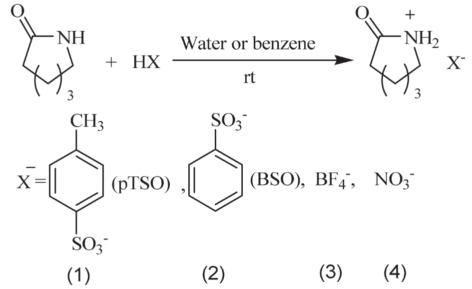
EXPERIMENTAL SECTION

Preparation and Characterization of Caprolactam-Based Ionic Liquids

The preparation of caprolactam-based ILs is illustrated in Scheme 1. The ILs were prepared according to the method in Ref. 4.

^1H NMR spectra were recorded on a Bruker Advanced Digital 300-MHz NMR spectrometer, and mass spectra were recorded on a Finnigan TSQ Quantun Ultra AM spectrometer. IR spectra were recorded on a Bruker Equinox 55 IR spectrometer; melting points were measured on a XT4 micro-melting point instrument made by Beijing Keyi Dianguang Instrument Plant.

Using pyridine as IR probe molecule, pyridine and ILs were mixed in a given ratio (1:1 by molar) and then spread into KBr liquid films; the Brønsted acidities of these ILs were determinated by IR spectrometer.



Scheme 1. Preparation of caprolactam-based ILs.

Nitration of Aromatic Compounds with NO_2 under Air in the Presence of Ionic Liquids: General Procedure

To a cooled (0 or −15°C), vigorously stirred mixture of the IL (quantities indicated in the tables) and the substrate (10.0 mmol) under an air atmosphere, 0.5 mL of liquid nitrogen dioxide was added all at once. After a given time, the reaction was quenched by addition of deionized water (ca. 5 mL), and then the internal standard (nitrobenzene for toluene, anisole, and chlorobenzene, and hexadecane for benzene, 0.2 mL) was added, followed by addition of hexane (5 mL × 4). Two phases formed once the stirring was stopped. The bottom one was an aqueous phase containing the IL, and the upper one was an organic phase. The upper phase was removed by simple decantation from the aqueous phase. The organic layers were combined and washed with a saturated solution of sodium bicarbonate (5 mL), water (5 mL × 3), and brine (5 mL × 2) in turn, dried with Na_2SO_4, and then analyzed by GC. (When in preparative scale, the dried organic layers were distilled under reduced pressure to remove solvent and the unreacted substrates.) The recovered IL was dried at 65°C under reduced pressure for 5 h to remove water accumulated during the workup and employed for further use.

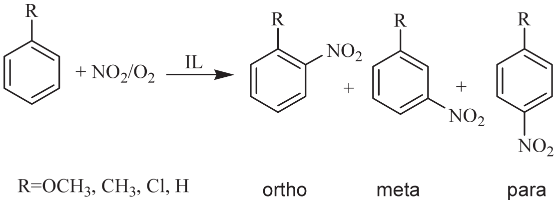
RESULTS AND DISCUSSION

Preparation and Characterization of Caprolactam-Based Ionic Liquids

All of the caprolactam-based ILs were prepared with high yields of 85–92%. They are moisture stable. Among them, [caprolactam]pTSO is a white solid with a melting point of 69°C, [caprolactam]BSO is a yellow liquid of high viscosity, [caprolactam]BF_4 is a colorless liquid with good fluidity, and [caprolactam]NO_3, is a white solid with a melting point of 30°C. All of them are easily soluble in water and have good moisture absorption (Scheme 2).

Data

The ^{1}H NMR data and MS spectra of the four ILs were shown as following. The data were similar with that reported in Ref. 4. In the ^{1}H NMR ($CDCl_3$) spectra, there are two active hydrogen in the range of δ 6.80–16.24 ppm, indicating that they all formed N-protonated caprolactam cation.



Scheme 2. Nitration of simple aromatics with NO_2/air catalyzed by ILs.

[Caprolactam]pTSO: ^{1}H NMR ($CDCl_3$): δ 1.73–1.83 (m, 6H), 2.38 (s, 3H), 2.68 (t, $J = 4.3$, 2H), 3.46 (s, 2H), 7.22 (d, $J = 7.5$, 2H), 7.76 (d, $J = 7.7$, 2H), 9.92 (s, 1H), 10.91 (s, 1H). ^{1}H NMR (D_2O): 1.61–1.77 (m, 6H), 2.41 (s, 3H), 2.49 (t, $J = 3.6$, 2H), 3.26 (t, $J = 4.6$, 2H), 7.38 (d, $J = 7.9$, 2H), 7.71 (d, $J = 7.9$, 2H). MS (ESI): m/z 114.12 (cation); calculated for cation ($C_6H_{12}NO$) 114.09.

[Caprolactam]BSO: ^{1}H NMR ($CDCl_3$): δ 1.74–1.85 (m, 6H), 2.65 (d, $J = 9.1$, 2H), 3.43 (s, 2H), 6.80 (s, 1H), 7.45 (s, 3H), 7.90 (d, $J = 5.9$, 2H), 10.03 (s, 1H). ^{1}H NMR (D_2O): δ 1.47–1.63 (m, 6H), 2.33 (t, $J = 5.3$, 2H), 3.11 (t, $J = 4.5$, 2H), 7.44 (t, $J = 7.7$, 3H), 7.68 (d, $J = 7.6$, 2H). MS (ESI): m/z 114.13 (cation); calculated for cation ($C_6H_{12}NO$) 114.09.

[Caprolactam]BF_4: ^{1}H NMR ($CDCl_3$): δ 1.74–1.88 (m, 6H), 2.71–2.76 (q, $J = 5.6$, 2H), 3.52–3.57 (t, $J = 7.1$, 2H), 3.46 (s, 2H), 8.49 (s, 1H), 9.79 (s, 1H). ^{1}H NMR (D_2O): 1.37–1.58 (m, 6H), 2.29–2.33 (t, $J = 5.7$, 2H), 3.05–3.09 (t, $J = 5.0$, 2H). MS (ESI): m/z 114.09 (cation); calculated for cation ($C_6H_{12}NO$) 114.09.

[Caprolactam]NO_3: ^{1}H NMR ($CDCl_3$): δ 1.64–1.84 (m, 6H), 2.62–2.65 (t, $J = 5.6$, 2H), 3.40–3.43 (t, $J = 4.5$, 2H), 8.54 (s, 1H), 16.24 (s, 1H); ^{1}H NMR (D_2O): δ 1.35–1.54 (m, 6H), 2.25–2.29 (t, $J = 5.7$, 2H), 3.01–3.04 (t, $J = 5.0$, 2H). MS (ESI): m/z 114.10 (cation); calculated for cation ($C_6H_{12}NO$) 114.09.

Using pyridine as IR probe molecule, the IR spectra of the caprolactam-based ILs were obtained. According to Refs. 7 and 8, the presence of a band near 1450 cm^{-1} is indicative of pyridine coordinated to Lewis acid sites, where a band near 1540 cm^{-1} is an indication of the formation of pyridinium ions resulting from the presence of Brønsted acidic sites. From each probe IR spectra of these ILs, a band is observed near

1540 cm^{-1}, confirming that Brønsted acidic sites are all present in the ILs synthesized. The wavenumber of the band corresponding to coordination at Brønsted acidic sites increases from 1541.59 cm^{-1} for [caprolactam]BSO to 1543.69 cm^{-1} for [caprolactam]pTSO, 1544.61 cm^{-1} for [caprolactam]NO_3 and 1549.39 cm^{-1} for [caprolactam]BF_4, indicating that the Brønsted acidity increases in the order [caprolactam]BSO < [caprolactam]pTSO < [caprolactam]NO_3 < [caprolactam]BF_4.

NO_2 Nitration of Simple Aromatics under Air in the Presence of Brønsted Acidic ILs

Some results of NO_2 nitration of simple aromatics under an air atmosphere in the presence of Brønsted acidic ILs are listed in Table 1.

The data in Table 1 indicated that the prepared caprolactam-based ILs all had catalytic acitivity for NO_2/air nitration of aromatics, and among them,

Table 1. Results of NO_2–air nitration of simple aromatics catalyzed by caprolactam-based ILs

Entry	Ionic liquid	R	Yield (%)[c]	Product distribution (%)			Ortho/para
				Ortho	Meta	Para	
1[a]	IL1	CH_3	61.4	57.1	3.9	39.0	1.46
2[a]	IL2	CH_3	44.7	49.9	6.3	43.8	1.14
3[a]	IL3	CH_3	46.5	56.8	4.7	38.4	1.48
4[a]	IL4	CH_3	31.8	56.2	7.9	35.8	1.57
5[a]	IL1	OCH_3	91.3	40.4	2.3	57.3	0.70
6[b]	IL1	Cl	48.7	19.9	3.7	76.4	0.26
7[b]	IL2	Cl	37.4	19.8	0.3	79.8	0.25
8[b]	IL3	Cl	38.2	24.3	1.9	73.7	0.33
9[b]	IL4	Cl	25.3	22.5	9.0	68.4	0.33
10[b]	IL1	H	55.4				
11[b]	IL2	H	41.4				
12[b]	IL3	H	43.8				
13[b]	IL4	H	29.2				
14[b]	None	H	9.2				
15[b]	None	Cl	4.9	39.8	0	60.1	0.66
16[a]	None	CH_3	13.4	57.9	5.7	36.4	1.59

[a] Substrate 10 mmol, IL 10 mol%, NO_2 0.5 mL (ca. 14 mmol), −15°C/30 min, then 0°C/6 h, and rt/24 h (when the air balloon was removed).

[b] Substrate 10 mmol, IL 10 mol% of substrate, NO_2 0.5 mL (ca. 14 mmol), −15°C/30 min, then 0°C/6 h, and rt/60 h (when the air balloon was removed).

[c] Calculated by quantitative GC.

Table 2. Recycling of IL1 for NO_2–air nitration of toluene[a]

Run	Yield (%)[b]	Product distribution (%) Ortho	Meta	Para	Ortho/para
1	61.4	57.1	3.9	39.0	1.46
2	60.7	56.3	4.6	39.1	1.44
3	57.3	54.2	6.8	39.0	1.39
4	57.8	54.3	7.7	37.9	1.43
5	54.8	52.6	5.7	41.7	1.26

[a] Substrate 10 mmol, IL 10 mol%, NO_2 0.5 mL (ca. 14 mmol), −15°C/30 min, then 0°C/6 h, and rt/24 h (when the air balloon was removed).

[b] Calculated by quantitative GC.

[caprolactam]pTSO had the best affinity to aromatics. Comparing the result of entry 1 with the result of entry 2, the latter showed a little lower yield but a slight higher paraselectivity than the former. This could be explained by the stronger polarization ability of IL2 than IL1, which because BSOs had stronger polarity than pTSOs. Under the condition indicated in the table, nitration of chlorobenzene had a smaller yield (and also benzene) but gave better paraselectivity than without IL. From analyzing the results of NO_2/air nitration of toluene catalyzed by different ILs (entries 1–4 in Table 1) and the Brønsted acidity of the ILs (which increases in the order [caprolactam] BSO < [caprolactam]pTSO < [caprolactam]NO_3 < [caprolactam]BF_4), it can be seen that the acidity and affinity to aromatics of ILs have important roles on their catalytic activity.

Table 3. Synthesis of nitro compounds in preparative scale using the method upon

Entry	R	Amount of products (g)	Yield (%)[c]	Product distribution (%)[d] Ortho	Meta	Para	Ortho/para
1[a]	OCH_3	26.3	85.9	39.6	2.9	57.5	0.69
2[a]	CH_3	17.0	62.0	54.2	3.4	42.4	1.28
3[b]	H	13.1	53.4				
4[b]	Cl	14.6	44.6	22.3	3.5	74.2	0.30

[a] Substrate 0.2 mol, IL1 10 mol%, NO_2 10 mL, −15°C/30 min, then 0°C/6 h, and rt/24 h (when the air balloon was removed).

[b] Substrate 0.2 mol, IL1 10 mol% of substrate, NO_2 10 mL, −15°C/30 min, then 0°C/6 h, and rt/60 h (when the air balloon was removed).

[c] Isolated yield.

[d] Calculated by quantitative GC.

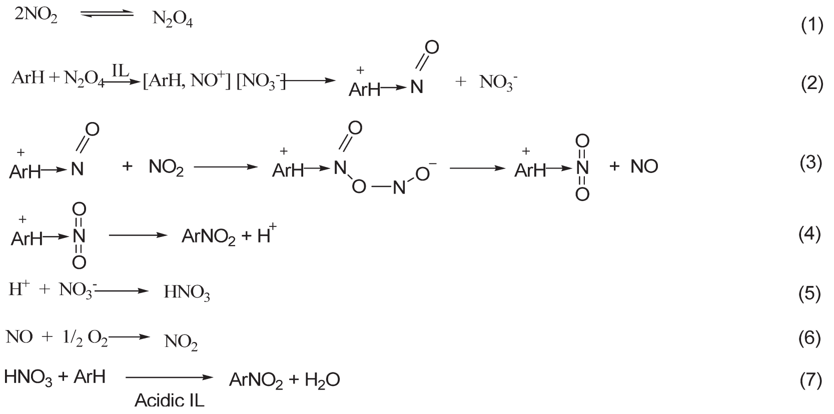


Figure 1. Possible pathway for NO_2–air nitration of aromatics catalyzed by Brønsted acidic ILs.

Recycling of IL1 for NO_2/air nitration of toluene was studied, and the results are listed in Table 2. Though the yield decreased and ortho/para ratio lowered after each recycling because of the loss of IL in the disposal process, the IL still had catalytic activity after four runs.

To check the utility of this process for mass production, nitro compounds were synthesized with good yields using this method in preparative scale. The details are shown in Table 3.

The mechanism of the present process at this stage is mysterious. The nitration of aromatic compounds with N_2O_5 is very reasonable. N_2O_4 is partially converted to N_2O_5 with O_2. Meanwhile, knowing that dinitrogen tetroxide is almost completely ionized in anhydrous nitric acid,[9] we imagine that NO_2-air nitration of simple aromatic compounds catalyzed by Brønsted acidic ILs may also proceed via the pathway showed in Fig. 1. As shown in the figure from formula (1) to formula (6), nitration products are produced, and the side-product is nitric acid. When reaction temperature rises, catalyzed by Brønsted acidic ILs, NO_2^+ is generated by HNO_3 and reacts with the aromatics. Thus, the usage of nitrogen dioxide is increased. The most ideal result is that water is the only by-product.

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