南京理工大学
Nanjing University of Science and Technology

Nitration of Aromatic Compounds in Ionic Liquids

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南京理工大学
Nanjing University of Science and Technology

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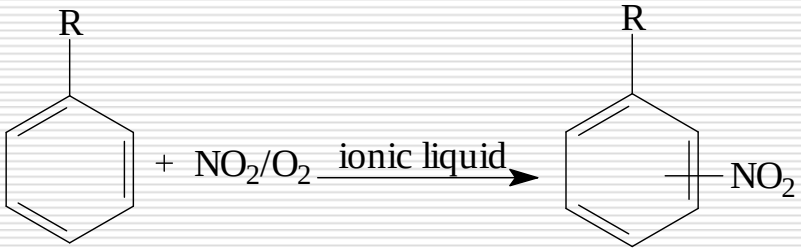
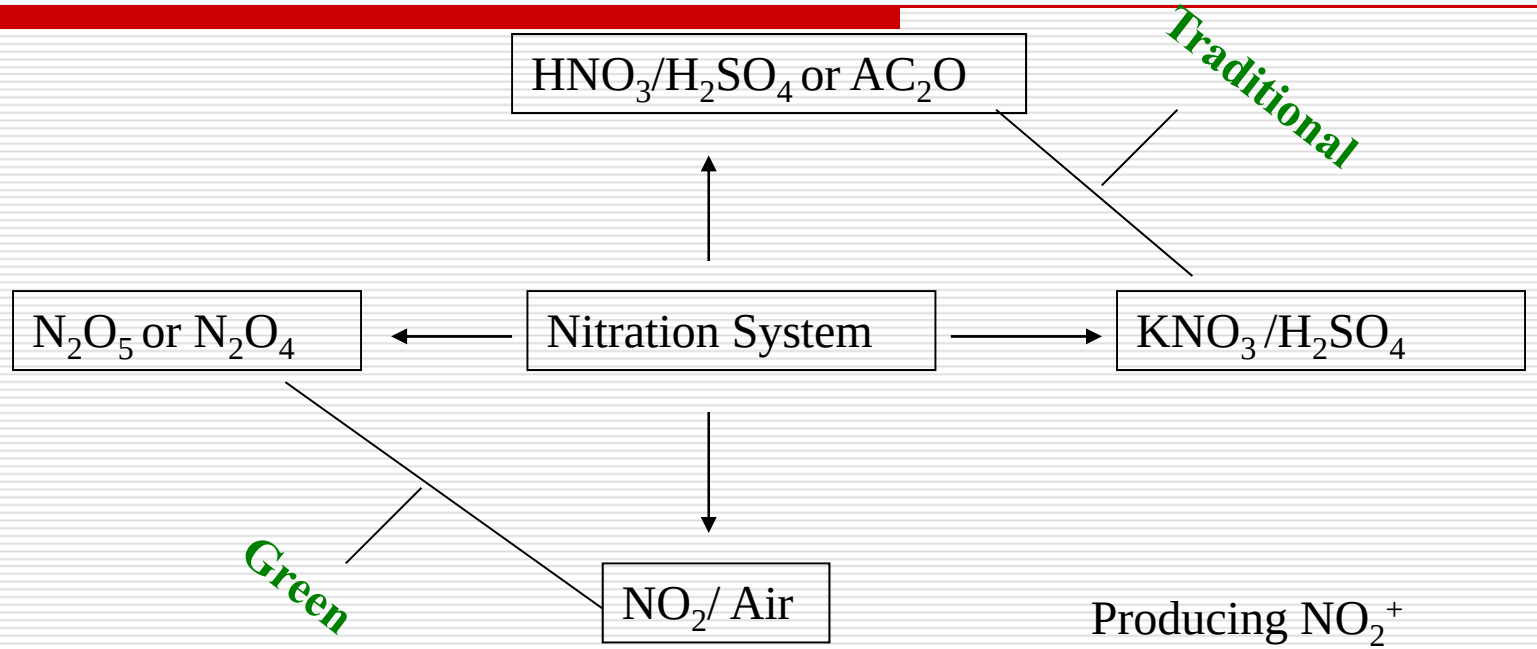
Nitration of simple aromatic compounds



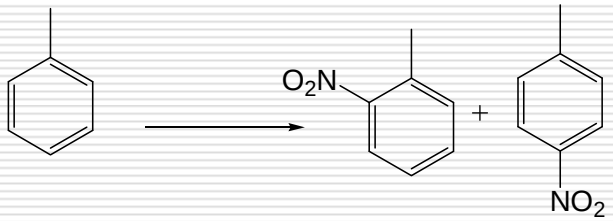
R = CH_3, H, Cl

Mono-nitro product: ***Key organic intermediates or energetic materials***


HNO_3/H_2SO_4 or AC_2O
Traditional
N_2O_5 or N_2O_4
Nitration System
KNO_3/H_2SO_4
Green
NO_2/ Air
Producing NO_2^+

Ionic liquid(IL): a salt in the liquid state, organic cations and inorganic anions
Solvent free: solvent and catalyst; recycled, easier to separated

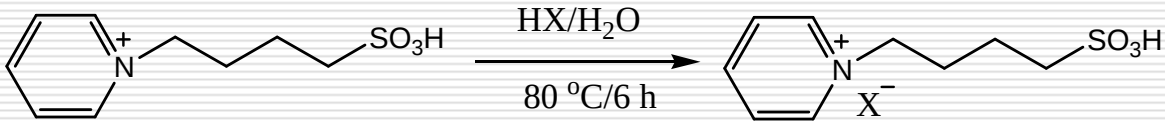
Nitration system: NO_2/ Air



Demanding higher

o/p : 1.96 in HNO_3/H_2SO_4

ILs:



[BSPy][HSO_4] $X^- = HSO_4$
[BSPy][OTf] $X^- = CF_3SO_3^-$

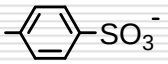
[BSPy][pTSA] X^- = 

Table 1 nitration of toluene in [BSPy][HSO_4] under different conditions[a]

Entry	[BSPy][HSO_4][d] (mol%)	NO_2 (mL)	Yield[e] (%)	Product distribution (%)			Ortho/ Para
				Ortho	Meta	Para	
1	0	0.5	11.4	57.9	5.7	36.4	1.59
2	5	0.5	33.0	55.4	3.9	40.7	1.36
3	10	0.5	33.3	53.7	3.7	42.6	1.26
4	15	0.5	77.0	54.2	3.3	42.5	1.27
5	20	0.5	52.8	54.1	3.5	42.4	1.27
6	15	0.2	16.7	54.2	4.3	41.5	1.31
7	15	0.8	35.9	54.3	3.7	42.0	1.29
8	15	1	28.7	54.5	3.5	42.0	1.30
9[b]	15	0.5	35.7	51.0	3.9	45.1	1.13
10[c]	15	0.5	4.6	56.0	0	44.0	1.27

Substrate 10 mmol; reaction time and temperature: [a]-15 °C /30 min, then 0 °C /5 h, and rt/20 h (when the air balloon was removed). [b]-15 °C /30 min, then 0 °C /5 h, and 45 °C /20 h (when the air balloon was removed). [c]-15 °C /30 min, then 0 °C /5 h. [d]mole ratio to toluene. [e]Calculated by quantitative GC.

Table 2 nitration of simple aromatic compounds catalyzed by different ionic liquids

Entry	IL	R	Yield[c] (%)	Product distribution (%)			Ortho/Para
				Ortho	Meta	Para	
1[a]	[BSPy][HSO_4]	CH_3	77.0	54.2	3.3	42.5	1.27
2[a]	[BSPy][OTf]	CH_3	63.6	53.0	3.3	43.7	1.21
3[a]	[BSPy][pTSA]	CH_3	30.8	53.2	6.5	40.3	1.32
3[1a]	[hexPy][PTSA]	CH_3	13.4	54.5	8.0	37.5	1.45
4[b]	[BSPy][HSO_4]	Cl	34.7	22.5	2.2	75.3	0.30
5[b]	[BSPy][OTf]	Cl	32.6	19.8	0.5	79.7	0.25
6[b]	[BSPy] [pTSA]	Cl	16.4	24.3	1.8	73.8	0.33
7[b]	[BSPy] [HSO_4]	H	38.9	-			
8[b]	[BSPy][OTf]	H	28.6	-			
9[b]	[BSPy][pTSA]	H	15.4	-			
10[a]	-	CH_3	11.4	57.9	5.7	36.4	1.59
11[b]	-	Cl	4.5	39.8	0	60.1	0.66
12[b]	-	H	8.6	-			

Substrate 10 mmol, NO_2 0.5 mL; reaction time and temperature

a. -15 °C /30 min, then 0 °C /5 h, and rt/20 h (when the air balloon was removed).

b. -15 °C /30 min, then 0 °C /5 h, and rt/40 h (when the air balloon was removed).

c. Calculated by quantitative GC.

Table 3 Reusability of [BSPy][HSO_4] for nitration of toluene[a]

Entry	times	Yield[b](%)	Product distribution (%)			Ortho/Para
			Ortho	Meta	Para	
1	1	77.0	54.2	3.3	42.5	1.27
2	2	76.3	53.3	3.9	42.8	1.25
3	3	74.9	54.0	4.4	41.6	1.30
4	4	70.1	53.3	4.8	41.9	1.27
5	5	67.6	53.5	4.2	42.3	1.26

[a]Substrate 10 mmol, -15 ^oC /30 min, then 0 ^oC /5 h, and rt/20 h (when the air balloon was removed). [b]Calculated by quantitative GC.

[BSPy][HSO4] has excellent reusability

Conclusion

1. sulfonic acid-functionalized ionic liquid shows good catalytic activity in Nitration of aromatic compounds with NO2/air (77% yield, 1.27 of ratio of o/p)

2. ILs could be conveniently separated with the products and reused for five times with excellent yield of mono-nitration products and paraselectivity. (77% yield, 1.27 of ratio of o/p for the first run; 67% yield and 1.26 of ratio of o/p for the fifth run)

Papers about ionic liquid

1. Xiufang Qi, **Guangbin Cheng,** Chunxu Lu, Desheng Qian. *Synthetic Communications*, **2008**, 38(4): 537~545

2. Xiufang Qi, **Guangbin Cheng,** Chunxu Lu, Desheng Qian. *Central European Journal of Energetic Materials*，**2007**, 4(3): 105~113

3. **Guangbin Cheng,** Xiufang Qi, Chunxu Lu. *Central European Journal of Energetic Materials*，**2007**, 4(4): 59~65

4. Xiufang Qi, **Guangbin Cheng**, Chunxu Lu, Desheng Qian. *Chinese Journal of Applied Chemistry*, **2008**, 25(2): 147~151

5. Xiufang Qi, **Guangbin Cheng,** Xuelei Duan, Chunxu Lu, Chinese Journal of Explosive & Propellants, **2007**, 30(5):12~15

6. Xiufang Qi, **Guangbin Cheng,** Chunxu Lu, *Chinese Journal of Energetic Materials*, **2008**, 16(4): 398~400

7. Xiufang Qi, **Guangbin Cheng,** Desheng Qian. Chunxu Lu, *Chinese Journal of Applied Chemistry,* **2007**, 24(11): 1255~1259

8. Xuelei Duan, **Guangbin Cheng,** Xiufang Qi, Chunxu Lu. *Chinese Journal of Applied Chemistry*, **2009**, **26**(2)

9. **Guangbin Cheng,** Xuelei Duan, Xiufang Qi, Chunxu Lu. *Catalysis Communications*, **2008**, 10, 201–204

THANKS