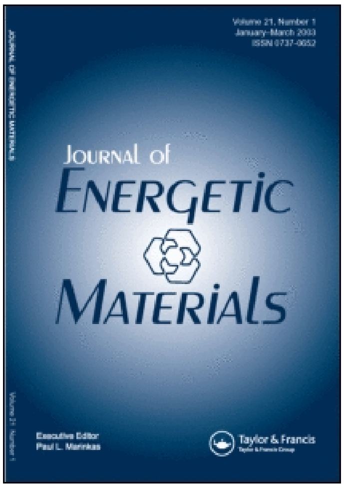

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Synthesis of RDX Catalyzed by Brønsted Acidic Ionic Liquids

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The experimental study was carried out on the direct nitrolysis of hexamethylenetetramine (HA) to synthesize hexahydro-1,3,5-trinitro 1,3,5-triazine (RDX) with nitric acid (95%) catalyzed by Brønsted acidic ionic liquids. Various ionic liquids, such as [HMim]X, [$(CH_2)_4SO_3H$-Mim]X, and [$(CH_2)_4SO_3HPy$]X ($X^- = pTSO^-$, NO_3^-, CF_3COO^-), and various parameters, such as equivalents of ionic liquid, mass ratio of nitric acid (95%) to the starting material, and reaction time, were investigated. Ionic liquid [$(CH_2)_4$ SO_3HPyr]NO_3 showed good catalytic activity. In the presence of 3.0% mol ratio [$(CH_2)_4SO_3HPyr$]NO_3 ionic liquid to HA, the yield of RDX was improved by 10.5% compared to the system without ionic liquid.

Keywords: hexamethylenetetramine, ionic liquid, nitrolysis, RDX

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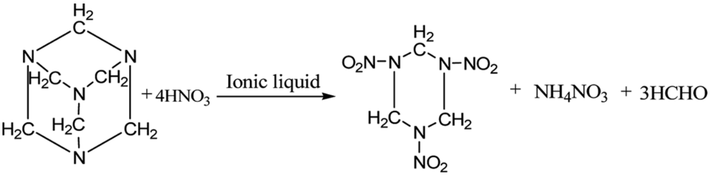
Introduction

For about two decades, ionic liquids have attracted much attention in synthetic organic chemistry as green solvents and catalysts [1–7]. In the presence of ionic liquids, the conversions and the selectivities of the nitration of aromatic compounds have quite often seen a significant improvement [8–12]. Our previous research also showed that acidic ionic liquid could promote both the yield and selectivities of the nitration reactions of aromatic compounds [13,14].

Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) is an energetic compound that is commonly used as a military explosive. The conventional processes for making RDX are direct nitrolysis of hexamethylenetetramine (HA) with concentrated nitric acid (HNO_3) (Woolwich process) [15,16] or with the mixture of concentrated nitric acid and ammonium nitrate (NH_4NO_3) in an acetic anhydride medium (Bachmann process) [17]. The former requires a large excess of nitric acid (22–26 eq.) with the plague of waste nitric acid and by-products resulting from oxidation, and the latter requires ammonium nitrate and acetic anhydride (7–8 eq.), which add considerable expense, although the amount of nitric acid (4–5 eq.) is reduced [18].

Having gained success in applying acidic ionic liquids in nitration of aromatic compounds we would like to further expand our experience to the synthesis of RDX in an attempt to improve the direct nitrolysis procedure (for example, to reduce amounts of nitric acid; Scheme 1).



Scheme 1. Synthesis of RDX in the presence of ionic liquids. Ionic liquids: [HMim]X, [$(CH_2)_4SO_3$HMim]X, [$(CH_2)_4SO_3$HPyr]X; $X^- = NO_3^-$, pTSO$^-$, CF3COO$^-$.

Experimental

Reagents and Instrument

All the reagents used were analytical grade. The melting point of RDX was obtained with a WRS-1B Digital Melting Apparatus (Shanghai Precision & Scientific Instrument Co., Ltd., Shanghai, China). ^{1}H NMR spectra were recorded on Bruker Advanced Digital 300 MHz NMR spectrometer (Switzerland).

Preparation of Brønsted Acidic Ionic Liquids

[HMim]X ($X^- = pTSO^-$, NO_3^-, CF_3COO^-) were synthesized following the general procedure: *N*-methylimidazole (1.64 g, 20 mmol) was added to deionized water (5 mL) in a 25-mL glass flask under vigorous stirring. Then an equivalent molar amount of acid (4-toluene sulfonic acid [pTSA], nitric acid [65–68%], trifluoroacetic acid) was added. The mixture was stirred at 40°C for 10 h and then the water was removed under vacuum (0.1 MPa) at 75°C. The viscous liquid obtained was washed with diethyl ether three times and dried at 75°C for 5 h under vacuum (0.1 MPa). [HMim]pTSO: ^{1}H NMR (300 MHz, D_2O, TMS) δ 2.21 (s, 3H), 3.69 (s, 3H), 7.17 (d, 2H, J = 7.8 Hz), 7.20 (d, 2H, J = 7.6 Hz), 7.54 (s, 2H), 8.31 (s, 1H). [HMim]NO_3: ^{1}H NMR (300 MHz, D_2O, TMS), δ 3.80 (s, 3H), 7.46 (s, 2H), 8.70 (s, 1H). [HMim]CF_3COO: ^{1}H NMR (300 MHz, D_2O, TMS), δ 3.89 (s, 3H), 7.40 (s, 2H), 8.64 (s, 1H). [$(CH_2)_4SO_3$HMim]X ($X^- = NO_3^-$, $pTSO^-$, CF_3COO^-) were synthesized according to Qi et al. [19]. [$(CH_2)_4SO_3$HPyr]X ($X^- = NO_3^-$, $pTSO^-$, CF_3COO^-) were synthesized according to Qi et al. [20].

General Procedure for the Synthesis of RDX Catalyzed by Brønsted Acidic Ionic Liquids

At 0–5°C with an ice bath, an indicated amount of ionic liquid was added into HNO_3 (95%) in a 250-mL three-necked flask. A given amount of HA was added under vigorous stirring within 5–10 min. The reaction was continued until the yellow color faded off. Deionized water was added drop-wise to dilute the concentration of HNO_3 to 30–35%. The product RDX precipitated as crystals. The suspension was filtered and the crystals were washed with water until the washed water was neutral. The crystals were dried for 10 h under vacuum (0.06 MPa) at 35°C.

Results and Discussion

Effect of the Equivalents of Ionic Liquid on the Nitrolysis of HA

The effect of equivalents of ionic liquid on the nitrolysis of HA was investigated with $[\mathrm{HMim}]\mathrm{NO}_3$ in the range of 1.0–7.0% mol ratio of ionic (IL) to HA, and the results are shown in Table 1.

It can be seen from Table 1 that the yield of RDX increased with an increase in the equivalents of IL; once the equivalents of IL reached 3.0%, continuing to increase the equivalents of IL had an adverse effect on the yield of RDX. The highest yield of RDX was 71.2%; the mass ratio of HNO_3 (95%) to HA was 13:1 and reaction time was 90 min.

Table 1

The effect of the equivalents of ionic liquid on the nitrolysis of HA[a]

Entry	IL (%)	Nitric acid (95%)/g	HA (g)	RDX (g)	Melting point (°C)	Yield (%)[b]
1	0	18.20	1.40	1.33	203.5–203.7	62.2
2	1.0	18.20	1.40	1.36	203.1–203.2	62.6
3	1.5	18.20	1.40	1.52	204.5–204.7	69.9
4	2.0	18.20	1.40	1.51	204.8–204.8	69.5
5	3.0	18.20	1.40	1.56	203.7–204.0	71.2
6	5.0	17.87	1.37	1.42	204.5–204.7	66.7
7	7.0	17.82	1.37	1.34	204.0–204.3	63.0

[a] Mass ratio of HNO_3 (95%) to HA: $\mathrm{m}(\mathrm{HNO}_3(95\%)/\mathrm{m}(\mathrm{HA}) = 13{:}1$, reaction time: 90 min.

[b] Yield of RDX: $\mathrm{Yield}/\% = 1.021 \times \mathrm{m}(\mathrm{RDX}) \times 140/[\mathrm{m}(\mathrm{HA}) \times 222] \times 100\%$.

Effect of the Mass Ratio of Nitric Acid (95%) to HA on the Nitrolysis of HA in the Presence of IL

The effect of mass ratio of nitric acid to HA was investigated with 3.0 mol% of IL [HMim]NO_3. The results are shown in Table 2.

When the mass ratio of HNO_3 (95%) to HA was 10:1, the yellow color of the reaction faded away within 5 min and white insoluble substrate precipitated. Increasing the amount of HNO_3 enhanced the yield of RDX although the reaction time was extended as well. The highest yield of RDX was 69.0% when the mass ratio of HNO_3 (95%) to HA was 13:1. When the mass ratio of HNO_3 (95%) to HA was 14:1, the yellow color of the reaction still remained after 60 min and the yield of RDX dropped.

Effect of Different Ionic Liquids on the Nitrolysis of HA

The effect of different ILs on the nitrolysis of HA was studied with 3.0% mol ratio of IL to HA, 12:1 mass ratio of nitric acid (95%) to HA. The ILs investigated in this reaction series were [HMim]X, [$(CH_2)_4SO_3$HMim]X, [$(CH_2)_4SO_3$HPyr]X ($X^- =$ pTSO$^-$, NO_3^-, CF_3COO^-). The results are shown in Table 3.

Based on the data in Table 3, the conclusion could be drawn that all ILs have catalytic activities in the nitrolysis of HA. Compared to the system without IL, the yield of RDX was increased by adding 4.2–9.2% under the conditions indicated in Table 3. The anions of IL had no obvious effect on the nitrolysis of HA. On the other hand, the cations of IL played a larger role. The IL [$(CH_2)_4SO_3$HPyr]X showed better catalytic activity than other ILs. This might be related to the acidities of the cations. Among all the ionic liquid used, [$(CH_2)_4SO_3$HPyr]NO_3 showed the best catalytic activity with the yield of RDX 69.9% and the color of the reaction faded away within 5 min after HA was added.

Table 2
The effect of the mass ratio of nitric acid (95%) on the nitrolysis of HA in the presence of ionic liquid[a]

Entry	Mass ratio of HNO_3 (95%) to HA	HNO_3 (95%) (g)	HA (g)	Time[b] (min)	Time[c] (min)	RDX (g)	Melting point (°C)	Yield (%)[d]
1	10:1	14.00	1.40	8[e]	25	1.32	204.7–204.9	60.7
2	11:1	15.40	1.40	10	30	1.40	204.7–204.8	64.4
3	12:1	16.80	1.40	20	40	1.46	204.7–204.9	65.2
4	13:1	18.20	1.40	40	60	1.50	204.7–204.9	69.0
5	14:1	19.60	1.40	60[f]	60	1.27	204.7–204.9	58.4

[a] Amount of ionic liquid: 3.0 mol% of HA.

[b] Yellow fading time.

[c] Reaction time.

[d] Yield of RDX: $\text{Yield}/\% = 1.021 \times \text{m(RDX)} \times 140/[\text{m(HA)} \times 222] \times 100\%$.

[e] The yellow of the reaction system faded away within 5 min and white insoluble substrate appeared.

[f] The yellow did not fade away within 60 min and produced a lot of NO_2 after water was added.

Table 3
The effect of different ionic liquids on the nitrolysis of HA[a]

Entry	IL	Reaction time (min)	Time (min)[b]	RDX (g)	Melting point (°C)	Yield (%)[c]
1	[HMim]pTSO	40	30	1.50	204.4–204.8	69.0
2	[HMim]NO_3	40	20	1.41	204.4–204.7	64.9
3	[HMim]CF_3COO	40	20	1.46	204.7–204.9	67.2
4	[$(CH_2)_4SO_3$HMim]NO_3	40	8	1.41	204.5–204.8	64.9
5	[$(CH_2)_4SO_3$HMim pTSO	40	5	1.42	204.6–204.9	65.3
6	[$(CH_2)_4SO_3$HMim]CF_3COO	40	5	1.45	204.4–204.8	66.6
7	[$(CH_2)_4SO_3$HPyr]NO_3	40	5	1.52	204.5–204.7	69.9
8	[$(CH_2)_4SO_3$HPyr]pTSO	40	20	1.50	204.6–204.8	69.0
9	[$(CH_2)_4SO_3$HPyr]CF_3COO	40	10	1.51	204.5–204.7	69.5
10	none	40	15	1.32	204.3–204.5	60.7

[a] n(IL)/n(HA) = 3.0%, m(95% HNO_3)/m(HA) = 12:1, m(95% HNO_3): 16.80 g, m(HA): 1.40 g.

[b] Yellow fading time.

[c] The yield of RDX: Yield/% = 1.021 × m(RDX) × 140/[m(HA) × 222] × 100%.

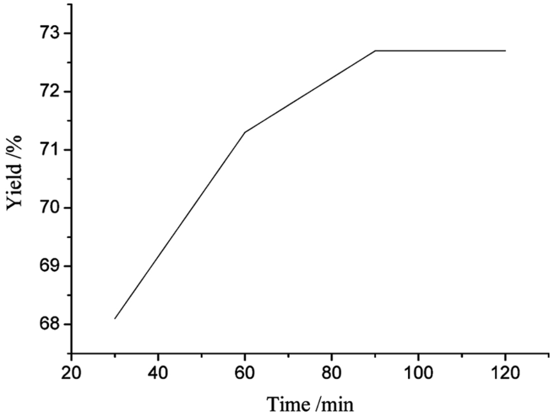


Figure 1. The effect of reaction time on the nitrolysis of HA in the presence of ionic liquid.

Effect of Reaction Time on the Nitrolysis of HA in the Presence of Ionic Liquid

The effect of reaction time on the nitrolysis of HA was investigated with the 13:1 mass ratio of nitric acid (95%) to HA and 3.0 mol% ionic liquid $[(CH_2)_4SO_3HPyr]NO_3$. The results are shown in Fig. 1.

It can be seen from Fig. 1 that the yield of RDX increased and the reaction rate decreased gradually with time. Most of the reaction was finished within 30 min. The yield showed no change after 90 min. Reacting for 90 min, the yield of RDX reached 72.7% in the presence of $[(CH_2)_4SO_3HPyr]NO_3$ ionic liquid.

Conclusions

Three types of IL, [HMim]X, $[(CH_2)_4SO_3HMim]X$, and $[(CH_2)_4SO_3HPyr]X$ ($X^- = pTSO^-$, NO_3^-, CF_3COO^-), were investigated in the nitrolysis of HA. The ILs all showed catalytic activities. Among them $[(CH_2)_4SO_3HPyr]NO_3$ showed the best catalytic activity. In the presence of 3.0% mol ratio $[(CH_2)_4SO_3HPyr]NO_3$ to HA the yield of RDX was 72.7%

within 90 min at 0–5°C with the 13:1 mass ratio of concentrated nitric acid (95%) to HA. Compared with the system without ionic liquid, the yields of RDX were improved by 10.5%.

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