



## Synthesis of HMX via Nitrolysis of DPT Catalyzed by Acidic Ionic Liquids

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**Abstract:** The direct nitrolysis of DPT to synthesize HMX with ionic liquids (ILs) as catalysts was investigated. The results showed that  $[\text{Et}_3\text{NH}]\text{HSO}_4$  was the best catalyst among 18 ILs used and the yield of HMX was up to 61% against 45% without IL. The ILs could be efficiently recovered by simple distillation and extraction after reaction without any apparent loss of catalytic activity even after 10 times recycling.

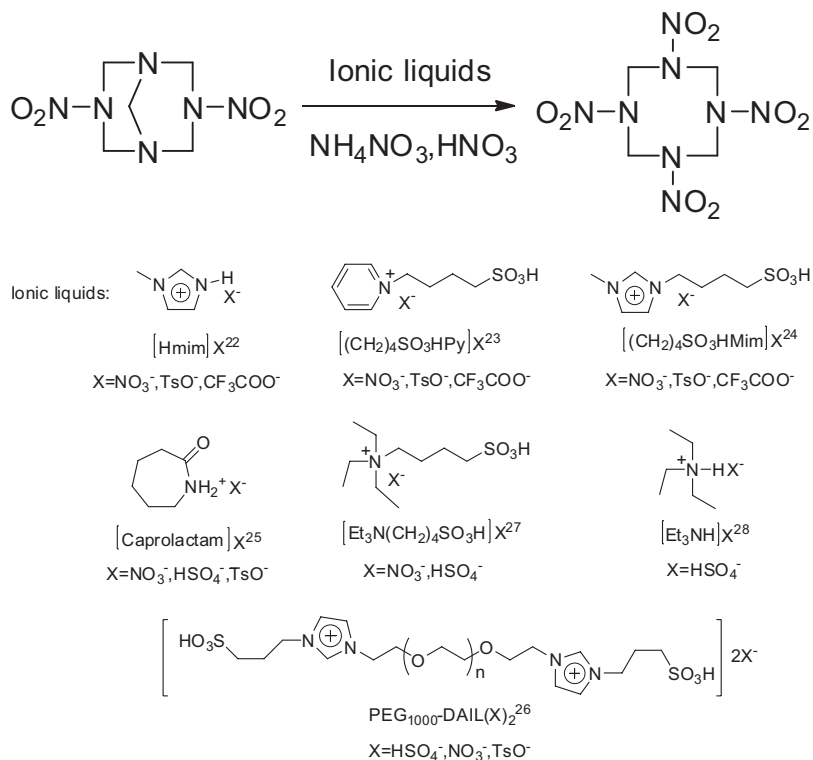
**Keywords:** DPT, HMX, nitrolysis, ionic liquid

### Introduction

1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane (HMX) is one of the most powerful military explosives [1-3], but its application is limited owing to high cost. The conventional methods to synthesize HMX involve the nitrolysis of hexamine (HA) [4], 3,7-dinitro-1,3,5,7-tetraazabicyclo[3,3,1]nonane (DPT) [5], 1,3,5,7-tetraacetyl-1,3,5,7-tetraazacyclooctane (TAT) [6], 1,5-diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane (DADN) [7], etc. Some substrates such as TAT and DADN can afford HMX in high yields but need three or more steps, and they are not economical or environmental friendly.

DPT can be obtained with high yield from broadly available and inexpensive

urea via nitrourea and/or dinitrourea [4, 5, 8, 9], and then HMX can be produced from DPT by direct nitrolysis. This process avoids the use of large excess of acetic acid and acetic anhydride, so the total cost could be reduced remarkably. However, traditional nitrolysis of DPT by  $\text{HNO}_3\text{-NH}_4\text{NO}_3$  only gave HMX in a low yield of 45% even when more than 30 equiv. of  $\text{HNO}_3$  was used [10]. Some other  $\text{HNO}_3\text{-NH}_4\text{NO}_3$ -base systems were also investigated to afford HMX in moderate or low yields of 60%, 62% and 39% when  $\text{MgO}$  [11],  $\text{P}_2\text{O}_5$  [12],  $\text{SO}_3$  [13] were added, respectively. It was well known that better yields could be obtained with a mixture of acetic acid with acetic anhydride in the presence of  $\text{HNO}_3\text{-NH}_4\text{NO}_3$  [14, 15]. Unfortunately, these methods inevitably showed some drawbacks such as environmental pollution and tedious workup.



**Scheme 1.** Nitrolysis of DPT catalyzed by ionic liquids.

Up to now, ionic liquids (ILs) have attracted much attention as environmentally benign media or catalysts thanks to many interesting properties such as wide liquid range, negligible vapor pressure, high thermal stability, and

good solvating ability for a wide range of substrates and catalysts [16-18]. Qiao et al. developed a silica gel-immobilized Brønsted ionic liquid and used it as recyclable solid catalyst in the nitration of aromatic compounds, which offered practical convenience for the separation of product from catalyst [19]. Qian et al reported the ultrasonic assisted nitrolysis of DAPT in [BMIM]PF<sub>6</sub> to achieve HMX in a high yield of 66.8% [20]. Little attention has been paid to the nitrolysis of DPT in an acidic ionic liquid based system. Zhi et al reported a new method to synthesize HMX from DPT via nitrolysis using N<sub>2</sub>O<sub>5</sub>/HNO<sub>3</sub> catalyzed with a new dicationic acidic ionic liquid PEG<sub>200</sub>-DAIL with 64% yield [21]. In this paper, we investigated the application of a series of acidic ILs in the synthesis of HMX by nitrolysis of DPT with HNO<sub>3</sub> (see Scheme 1).

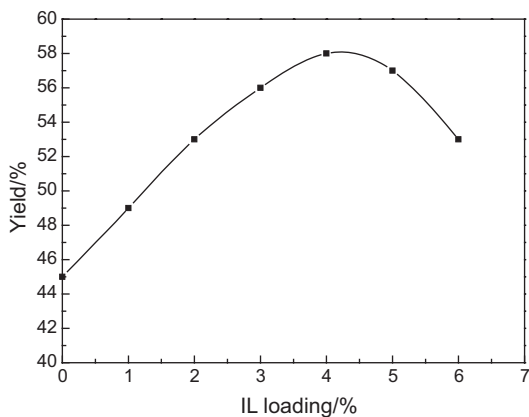
## Materials and Methods

ILs were prepared by reported methods, DPT was prepared from urea by known method with a purity of more than 99% [4]. Melting points were determined on a Perkin-Elmer differential scanning calorimeter. The IR spectra was recorded on a Nicolette spectrometer and expressed in cm<sup>-1</sup> (KBr). Proton NMR was recorded on Bruker DRX300 (500MHz) spectrometer. The HPLC (Waters) was recorded on a SPD-6AV UV detector and mobile phase was methanol and water (70:30), velocity of flow was 1mL/min.

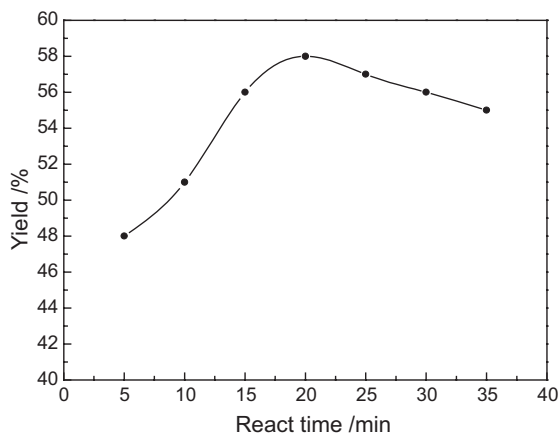
Typical nitrolysis procedure: 0.1 g IL was dissolved in 21.9 g nitric acid (98%) and cooled below 0 °C, 1.9 g ammonium nitrate (AN) was added, then 2 g DPT was added in parts to keep the temperature below 0 °C, and the result mixture was let stand at definite temperature for certain time to ensure complete reaction. The mixture was poured into an additional funnel and added dropwise into a flask containing 0.3 mL of water over 20 minutes keeping the reaction temperature between 60-65 °C. The resulting mixture was stirred for another 20 minutes, then cooled to 40 °C and additional water was added. After an additional stirring for 10 minutes the mixture was cooled to 20 °C and let standing for 10 minutes, the solid product was collected by filtration and rinsed by water, affording pure HMX after crystallization from acetone and drying in vacuum. IR (KBr, cm<sup>-1</sup>) 1560, 1462, 1395, 1203, 1144, 1086, 947, 760, 600. <sup>1</sup>H NMR(DMSO-d<sub>6</sub>), δ: 6.03(s, 8H, CH<sub>2</sub>).

## Results and Discussion

Initially experiments for direct nitrolysis of DPT were carried out in  $\text{NH}_4\text{NO}_3/\text{HNO}_3$  system in the presence of  $[(\text{CH}_2)_4\text{SO}_3\text{HPy}]\text{NO}_3$ . Reaction conditions such as the amount of IL and reaction time were investigated at  $25\text{ }^\circ\text{C}$ , and the results was illustrated in Figure 1 and Figure 2. It was observed that the yield of HMX increased up to 58% when catalyzed by  $[(\text{CH}_2)_4\text{SO}_3\text{HPy}]\text{NO}_3$  while only 45% was obtained without the IL (see Figure 1). However, the yield decreased with increasing IL concentration. The reduced yields may arise from an inappropriate acidity created during the nitrolysis reaction. At the same time, a shorter reaction time of 20 minutes was needed for nitrolysis in  $[(\text{CH}_2)_4\text{SO}_3\text{HPy}]\text{NO}_3$  against a minimum 30 minutes for traditional nitrolysis in  $\text{NH}_4\text{NO}_3/\text{HNO}_3$  (see Figure 2). The yield would decrease with prolonged time owing to HMX decomposition [13]. Thus, the IL  $[(\text{CH}_2)_4\text{SO}_3\text{HPy}]\text{NO}_3$  proved to be an efficient catalyst which accelerate the reaction rate.



**Figure 1.** The effect of amount of ionic liquid on nitrolysis of DPT. Reaction conditions: 21.9 g  $\text{HNO}_3$ , 2 g DPT, 1.9 g  $\text{NH}_4\text{NO}_3$ ,  $25\text{ }^\circ\text{C}$ , 30 min.



**Figure 2.** The effect of reaction time on nitrolysis of DPT. Reaction conditions: 21.9 g HNO<sub>3</sub>, 2 g DPT, 1.9 g NH<sub>4</sub>NO<sub>3</sub>, 25 °C, 4 (wt)% of [(CH<sub>2</sub>)<sub>4</sub>SO<sub>3</sub>HPy]NO<sub>3</sub>

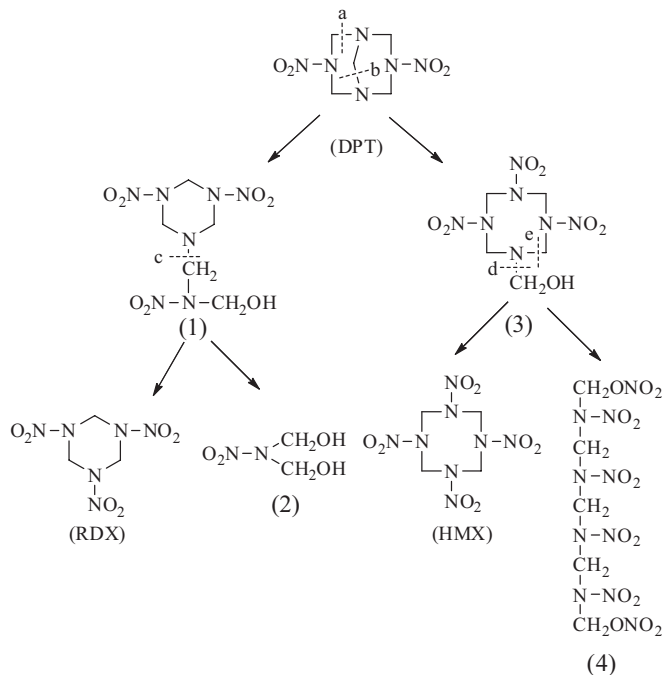
**Table 1.** The effect of different ionic liquids on the nitrolysis of DPT<sup>a</sup>

Entry	IL	HMX (g)	Melting point °C	Yield (%) <sup>b</sup>
1	0	1.23	274.1 ~ 274.4	45
2	[HMim]NO <sub>3</sub>	1.47	273.6 ~ 273.9	54
3	[HMim]TsO	1.49	274.1 ~ 274.3	55
4	[HMim]CF <sub>3</sub> COO	1.47	273.8 ~ 274.0	54
5	[(CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> HPy]NO <sub>3</sub>	1.60	274.2 ~ 274.5	59
6	[(CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> HPy]TsO	1.63	274.4 ~ 274.6	60
7	[(CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> HPy]CF <sub>3</sub> COO	1.58	274.1 ~ 274.5	58
8	[(CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> HMim]NO <sub>3</sub>	1.49	274.2 ~ 274.4	55
9	[(CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> HMim]TsO	1.52	274.4 ~ 274.5	56
10	[(CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> HMim]CF <sub>3</sub> COO	1.49	274.0 ~ 274.3	55
11	[Et <sub>3</sub> NH]HSO <sub>4</sub>	1.66	274.1 ~ 274.4	61
12	[Et <sub>3</sub> N(CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> H]NO <sub>3</sub>	1.49	274.3 ~ 274.7	55
13	[Et <sub>3</sub> N(CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> H]HSO <sub>4</sub>	1.49	274.1 ~ 274.4	55
14	[Caprolactam]NO <sub>3</sub>	1.52	274.0 ~ 274.2	56
15	[Caprolactam]HSO <sub>4</sub>	1.52	273.9 ~ 274.3	56
16	[Caprolactam]TsO	1.55	274.3 ~ 274.6	57
17	PEG <sub>1000</sub> -DAIL(NO <sub>3</sub> ) <sub>2</sub>	1.47	274.1 ~ 274.3	54
18	PEG <sub>1000</sub> -DAIL(HSO <sub>4</sub> ) <sub>2</sub>	1.47	274.0 ~ 274.3	54
19	PEG <sub>1000</sub> -DAIL(TsO) <sub>2</sub>	1.49	274.2 ~ 274.5	55

<sup>a</sup> 2.0 g DPT, 1.9 g NH<sub>4</sub>NO<sub>3</sub>, 21.9 g HNO<sub>3</sub>, 4 (wt)% of IL, 25 °C/20 min, 65-70 °C/20 min.

<sup>b</sup> Calculated by HPLC.

A series of acidic ionic liquids were then applied as catalysts in the direct nitrolysis of DPT in  $\text{NH}_4\text{NO}_3/\text{HNO}_3$  mixture (see Table 1). The product yields (54%~61%) were significantly better when using acidic ionic liquids as compared to control experiment (45%). The anions of ILs did not show distinct effect on the catalytic activity for nitrolysis of DPT. However, the cations had a more direct effect on the yields. The catalytic activities of  $[(\text{CH}_2)_4\text{SO}_3\text{HPy}]\text{TsO}$  and  $[\text{Et}_3\text{NH}]\text{HSO}_4$  were superior than other ILs. Studies on the nitrolysis mechanism for HMX preparation has shown that esterification (O-nitration) is a competing side reaction which occurs during the formation of HMX in the nitrolysis of DPT, and that the bridge C-N bonds are the weakest ones which resulting in the formation of HMX. The choice may depend on the rapidity and completeness with which the free hydroxyl group is esterified (see Figure 3). If compound 3 is esterified quickly enough, the straight-chain product 4 would form. However, ammonium nitrate appears to favor formaldehyde removal (demethylolation) or hindered esterification, which facilitated the formation of HMX [29]. All the cations of the ILs used in this research were organic ammoniums, which might have the similar function of ammonium nitrate. This might be a reason for the nitrolysis modification affording higher yields against traditional methods.



**Figure 3.** Nitration of DPT.

The recoverability and recyclability of the acidic ILs was then studied. Table 2 lists the results of repeat experiments using  $[\text{Et}_3\text{NH}]\text{HSO}_4$  as catalysts. The results indicated that the yield was reproducible.

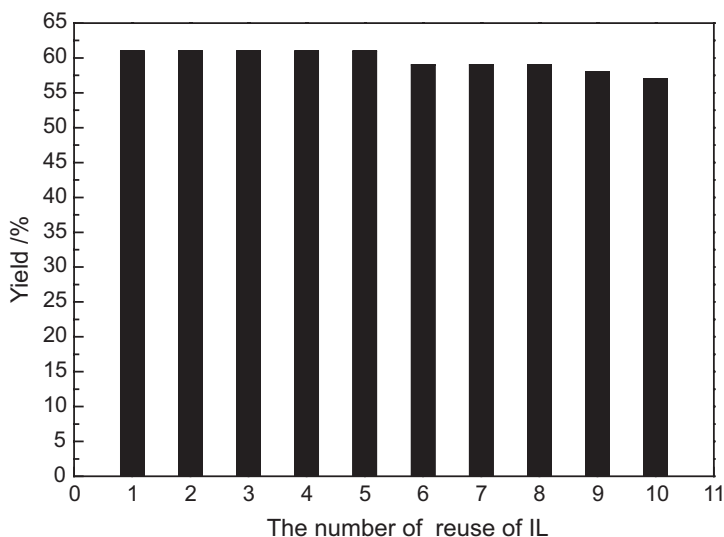
**Table 2.** Repeated experiments of the nitrolysis<sup>a</sup>

Entry	Dosage of IL (%)	HMX (g)	Melting point °C	Yield (%) <sup>b</sup>
1	4	1.67	274.4 ~ 274.6	61
2	4	1.66	274.2 ~ 274.3	61
3	4	1.67	274.3 ~ 274.5	61
4	4	1.65	274.1 ~ 274.4	61
5	4	1.66	274.3 ~ 274.5	61

<sup>a</sup> 2.0 g DPT, 1.9 g  $\text{NH}_4\text{NO}_3$ , 21.9 g  $\text{HNO}_3$ , 4 (wt)% of  $[\text{Et}_3\text{NH}]\text{HSO}_4$ , 25 °C/20 min, 65-70 °C/20 min.

<sup>b</sup> Calculated by quantitative HPLC.

After reaction, IL was extracted from the filtrate with 50 mL methylene chloride, and it was recovered after removing methylene chloride. The recovered IL was reused in the next nitrolysis reaction after loading refresh substrates. The yield of HMX was unchanged after five recycles of acidic ionic liquid  $[\text{Et}_3\text{NH}]\text{HSO}_4$  and then decreased slightly with continued recycling for up to ten cycles (see Figure 4).



**Figure 4.** Repeating experiments using recovered  $[\text{Et}_3\text{NH}]\text{HSO}_4$ .

## Conclusions

An efficient process for the preparation of HMX from DPT in a  $\text{NH}_4\text{NO}_3/\text{HNO}_3$  nitrolysis mixture catalyzed by a series of acidic ionic liquids was demonstrated. The ionic liquids could be reused for at least 10 cycles reproducibly affording HMX in yields up to 61%.

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