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Preparation of HMX by Catalytic Nitrolysis of DPT in AIL-N_2O_5-HNO_3 System

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Direct nitrolysis of 3,7-dinitro-1,3,5,7-tetraazabicyclo[3,3,1]nonane (DPT) is a feasible way to synthesize HMX, and it has multiple practical applications. In this paper, a new nitrolysis process involving the use of an N_2O_5-HNO_3 system catalyzed by acidic ionic liquids (AILs) was developed. The results show that $[Et_3NH]TsO$ was the best catalyst among the 28 AILs used and that HMX was formed at a higher yield of 61%, compared to 45% without any AIL. Moreover, with the addition of N_2O_5, the yield was further increased to a maximum value of 69%. The AILs were also efficiently recovered by simple extractions without any apparent loss of catalytic activity, even after five runs.

Key Words : DPT, HMX, Nitrolysis, N_2O_5, Acidic 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 because of its high cost. The conventional synthesis of HMX involves nitrolysis of one of the following: hexamine (HA),[4,5] 1,3,5,7-tetraacetyl-1,3,5,7-tetraazacyclooctane (TAT),[6] or 1,5-diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane (DADN).[7] TAT and DADN can be used to achieve high yields; however, they require three or more steps, and their preparations are neither economical nor eco-friendly.

DPT, prepared from nitrourea and/or dinitrourea,[4,8-10] can also synthesize HMX by direct nitrolysis. This process avoids using excess acetic acid and acetic anhydride, which can reduce the total cost remarkably. Unfortunately, traditional nitrolysis of DPT by HNO_3-NH_4NO_3 system only afforded HMX in low yield (45%), even when more than 30 molar equivalents of HNO_3 were used.[11] Other HNO_3-NH_4NO_3-based systems have also been investigated and have resulted in moderate to low yields (60%, 62% and 39%) when MgO, P_2O_5 and SO_3 were added, respectively.[12-14] It is well known that better yields can be obtained in a mixture of acetic acid and acetic anhydride in the presence of HNO_3-NH_4NO_3.[15,16] Unfortunately, these methods inevitably have shown some drawbacks, such as environmental pollution and tedious workup.

At present, ionic liquids have attracted significant attention as eco-friendly solvents or catalysts because they possess many interesting properties, including a wide liquid range, negligible vapor pressure, high thermal stability, high design ability, and good solvating ability for a wide range of substrates and catalysts.[17-27] Qiao and co-workers prepared a silica gel immobilized Brønsted ionic liquid and used it as a recyclable catalyst in the nitration of aromatic compounds.[28]

N_2O_5 has been widely used as a clean, efficient nitrating agent and has many advantages in comparison to mixed acids.[29] Its advantages include (1) reactions that are considerably faster, less exothermic, easier to control, and cleaner; (2) higher yields; (3) product isolation that is often easier; (4) almost no acid waste requiring treatment and disposal; and (5) the synthesis of high energy materials, such as nitrated hydroxy-terminated polybutadiene (NHTPB), poly[NIMMO], poly[GLYN] and ammonium dinitramide (ADN), that can not be synthesized using conventional nitrating agents. In fact, N_2O_5 can perform all of the reactions that conventional nitrating agents can, but it usually does so more efficiently. For example, TAT and DADN efficiently transferred to HMX in high yields when a solution of N_2O_5 in nitric acid was used as a nitrolyzing system; however, these same reactions failed when conventional nitrating agents were applied.[1,29] We have also reported that an N_2O_5-HNO_3 system worked in the nitrolysis of DPT, affording HMX a yield of 58%.[30] With the help of ultrasonic radiation, DAPT was nitrolyzed efficiently in an N_2O_5-HNO_3 system to provide HMX at a higher yield of 66.8%.[31] Furthermore, CL-20 was synthesized *via* nitration and nitrolysis of 2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazatetracyclo[5,5,0,$0^{3,11}0^{5,9}$]dodecane (TAIW) in a N_2O_5-HNO_3 system to give a yield of 86.1% and purity of 99%.[32]

Unfortunately, this same attention has not been paid to nitrolysis with the use of both acidic ionic liquids and N_2O_5. From the few research results reported, we have found that the combined use of ionic liquids and N_2O_5 in nitrations, especially in the nitrolysis of amines, has some merits. For example, Cheng and co-workers investigated the application of N_2O_5 and Brønsted acidic ionic liquids in the synthesis of RDX by direct nitrolysis of urotropine, and the yield was as high as 84%.[33] Additionally, our team reported a new method to synthesize HMX from DPT in a N_2O_5-HNO_3 system catalyzed by a novel dicationic acidic ionic liquid PEG_{200}-DAIL.[34] The attractive merits of this technique are

that the yield of HMX was promoted to 64% and the loading quantity of HNO_3 was decreased dramatically.

In this paper, we report a process to prepare HMX by the nitrolysis of DPT in an N_2O_5-HNO_3 system catalyzed by a large variety of AIL.

Experimental Section

Materials and Methods. N_2O_5 was prepared from HNO_3 by dehydration with P_2O_5 and stored at −60 °C before use. AILs were prepared by reported methods.[35-41] DPT was prepared by a known method from urea with a purity of more than 99%.[4] All other chemicals (AR grade) were commercially available and used without further purification. The purity of HMX was tested by high performance liquid chromatography (HPLC) with a reverse phase micro C18 column (Waters Alliance HPLC system), and the eluent was a mixture of methanol and water (70:30) with a flow rate of 1 mL/min. Melting points were determined on a Perkin-Elmer differential scanning calorimeter and are uncorrected. IR spectra were recorded on a Nicolete spectrometer (KBr), and ^{1}H NMRs were recorded on a Bruker DRX300 (500MHz) spectrometer. The crystal structure of HMX was recorded on a four-circle single crystal X-ray diffraction apparatus (CAD4/PC) from Netherlands Enraf Noius & Enraf Noius Inc.

Typical Nitrolysis Procedure. N_2O_5 (2.0 g, 0.0158 mol) was dissolved in 98% nitric acid (11.0 g, 0.1711 mol), and the solution was cooled to below 0 °C. Next, AIL (0.0088 mol) and ammonium nitrate (1.9 g, 0.0238 mol) were added in one portion, and DPT (2.0 g, 0.0092 mol) was then added in parts to keep the temperature below 0 °C. The mixture was kept at 25 °C for 20 min to ensure the reaction went to completion. Once complete, the reaction was transferred into an addition funnel and added dropwise into 0.3 mL of water over 20 min to keep the temperature between 60-65 °C. The mixture was stirred for another 20 min and cooled to 40 °C; additional water (7 mL) was then added. The reaction mixture was stirred for 10 min, cooled to 20 °C and let to stand for another 10 min. The solid product was collected by filtration and rinsed with water. Pure HMX was obtained by crystallization from ethyl acetate and drying under vacuum. IR (KBr, cm^{-1}) 3037, 1526, 1261, 759; ^{1}H NMR (DMSO-d_6) δ 6.02 (s, 8H, CH_2); mp 274.8-275.1 °C.

Results and Discussion

Characterization of HMX. The high-performance liquid chromatogram shows a single peak at retention time 2.98 min as HMX with a purity of 99.9% (Figure 1). The IR spectrum (Figure 2) also exhibits two characteristic peaks at 1526 cm^{-1} and 1261 cm^{-1}, which are due to the asymmetric and symmetric stretching vibrations of the nitro group. Furthermore, the small peak at 3037 cm^{-1} is representative of the symmetric vibrations of the methylene groups of HMX.

According to reference,[42] β-HMX has only one strong transmittance peak in the fingerprint area, while α- and γ-

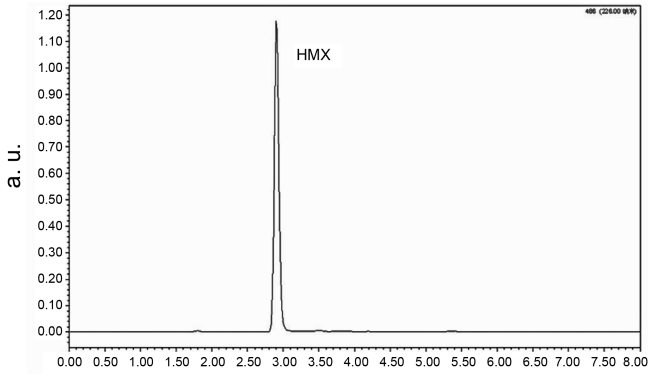


Figure 1. High Performance Liquid Chromatogram of β-HMX.

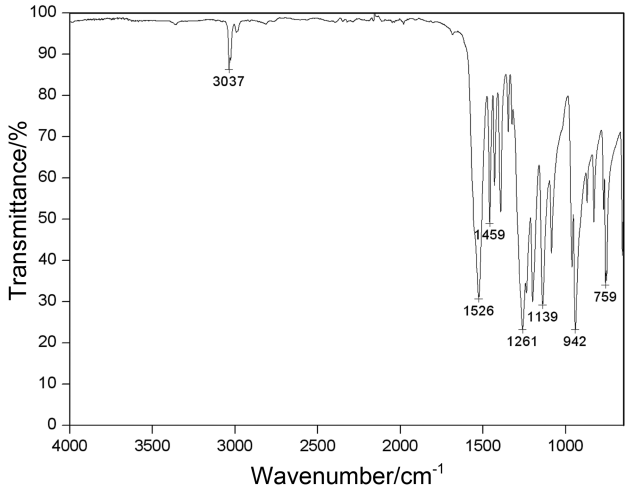


Figure 2. FT-IR spectra of β-HMX.

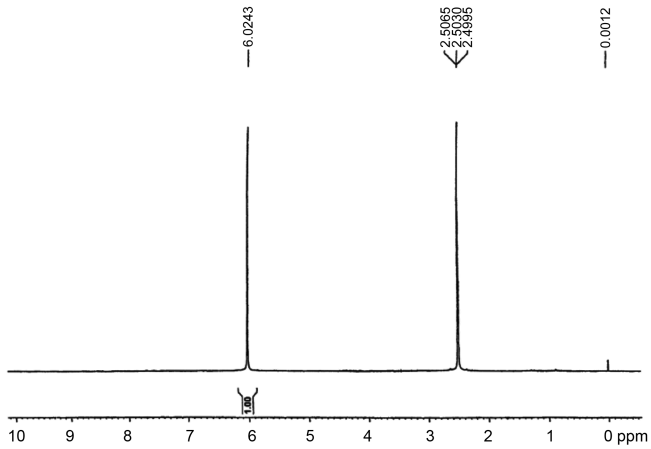


Figure 3. ^{1}H NMR of β-HMX (DMSO-d_6).

HMXs have three weak transmittance peaks in the fingerprint area. Based on these findings, the strong peak at 759 cm^{-1} in Figure 2 indicates that the HMX obtained from this work is of the beta crystal form. Additionally, the ^{1}H NMR spectrum of HMX (Figure 3) exhibits a single chemical shift (δ 6.02 pm) for the methylene protons.

The single crystal of HMX was obtained after very slow crystallization from ethyl acetate at ambient temperature. The molecular packing diagram and stereo structure for

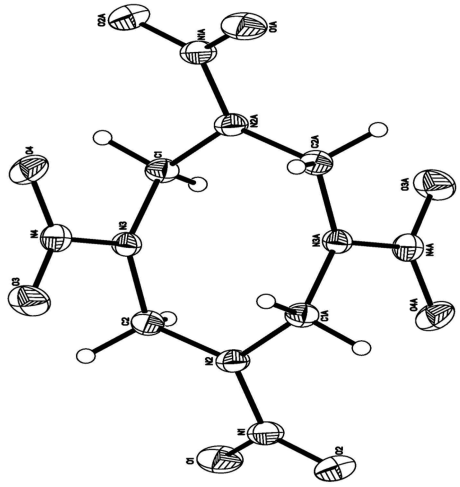


Figure 4. Molecular structure of β-HMX.

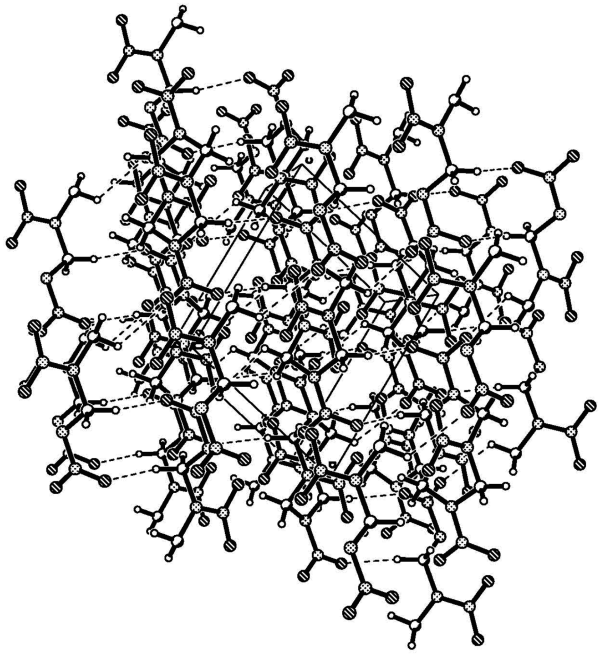


Figure 5. Molecular packing diagram of β-HMX.

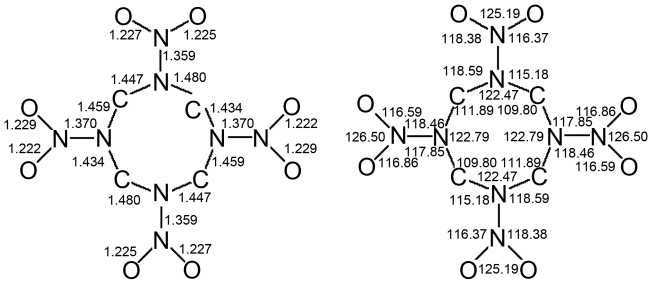


Figure 6. Bond length and bond angle data of β-HMX.

HMX were determined by X-ray crystal structure analysis (Figures 4 and 5). The bond lengths, bond angles and dihedral angles defining the exact conformation of HMX are included in Figure 6 and Table 1. The X-ray diffraction data obtained for the synthesized HMX using acidic ionic liquid matches with the literature data.[43]

Table 1. Dihedral angle obtained from four-circle single crystal X-ray diffraction

Atoms	Dihedral angle	Atoms	Dihedral angle
D(O1 N1 N2 C1)	−160.38	D(N2 C2 N3 C1)	102.59
D(O2 N1 N2 C1)	22.3	D(N2 C1 N3 N4)	72.3
D(O1 N1 N2 C2)	−1.7	D(N2 C1 N3 C2)	−118.75
D(O2 N1 N2 C2)	−178.98	D(C2 N3 N4 O3)	11.9
D(N1 N2 C2 N3)	−174.84	D(C1 N3 N4 O3)	−178.66
D(C1 N2 C2 N3)	−17.1	D(C2 N3 N4 O4)	−170.63
D(N2 C2 N3 N4)	−88.44	D(C1 N3 N4 O4)	−1.2

Nitrolysis of DPT in AIL-N_2O_5-HNO_3 System. Initial nitrolysis experiments of DPT to prepare HMX were performed in an N_2O_5-HNO_3 system and in the presence of $[(CH_2)_4SO_3HPy]NO_3$. The reaction conditions used, such as the amount of AIL and reaction time, were investigated at 25 °C, and the results are presented in Tables 2 and 3. From Table 2, it is observed that the yield of HMX increased to 65% when $[(CH_2)_4SO_3HPy]NO_3$ was applied as a catalyst, while only a yield of 58% was obtained without any AIL. Furthermore, the yields further decreased with increasing percentage of AIL used when above 4%. This phenomenon may have arisen from an acidity created during the nitrolysis reaction when the loading amount of AIL was above 4%; the acidity elevated to a level where more by-product **5** (Figure. 7) was produced. With regard to reaction time, a shorter reaction time of 20 min was required for nitrolysis with $[(CH_2)_4SO_3HPy]NO_3$; this time gave an increased yield of 67% for HMX. Comparatively, a minimum time of 30 min

Table 2. The effect of the amount of ionic liquid on nitrolysis of DPT

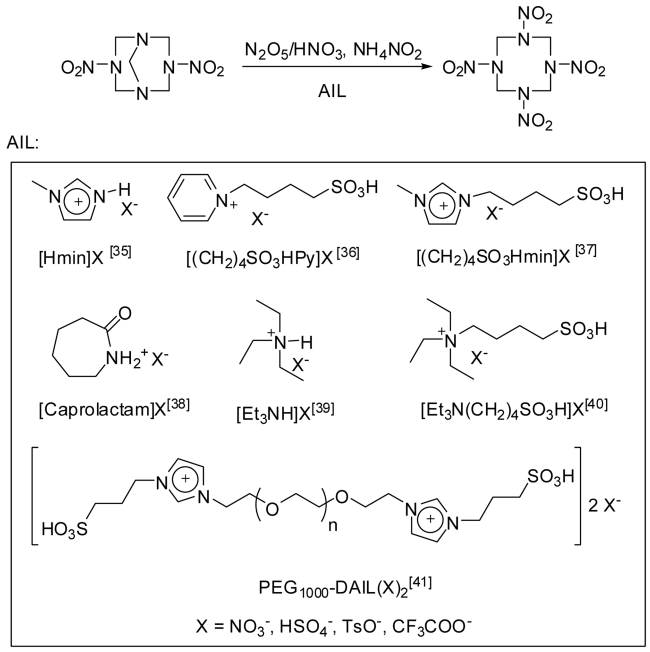
Entry	IL loading (%)	Yield (%)[a]
1	0	58
2	1	59
3	2	62
4	4	65
5	6	64
6	8	62

[a]2 g N_2O_5, 2 g DPT, 1.9 g NH_4NO_3, 11 g HNO_3, 25 °C, and 30 minutes.

Table 3. The effect of the reaction time on nitrolysis of DPT

Entry	Reaction time (min)	Yield (%)[b]
1	5	50
2	10	55
3	15	61
4	20	67
5	25	66
6	30	65
7	35	63

[b]2 g N_2O_5, 2 g DPT, 1.9 g NH_4NO_3, 11 g HNO_3, 25 °C, and 4% of $[(CH_2)_4SO_3HPy]NO_3$



Scheme 1. Nitrolysis of DPT in AIL-N_2O_5-HNO_3 system.

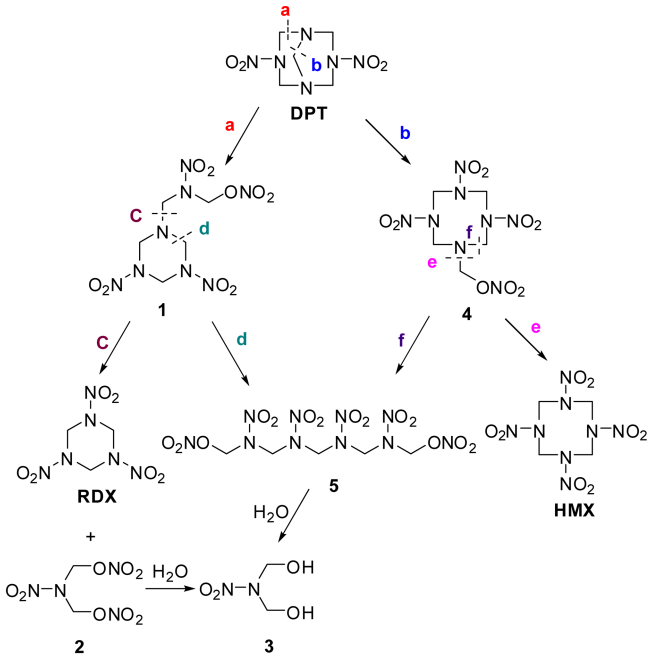


Figure 7. Main nitrolysis process of DPT.

was needed for nitrolysis in an N_2O_5-HNO_3 system (Table 3). The yield decreased with prolonged time, possibly because of the decomposition of HMX[14]. Thus, $[(CH_2)_4SO_3HPy]NO_3$ proved to be an efficient catalyst.

A series of acidic ionic liquids were also applied as catalysts in the nitrolysis of DPT in a N_2O_5-HNO_3 system (Scheme 1. and Table 4). The yields (58%-69%) achieved from the AIL-N_2O_5-HNO_3 systems were significantly higher than the control experiment without any AIL (Table 4, entry 1). It is also obvious from Table 4 that the anions of the ILs did not show remarkable effects on the catalytic activity for

Table 4. Preparation of HMX from DPT catalyzed by different acidic ionic liquids[a]

Entry	IL	Yield (%)[c]	
		HNO_3	N_2O_5-HNO_3
1	/	45	58
2	$[HMim]NO_3$	54	62
3	$[HMim]HSO_4$	56	64
4	$[HMim]CF_3COO$	54	60
5	[HMim]TsO	55	65
6	$[(CH_2)_4SO_3HPy]NO_3$	59	67
7	$[(CH_2)_4SO_3HPy]\ HSO_4$	58	66
8	$[(CH_2)_4SO_3HPy]CF_3COO$	58	66
9	$[(CH_2)_4SO_3HPy]TsO$	59	68
10	$[(CH_2)_4SO_3HMim]NO_3$	55	63
11	$[(CH_2)_4SO_3HMim]HSO_4$	56	64
12	$[(CH_2)_4SO_3HMim]CF_3COO$	55	64
13	$[(CH_2)_4SO_3HMim]TsO$	56	66
14	$[Et_3NH]NO_3$	58	66
15	$[Et_3NH]HSO_4$	58	67
16	$[Et_3NH]CF_3COO$	59	68
17	$[Et_3NH]TsO$	60	69
18	$[Et_3N(CH_2)_4SO_3H]NO_3$	55	63
19	$[Et_3N(CH_2)_4SO_3H]HSO_4$	55	66
20	$[Et_3N(CH_2)_4SO_3H]CF_3COO$	56	65
21	$[Et_3N(CH_2)_4SO_3H]\ TsO$	57	67
22	$[Caprolactam]NO_3$	56	64
23	$[Caprolactam]HSO_4$	56	65
24	$[Caprolactam]CF_3COO$	55	63
25	[Caprolactam]TsO	57	65
26	PEG_{1000}-$DAIL(NO_3)_2$	54	66
27	PEG_{1000}-$DAIL(HSO_4)_2$	54	64
28	PEG_{1000}-$DAIL(CF_3COO)_2$	55	64
29	PEG_{1000}-$DAIL(TsO)_2$	56	67

[c]2 g DPT, 2 g N_2O_5,1.9 g NH_4NO_3, 11 g HNO_3, 4% of IL, 25 °C/20 min, then 65-70 °C/20 min.

the nitrolysis of DPT. In contrast, the cations had a relatively more notable effect on the yields. Specifically, the catalytic activities of $[(CH_2)_4SO_3HPy]TsO$ and $[Et_3NH]TsO$ were superior to any other AIL.

To explain this phenomenon, it would be better to discuss the nitrolysis mechanism that prepares HMX. Nitrolysis of DPT causes two fundamentally different bond breaks (Figure 7): breaking at *a* would result in the formation of products including mainly RDX and *N*-nitrodihydroxymethylamine (**3**) and breaking at *b* would lead to mainly HMX and some linear tetranitramines, such as 1,9-dinitroxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane (**5**). Esterification (O-nitration) might be a competing side reaction that could occur during the formation of HMX in the nitrolysis of DPT, and the bridge C-N bonds might be the weakest points, which would result in the formation of HMX. The first type of cleavage (at *a*) is of very low possibility. As a result, RDX and *N*-nitrodihydroxymethylamine (**3**) are rarely detected. The second type of breaking (at *b*) tends to occur with low acidity and/or with an appropriate nitrating agent at relative-

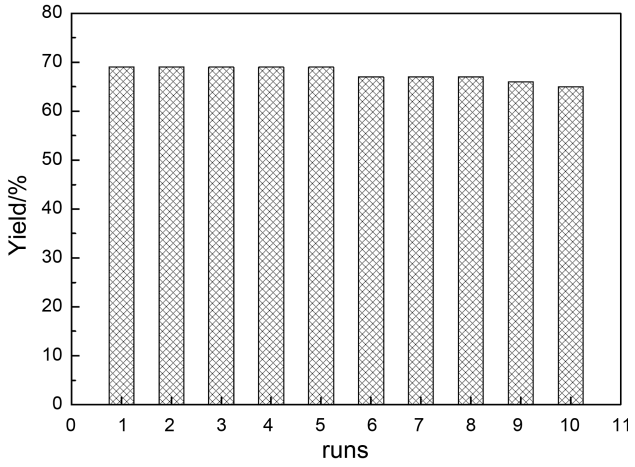


Figure 8. Recycling nitrolysis experiments of [Et_3NH]TsO.

ly low temperatures, particularly in the initial step with DPT. However, when the molar ratio of N_2O_5/DPT exceeds 2, the yield decreases. This decrease in yield is likely due to bond breaking occurring at *f* (in compound **4**) to form the straight chained by-product, compound **5**. However, the tendency may also depend on the rapidity and completeness of esterification of the free hydroxyl group. Fortunately, ammonium nitrate appears to favor the removal of formaldehyde or hindered esterification, which will favor the formation of HMX.

Based on the above discussion, we think that the AIL used in this work might have a similar function to ammonium nitrate because all of the cations of these ILs were organic ammoniums. It may be a reasonable explanation for the higher yields when AILs were used as catalysts, compared to traditional methods.

Recycling Application of the AIL. After each reaction, the final mixture was filtered, and the filtrate was extracted with 50 mL of methylene chloride. All of the AIL were recovered after the removal of water, and the recovered AILs were used in the next reaction after charging with fresh substrates. For example, a simple acidic ionic liquid, [Et_3NH]TsO, was used as a model catalyst, and the results of the recycling experiments are demonstrated in Figure 8. The yields of HMX showed almost no change after five runs; however, they slightly decreased after the fifth run. Nevertheless, a high yield of approximately 65% was still obtained after ten runs.

Conclusions

An efficient process for the preparation of HMX from DPT in an N_2O_5-HNO_3 system catalyzed by a series of acidic ionic liquids was developed. The yield of HMX was as high as 69%, and the acidic ionic liquids used could be reused. Specifically, the application of a simple acidic ionic liquid, [Et_3NH]TsO, afforded reproducibly yields of approximately 69% after five runs and 65% after ten runs.

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