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# Influence of Ammonium Ion on Nitrolysis of 3,7-Dinitro-1,3,5,7-tetraazabicyclo[3,3,1]nonane (DPT)

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**Abstract:** Based on the two mechanisms of 3,7-dinitro-1,3,5,7-tetraazabicyclo[3,3,1]nonane (DPT) nitrolysis via  $\text{HNO}_3\text{-NH}_4\text{NO}_3$  or  $\text{HNO}_3$ , the effects of  $\text{NH}_4^+$  in nitrolysis of DPT were studied by experiment and theoretical calculation. The effect of  $\text{NH}_4^+$  on the yield of HMX was studied with adding the ammonium salts including  $(\text{NH}_4)_2\text{HPO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{CH}_3\text{COONH}_4$  to nitrate solution system. Results show that the above-mentioned ammonium salts can improve the yield of HMX to 41.5%, 37.4% and 20.7%, respectively. Their function is similar to  $\text{NH}_4\text{NO}_3$ . In different nitric acid-ammonium salt systems, when the molar ratio of  $\text{NH}_4^+$  and DPT is close to 10, the yield of HMX reaches a maximum value of 56.3%, 52.2% and 35.5%, respectively. Results of the nitrolysis of DPT in nitric acid-ammonium salt systems and nitric acid-nitrate system are compared, finding that  $\text{NH}_4^+$  plays a dominant role in improving the yield of HMX. The reaction mechanism of  $\text{NH}_4^+$  in the nitrolysis process of DPT is theoretically explained by the density functional theory (DFT), deriving that the activation energy of DPT nitrolysis in  $\text{HNO}_3/\text{NH}_4^+$  is  $133.95 \text{ kJ} \cdot \text{mol}^{-1}$ , lower than  $376.73 \text{ kJ} \cdot \text{mol}^{-1}$  in  $\text{HNO}_3$ .

**Key words:** octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX); 3,7-dinitro-1,3,5,7-tetraazabicyclo[3,3,1]nonane (DPT); nitrate ammonium; nitrolysis; density functional theory (DFT); reaction mechanism

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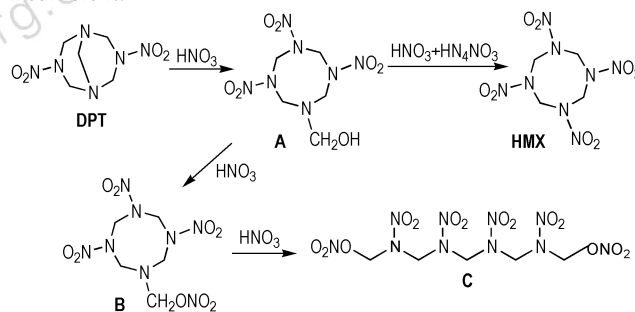
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## 1 Introduction

Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) is one of the most popular explosive compounds with high density, high energy and excellent thermal stability. Reported manufacturing process for HMX involves the nitrolysis of hexamine in the ternary systems including nitric acid, ammonium nitrate and acetic anhydride, among which the Bachmann process is the most classic method<sup>[1]</sup>. However the expensive acetic anhydride leads to a relatively high cost of HMX in Bachmann process, and then its application was greatly limited in high energetic explosive. Owing to the above reason, a new preparation process of HMX through the key precursor, 3,7-dinitro-1,3,5,7-tetraazabicyclo[3,3,1]nonane (DPT)<sup>[2-3]</sup>, has attracted great attention due to the low cost, high security and convenient performance. The nitrolysis of DPT is the committed step in DPT process. Different nitrolysis methods for DPT have been explored intensively, among which the  $\text{HNO}_3\text{-NH}_4\text{NO}_3$  method is most promising<sup>[4-8]</sup>. Compared to the Bachmann process, the cost of HMX is significantly reduced by employing the  $\text{HNO}_3\text{-NH}_4\text{NO}_3$  method.

$\text{NH}_4\text{NO}_3$  as additive plays a key role on the nitrolysis of DPT<sup>[9-10]</sup>. The yield of HMX in  $\text{HNO}_3\text{-NH}_4\text{NO}_3$  system is 40% higher than that in pure nitric acid in general<sup>[5-6]</sup>. However, the action mechanism of  $\text{NH}_4\text{NO}_3$  is poorly known in the nitrolysis of DPT. Currently, the nitrolysis process of DPT in  $\text{HNO}_3\text{-NH}_4\text{NO}_3$  or  $\text{HNO}_3$  is speculated as shown in

Scheme 1<sup>[7,9]</sup>. HMX and 1,9-dinitroxy-2,4,6,8-tetranitro-2,4,6,8-tetrazacyclononane (C) are two kinds of main products. When  $\text{NH}_4\text{NO}_3$  was absent in  $\text{HNO}_3$  solution, C got superior position. But by adding  $\text{NH}_4\text{NO}_3$  into  $\text{HNO}_3$  solution, HMX was prepared instead of C. McKay et al<sup>[9]</sup> considered that  $\text{NH}_4\text{NO}_3$  in nitrolysis system served to hinder esterification and promote demethylation on 1-hydroxymethyl-1,3,5,7-trinitro-1,3,5,7-tetrazacyclononane (A). Chen et al<sup>[4]</sup> found that nitrate can also improve the yield of HMX and hence inferred the common ion effect of  $\text{NO}_3^-$  was the main factor. And yet, the effect of  $\text{NH}_4^+$  has not been studied independently by now. Therefore the conjecture of former scholars was still far insufficient.



**Scheme 1** The nitrolysis of DPT in nitric acid-ammonium nitrate or pure nitric acid

Based on the two involved mechanisms (Scheme 1) of DPT nitrolysis via  $\text{HNO}_3\text{-NH}_4\text{NO}_3$  or  $\text{HNO}_3$ <sup>[7,9]</sup>, the role of  $\text{NH}_4\text{NO}_3$  was researched further by experiment and theoretical calculation in this study. Firstly, the role of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in DPT nitrolysis was investigated and compared in nitric acid-ammonium salt systems and nitric acid-nitrate systems respectively. Then on the basis of experiment research, two possible

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DPT nitrolysis mechanisms in  $\text{HNO}_3/\text{NH}_4^+$  and  $\text{HNO}_3$  were proposed. And the catalytic effect of  $\text{NH}_4^+$  was investigated theoretically through the density functional theory<sup>[11–12]</sup>.

## 2 Experiment section

### 2.1 Reagents and Instruments

DPT was prepared by Xi'an Modern Chemistry Research Institute<sup>[3]</sup>, with the purity over 99%.  $\text{HNO}_3$  was purified before use. Others are analytical reagents and commercially available without further purification.

Melting points were determined microscopically on an X-5 precision micro melting point apparatus.  $^1\text{H}$  NMR spectra were recorded on a Bruke AV-400 spectrometer, FT-IR (KBr) spectra were recorded on a PerkinElmer FT-IR spectrometer, and mass spectra were collected on a HP5989B mass spectrometer. The purity of HMX was checked on Shimadzu LC-2010 HPLC.

### 2.2 The nitrolysis of DPT in nitric acid-ammonium salt or nitric acid-nitrate

The preparation process of HMX as used in this research was a modification on the original  $\text{HNO}_3\text{-NH}_4\text{NO}_3$  method for the nitrolysis of DPT<sup>[5]</sup>. In a three necked round bottomed flask equipped with magnetic stirring assembly, 10.0 mL of  $\text{HNO}_3$  and a certain amount of ammonium salt or nitrate were mixed. The temperature of the nitrolysis system was maintained at  $(5.0 \pm 1.0)$  °C. 2.0 g of DPT was added slowly into flask, and the system temperature would rise to 7–8 °C. After DPT addition, the reaction was continued for another 30 min and then the temperature was increased to and kept at 25 °C for 40 min. Then, the reaction mixture was poured into ice water. The solution was neutralized by ammonia and pyrolyzed at 90 °C. HMX was washed several times with water and then dried.

The sample was characterized. Melting point: 279–281 °C; FT-IR ( $\nu/\text{cm}^{-1}$ ): 1559.28, 1461.88, 1394.96, 1201.94, 1143.63, 1086.52, 945.72, 760.31 and 599.70;  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ ),  $\delta = 6.02$  (8H, singlet); MS:  $[\text{M}+\text{Cl}]^- \sim 331$ ,  $[\text{M}+\text{HCOO}]^- \sim 341$ ,  $[\text{M}+\text{NO}_3]^- \sim 358$ . Purity: 98.6%.

### 2.3 Calculation methods

The optimized geometries and correlative energies of the reactants (R), transition states (TS), and products (P) were generally calculated at B3LYP/6-31G (d,p) level. The exchange-correlation potential in the B3LYP DFT method was constructed from Becke's three parameter formula (B3) for exchange<sup>[13]</sup> along with the Lee-Yang-Parr parameterization for correlation (LYP)<sup>[14]</sup>. 6-31G (d,p) was a split-valence double-zeta plus polarization basis set<sup>[15]</sup>. The structures and imaginary frequencies of transition states were confirmed by the calculation of both vibration analysis and the intrinsic reaction coordinate (IRC)<sup>[16–17]</sup> at the same level. All compounds had true minima on their potential energy surface without imaginary frequency and the transition state had only one imaginary frequency. All calculations were performed on a Lenovo T350 server with two Intel Xeron 5620 processors using the Gaussian 09 software package<sup>[18]</sup> in our laboratory.

## 3 Results and discussions

### 3.1 The nitrolysis of DPT via nitric acid-ammonium salt

The presence of  $\text{NH}_4\text{NO}_3$  served to hinder esterification and promote demethylation on **A** (Scheme 1), a key intermediate in the nitrolysis of DPT<sup>[9]</sup>, and the role of  $\text{NO}_3^-$  in improving the yield of HMX had been studied<sup>[4]</sup>. However, the role of  $\text{NH}_4^+$  had not been researched. In this section, various ammonium salts were used to investigate the role of  $\text{NH}_4^+$ . The nitrolysis of DPT was performed in nitric acid-ammonium salt including  $[(\text{NH}_4)_2\text{HPO}_4, (\text{NH}_4)_2\text{SO}_4$  and  $\text{CH}_3\text{COONH}_4]$  systems. The experiment was optimized furtherly by varying the concentration of  $\text{NH}_4^+$ , and repeated three times in one concentration. The results, compared to the yield via  $\text{HNO}_3\text{-NH}_4\text{NO}_3$  or pure nitric acid, were shown in Fig. 1.

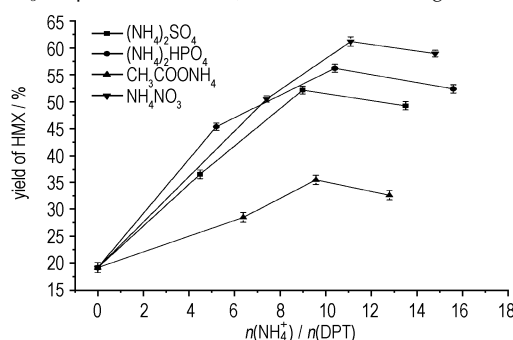


Fig. 1 The yield of HMX varying with  $n(\text{NH}_4^+)/n(\text{DPT})$

As shown in Fig. 1, the yield of HMX in pure nitric acid is 19.2%. By addition of the ammonium salt, the yield of HMX would be improved greatly. The highest yield of each lab group is 56.3%  $[(\text{NH}_4)_2\text{HPO}_4]$ , 52.2%  $[(\text{NH}_4)_2\text{SO}_4]$  and 35.5%  $(\text{CH}_3\text{COONH}_4)$ , respectively. Result shows the effect of  $(\text{NH}_4)_2\text{HPO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  are very significant, because their highest yields are close to that in  $\text{HNO}_3\text{-NH}_4\text{NO}_3$  (61.2%). And if the hygroscopicity of  $\text{CH}_3\text{COONH}_4$  decreases, the yield may much likely to be improved in  $\text{HNO}_3\text{-CH}_3\text{COONH}_4$ . To exclude from interference of  $\text{HPO}_4^{2-}$  and  $\text{SO}_4^{2-}$ , nitrolysis of DPT was done in  $\text{HNO}_3\text{-K}_2\text{HPO}_4$  and  $\text{HNO}_3\text{-K}_2\text{SO}_4$  systems separately. And  $\text{K}^+$  was considered to be no effect on improving the yield of HMX<sup>[4,9]</sup>. As expected, the yields of HMX are 28.3% ( $\text{K}_2\text{HPO}_4$ ) and 25.6% ( $\text{K}_2\text{SO}_4$ ), which are all much lower than those in  $\text{HNO}_3\text{-}(\text{NH}_4)_2\text{HPO}_4$  and  $\text{HNO}_3\text{-}(\text{NH}_4)_2\text{SO}_4$  systems. So it's believed that  $\text{NH}_4^+$  of the added ammonium salt greatly improves the yield of HMX. Moreover, Fig. 1 shows the yields of HMX in the four nitric acid-ammonium salt systems increase at the beginning and then decline with the increase of the molar ratio of  $\text{NH}_4^+$  and DPT. And the values of  $n(\text{NH}_4^+)/n(\text{DPT})$  at the highest yield of HMX are approximately the same as about 10 (9.6, 9.0, 10.4 and 11.1, respectively). Result is meaningful and further studies should be carried out to explore the underlying reasons.

### 3.2 Comparison of the role of $\text{NH}_4^+$ and $\text{NO}_3^-$ in DPT nitrolysis

Chen Li et al<sup>[4]</sup> had proven that the common ion effect of

$\text{NO}_3^-$  played a role in improving the yield of HMX. And at the previous section, the result also indicated that  $\text{NH}_4^+$  could improve the yield. So it is absolutely necessary to compare the affection of  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , and this is significative for further studying the effect mechanism of  $\text{NH}_4\text{NO}_3$ . In this section, the nitrolysis experiment of DPT was performed in various nitric acid-nitrate systems [including  $\text{KNO}_3$ ,  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Mg}(\text{NO}_3)_2$  and  $\text{Zn}(\text{NO}_3)_2$ ]. And the highest yield of each lab group was achieved by optimizing the preparation process. The comparison result between nitric acid-ammonium salt systems and nitric acid-nitrate systems was shown in Fig. 2.

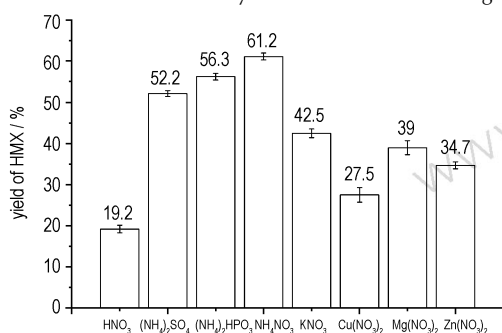


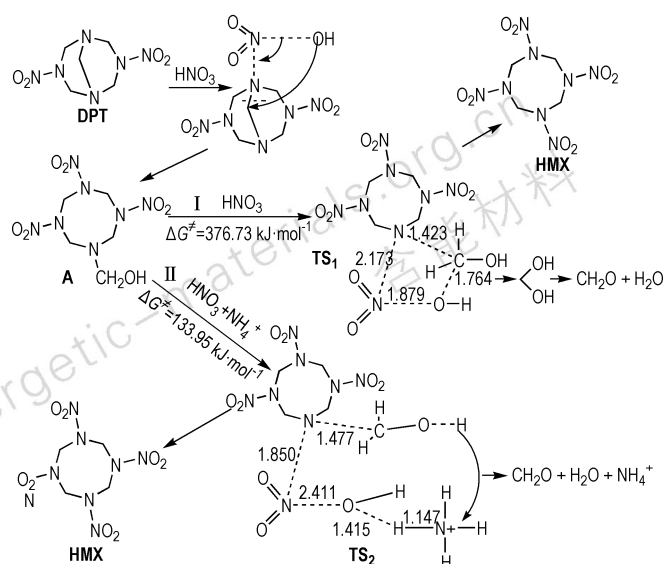
Fig. 2 Comparison of the role of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in nitrolysis of DPT

As shown in Fig. 2, the highest yield of HMX in various nitric acid-nitrate systems was 42.5% ( $\text{KNO}_3$ ), 27.5% [ $\text{Cu}(\text{NO}_3)_2$ ], 39.0% [ $\text{Mg}(\text{NO}_3)_2$ ] and 34.7% [ $\text{Zn}(\text{NO}_3)_2$ ], respectively, and little higher than that (19.2%) in pure nitric. But comparing to the highest yield (56.3% and 52.2%) in  $\text{HNO}_3$ - $\text{K}_2\text{HPO}_4$  and  $\text{HNO}_3$ - $\text{K}_2\text{SO}_4$ , there are obvious disparities. So the comparison shows the affection of  $\text{NH}_4^+$  in improving the yield of HMX is far higher than  $\text{NO}_3^-$ . According to the results above, it can be believed that the role of  $\text{NH}_4^+$  in  $\text{NH}_4\text{NO}_3$  was absolutely dominant.

### 3.3 Mechanism of $\text{NH}_4^+$ in the nitrolysis of DPT

The dominant role of  $\text{NH}_4^+$  in promoting the nitrolysis of DPT had been proved. Si et al.<sup>[19]</sup> studied theoretically the mechanism of  $\text{NH}_4^+$  catalysis in the nitrolysis of amides and also believed it could promote nitrolysis. Because of the inherent limits of quantum chemistry in the studies of the theoretical possibility of a reaction and its mechanism, recently, the density functional theory (DFT) based on the first principle had been increasingly used in the studies of molecular geometry, total energy, vibrational frequency and organic reaction mechanism<sup>[11-12]</sup>. So the mechanism of  $\text{NH}_4^+$  in hindering esterification and promoting demethylation on 1-hydroxymethyl-1,3,5,7-trinitro-1,3,5,7-tetraazabicyclo-octane (A) would be verified further by DFT in this section.

According to the proposed mechanisms, the transition state without  $\text{NH}_4^+$  ( $\text{TS}_1$ ) was designed to N—C—O—N tetraatomic ring geometry and the transition state with  $\text{NH}_4^+$  ( $\text{TS}_2$ ) was designed to N—C—O—H—N—O octatomic ring geometry (Scheme 2). The key bond lengths of transition states, activation energy barriers and potential energy profiles of reverse channels were all shown in Scheme 2. And the results were originally from IRC at B3LYP/6-31G\*\* level.



Scheme 2 The possible mechanisms for DPT nitrolysis in the absence or presence of  $\text{NH}_4^+$  (The A,  $\text{TS}_1$  and  $\text{TS}_2$  represent intermediate and transition states respectively. I and II represent the channels.)

As shown in Scheme 2, firstly, the amino nitrogen of  $-(\text{CH}_2)_3\text{N}$  group in DPT is attacked by nitric acid molecule and  $\text{CH}_2-\text{N}$  of the bridge methylene is broken to produce  $-(\text{CH}_2)_2\text{N}-\text{NO}_2$  and  $\text{CH}_2-\text{OH}$ . Then, 1-hydroxymethyl-1,3,5,7-trinitro-1,3,5,7-tetraazabicyclo-octane (A) is nitrated in two kind nitrolysis systems of  $\text{HNO}_3$  (channel I) and  $\text{HNO}_3/\text{NH}_4^+$  (channel II). In channel I, the nitrogen atoms of  $-\text{N}-\text{CH}_2\text{OH}$  is attacked directly by nitric acid molecule. And methanediol [ $\text{CH}_2(\text{OH})_2$ ] is produced and lost from hydroxymethyl and hydroxy of nitric acid, thus HMX is produced. Then methanediol is decomposed into formaldehyde and water. In channel II,  $\text{NH}_4^+$  is added into nitration solution, where  $\text{NH}_4^+$  would interact with nitric acid and hydroxymethyl.  $\text{H}_2\text{O}$  is lost from hydroxyl of nitric acid and hydrogen of  $\text{NH}_4^+$ . The hydroxymethyl ( $-\text{CH}_2\text{OH}$ ) is replaced by  $-\text{NO}_2$  of nitric acid. Then the proton of hydroxyl ( $-\text{OH}$ ) is transferred from hydroxymethyl to  $\text{NH}_4^+$  and formaldehyde is formed. In channel II, due to the effect of  $\text{NH}_4^+$  with nitric acid and hydroxymethyl, the bond length of N—OH is extended to 2.411 Å from 1.879 Å (without  $\text{NH}_4^+$ ). Therefore, it is easy for water molecule to split. Similarly, the bond length of N— $\text{CH}_2\text{OH}$  is extended to 1.477 Å from 1.423 Å (without  $\text{NH}_4^+$ ), which facilitates the removal of formaldehyde. Simultaneously,  $\text{NH}_4^+$ , from which a hydrogen atom is involved in generating water, attracts the proton of hydroxymethyl and thus hinders hydroxymethyl esterification with nitric acid.

Through the interaction of  $\text{NH}_4^+$  with hydroxymethyl and nitric acid, activation energy barrier of DPT nitrolysis in channel II decreases to 133.95  $\text{kJ} \cdot \text{mol}^{-1}$  from 376.73  $\text{kJ} \cdot \text{mol}^{-1}$  in the channel I.

## 4 Conclusions

(1) Similar to  $\text{NH}_4\text{NO}_3$ , ammonium salts can also improve the yield of HMX. And the yield of HMX synthesized in  $\text{HNO}_3$ - $(\text{NH}_4)_2\text{HPO}_4$  is the highest (56.3%), which is close to that in  $\text{HNO}_3$ - $\text{NH}_4\text{NO}_3$ . In different nitric acid-ammonium

salt systems, the molar ration of  $\text{NH}_4^+$  and DPT at the highest yield of HMX are very similar (about 10).

(2) The yield of HMX in nitric acid-ammonium salt is far higher than that in nitric acid-nitrate. It can be believed that  $\text{NH}_4^+$  of  $\text{NH}_4\text{NO}_3$  plays a dominant role in the nitrolysis of DPT to improving the yield of HMX.

(3)  $\text{NH}_4^+$  can act on 1-hydroxymethyl-3,5,7-trinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane (A, the key intermediate in DPT nitrolysis) and nitric acid, so as to hinder hydroxymethyl ( $\text{CH}_2\text{OH}$ ) esterification and promote the nitrification. The activation energy of DPT nitrolysis in  $\text{HNO}_3/\text{NH}_4^+$  is  $133.95 \text{ kJ} \cdot \text{mol}^{-1}$ , which is much lower than the  $376.73 \text{ kJ} \cdot \text{mol}^{-1}$  in  $\text{HNO}_3$ .

## References

- [1] Bachmann W E, Sheehan J C. A new method of preparing the high explosive RDX[J]. *Journal of the American Chemical Society*, 1949, 71(5): 1842-1845.
- [2] Radhakrishnan S, Talawar M B, Venugopalan S, et al. Synthesis, characterization and thermolysis studies on 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane (DPT): A key precursor in the synthesis of most powerful benchmark energetic materials (RDX/HMX) of today [J]. *Journal of hazardous materials*, 2008, 152(3): 1317-1324.
- [3] SONG Hong-yan, WANG Peng, QIN Guang-ming, et al. Reaction mechanism of one-pot synthesis of dinitro pentamethylene tetramine[J]. *Chinese Journal of Organic Chemistry*, 2010 (3): 414-418.
- [4] CHEN Li, CHEN Ze-min, CHEN Xin-hu. The exploration of DPT nitrolysis in nitrate - nitrate system[J]. *Chinese Journal of Explosives & Propellants*, 1986 (3): 1-5.
- [5] CHEN Li, FANG Zhi-jie, CHEN Zhe-min. The exploration of DPT nitrolysis kinetics in nitric acid - ammonium nitrate system[J]. *Chinese Journal of Explosives & Propellants*, 1987 (3): 1-6.
- [6] LI Quan-liang, CHEN Jun, WANG Jian-long. Synthesis craft of HMX from 1,5-Meth-ylene-3,7-dinitro-1,3,5,7-tetraazabicyclooctane[J]. *Chinese Journal of Energetic Materials (Hanneng Cailiao)*, 2007, 15(5): 509-510.
- [7] HE Zhi-yong, LUO Jun, Lü Chun-xu, et al. Mechanisms and by-products of nitrolysis of 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane[J]. *Chinese Journal of Energetic Materials*, 2012, 20(1): 5-8.
- [8] HE Zhi-yong, LUO Jun, Lü Chun-xu, et al. Synthesis of HMX from DPT by green nitrolysis with dinitrogen pentoxide[J]. *Chinese Journal of Explosives & Propellants*, 2010 (2): 1-4.
- [9] Mckay A F, Richmond H H, Wright G F. Nitrolysis of hexamethylenetetramine. II. nitrolysis of 1,5-endomethylene-3,7-dinitro-1,3,5,7-tetraazabicyclooctane (DPT) [J]. *Canada Journal of Research*, 1949, 27(B): 23-27.
- [10] Bachmann W E, Horton W J, Jenner E L, et al. Cyclic and linear nitramines formed by nitrolysis of hexamine[J]. *Journal of the American Chemical Society*, 1951, 73(6): 2769-2773.
- [11] Yu T, Chang H B, Lai W P, et al. Computational study of esterification between succinic acid and ethylene glycol in the absence of foreign catalyst and solvent[J]. *Polymer Chemistry*, 2011, 2(4): 892-896.
- [12] Klapötke T M, Krumm B, Scherr M, et al. Experimental and theoretical studies on some energetic functionalized trimethylamine derivatives[J]. *Chemistry-A European Journal*, 2009, 15(42): 11341-11345.
- [13] Becke A D. Density-functional thermochemistry. III. The role of exact exchange[J]. *The Journal of Chemical Physics*, 1993, 98: 5648-5652.
- [14] Lee C, Yang W, Parr R G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density [J]. *Physical Review B*, 1988, 37(2): 785-789.
- [15] Hehre W J, Radom L, Schleyer P. *Ab Initio Molecular Orbital Theory*[M]. New York: Wiley, 1986.
- [16] Gonzalez C, Schlegel H B. An improved algorithm for reaction path following[J]. *The Journal of Chemical Physics*, 1989, 90: 2154.
- [17] Gonzalez C, Schlegel H B. Improved algorithms for reaction path following: Higher-order implicit algorithms[J]. *The Journal of Chemical Physics*, 1991, 95(8): 5853-5860.
- [18] Frisch M J, Trucks G W, Schlegel H B, et al. Gaussian 09, Revision A. 02, Gaussian[CP]. Inc., Wallingford, CT.
- [19] Si Zhenmei. Study on the hydrolysis-nitration mechanism of amide compounds [D]. Beijing: Beijing Institute of Technology, 2011.

## 铵离子对 3,7-二硝基-1,3,5,7-四氮杂双环[3.3.1]壬烷(DPT)硝解反应影响

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**摘要:** 基于 3,7-二硝基-1,3,5,7-四氮杂双环[3.3.1]壬烷(DPT)在  $\text{HNO}_3\text{-NH}_4\text{NO}_3$  及  $\text{HNO}_3$  中两种硝解机理, 分别通过实验和理论计算方法对  $\text{NH}_4^+$  在 DPT 硝解反应中的作用进行了研究。将三种不同的铵盐 ( $\text{NH}_4$ )<sub>2</sub>HPO<sub>4</sub>, ( $\text{NH}_4$ )<sub>2</sub>SO<sub>4</sub> 和  $\text{CH}_3\text{COONH}_4$  添加到硝解体系中, 考察了  $\text{NH}_4^+$  对 HMX 产率的影响。结果表明, 与  $\text{NH}_4\text{NO}_3$  的作用相似, 以上三种铵盐可提高 HMX 产率, 提高率分别为 41.5%、37.4% 和 20.7%。在不同的  $\text{HNO}_3$ -铵盐体系中, 当  $\text{NH}_4^+$  与 DPT 的摩尔比接近 10 时, HMX 的产率均达到最大值, 分别为 56.3%、52.2% 和 35.5%。对比了  $\text{HNO}_3$ -铵盐和  $\text{HNO}_3$ -硝酸盐体系中 DPT 硝解反应的结果, 发现  $\text{NH}_4^+$  对 HMX 产率的提高起主导作用。采用密度泛函理论(DFT)对  $\text{NH}_4^+$  在 DPT 硝解反应过程中的作用机理进行了理论解释, 得出  $\text{HNO}_3/\text{NH}_4^+$  体系中 DPT 硝解反应的活化能为  $133.95 \text{ kJ} \cdot \text{mol}^{-1}$ , 低于  $\text{HNO}_3$  体系中的  $376.73 \text{ kJ} \cdot \text{mol}^{-1}$ 。

**关键词:** 1,3,5,7-四硝基-1,3,5,7-四氮杂环辛烷; 3,7-二硝基-1,3,5,7-四氮杂双环[3.3.1]壬烷(DPT); 硝酸铵; 硝化; 密度泛函理论(DFT); 反应机理

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