

doi:10.3969/j.issn.1001-8352.2019.01.001

# 三硝基乙醇及其脂肪族衍生物研究进展\*

高福磊 汪营磊 陆婷婷 刘亚静 潘永飞 闫峥峰

西安近代化学研究所(陕西西安,710065)

**[摘 要]** 三硝基乙醇及其脂肪族衍生物具有含氧量高、密度高等优点,是一类重要的含能材料。综述了三硝基乙醇及其脂肪族衍生物等 30 余种三硝基乙基类含能化合物的最新研究成果,重点阐述了三硝基乙醇及其脂肪族衍生物的合成、性能及应用研究进展;并结合三硝基乙基类含能化合物的性能特点,进一步探讨了在炸药、固体推进剂等含能材料领域中的应用前景。

**[关键词]** 物理化学;三硝基乙基类含能化合物;合成;性能

**[分类号]** TQ560; O62

## Research Progress of 2,2,2-Trinitroethanol and Its Aliphatic Derivatives

GAO Fulei, WANG Yinglei, LU Tingting, LIU Yajing, PAN Yongfei, YAN Zhengfeng

Xi'an Modern Chemistry Research Institute (Shaanxi Xi'an, 710065)

**[ABSTRACT]** 2,2,2-Trinitroethanol-based energetic material with high oxygen content and high density is an important category of energetic materials. The latest research advances in 2,2,2-Trinitroethanol (TNE) and its aliphatic derivatives were briefly reviewed, especially including synthesis, performance and application investigation of TNE-based energetic materials. Application prospects of TNE and its derivatives in insensitive high energy explosives and propellants were further investigated.

**[KEYWORDS]** physical chemistry; trinitroethanol-based energetic materials; preparation; property

## 引言

三硝基乙基类含能化合物因其结构中存在硝仿基而具有含氧量高、密度高等特点<sup>[1-4]</sup>,成为高能量密度材料的研究热点之一,对它在高能炸药、低特征信号推进剂等方面进行的研究引起了国内外学者的广泛关注。三硝基乙醇是一种多硝基化合物,将其引入到氮杂环中,可以大幅提高其密度和能量,更能改善其氧平衡,提高其燃烧热,得到高能量密度、高氧平衡的三硝基乙基三唑、四唑、四嗪、呋咱等氮杂环含能化合物<sup>[3-14]</sup>。另外,由于三硝基甲基的吸电子作用使羟基中氧原子的碱性降低,转变为酸性( $pK_a = 6.1$ )<sup>[15]</sup>,易与氨基、氯原子等基团发生亲核取代反应,从而构筑一系列结构新颖、含氧量高、爆轰性能优异的三硝基乙基脂肪族含能化合物<sup>[16-23]</sup>,可作为无卤高能氧化剂、高能量密度材料,在高能炸

药、低特征信号推进剂等领域都具有巨大的应用潜力<sup>[24-26]</sup>。

本文中,综述了三硝基乙醇及其脂肪族衍生物的制备方法、理化性能及应用,分析了该类化合物的优势与不足,以期该类化合物的研究和发展提供参考。

## 1 TNE 合成

三硝基乙醇(2,2,2-trinitroethanol,简称 TNE),也称 2,2,2-三硝基乙醇,是一种白色固体,密度为  $1.839\text{ g/cm}^3$ ,氧含量(质量分数)高达 61.86%,易溶于水、乙醇、乙醚、二氯甲烷、N,N-二甲基甲酰胺、二甲亚砜等<sup>[15-16,27]</sup>,其分子结构见图 1。

TNE 的合成,通常以硝仿、多聚甲醛或甲醛水溶液为原料,经 Henry 反应得到目标化合物<sup>[28-29]</sup>,反应式见图 2。

\* 收稿日期:2018-05-06

第一作者:高福磊(1985-),男,硕士,主要从事含能材料合成研究。E-mail: gfl198510@163.com

通信作者:汪营磊(1983-),男,博士,主要从事含能材料合成及性能研究。E-mail: wyl-204@163.com

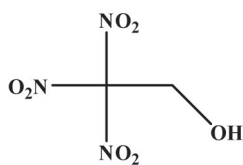


图 1 TNE 分子结构  
Fig. 1 Molecular structure of TNE

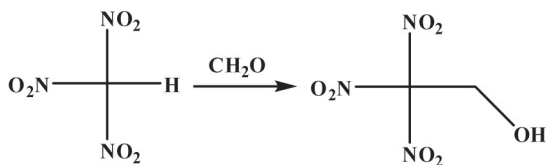


图 2 TNE 的合成路径  
Fig. 2 Synthetic path of TNE

20 世纪 50 年代,Marans 等<sup>[27]</sup>首次报道了以硝仿和多聚甲醛为原料合成 TNE,反应 12 h,倒入水中,煮沸,蒸馏,乙醚萃取,蒸除溶剂,得到 TNE,收率为 41%。但是,此法反应时间长、收率低、纯度低。

Hartman<sup>[30]</sup>对上述方法进行了改进,考察了不同反应溶剂(正己烷、甲苯、苯、四氯化碳)和反应物料比等对收率的影响,最佳工艺为:以正己烷为反应溶剂,回流反应 3 h,并用正己烷重结晶以提高产品的纯度,反应收率提高至 78%。

Epishina 等<sup>[31]</sup>以硝仿和多聚甲醛为原料,采用咪唑离子液体作为反应溶剂和催化剂,在常温条件下即可反应得到 TNE,将收率提高至 94%,且离子液体可以重复利用。

Kon'kova 等<sup>[32]</sup>对 TNE 的性能和结构进行了研究。从表 1 中可以看出,TNE 的密度(1.839 g/cm<sup>3</sup>)高于硝仿(NF)的密度(1.469 g/cm<sup>3</sup>)<sup>[32-39]</sup>,氧平衡较高(+13.3%);但是,其热分解温度较低,需要对其结构进行改进,引入杂环或氨基或氧原子,增加结构中氢键的数量,以提高热稳定性<sup>[40-43]</sup>,并降低敏感度。晶体结构分析表明:TNE 的晶体间群为正交晶系,晶胞参数: $a = 6.124\ 2\ \text{\AA}$ , $b = 18.822\ 3\ \text{\AA}$ , $c = 11.746\ 6\ \text{\AA}$ , $z = 8$ ,晶胞密度为 1.839 g/cm<sup>3</sup>,晶体结构中存在分子内的氢键 O—H $\cdots$ O,以及分子间的氢键 O—H $\cdots$ O 和 C—H $\cdots$ O。

2 三硝基乙基脂肪族化合物

Klapötke 团队<sup>[44-48]</sup>对 TNE 与—Cl 反应进行了系统的研究,将 TNE 分别与四氯化碳、氯仿、草酰氯等反应,制备得到了一系列氧平衡较高的 TNE 衍生物(1~4),以期获得可替代高氯酸铵(AP)的无卤氧化剂,反应路线如图 3 所示。其中,化合物(2)的密度为 1.897 g/cm<sup>3</sup>,氧平衡为 +10.1%,而且钝感。

表 1 TNE 与 NF 的物理化学性能<sup>[27,32-39]</sup>  
Tab. 1 Physical and chemical properties of TNE and NF<sup>[27,32-39]</sup>

化合物	密度/ (g · cm <sup>-3</sup> )	分解温度/ ℃	氧平衡/ %	生成焓/ (kJ · mol <sup>-1</sup> )	爆压/ GPa	爆速/ (m · s <sup>-1</sup> )	产气量/ (L · kg <sup>-1</sup> )
TNE	1.839	140	+13.3	-196.78	28.5	8 180	712
NF	1.469	80	+37.1	-48.50			

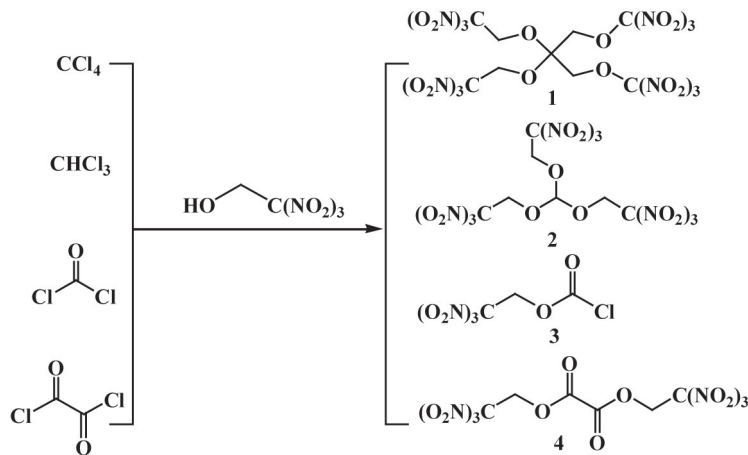


图 3 TNE 衍生物的合成  
Fig. 3 Synthesis of TNE derivatives

化合物(3)可作为中间体,直接叠氮化得到化合物(5);可氨化、硝化得到硝胺化合物(7);也可与肼进行取代反应得到化合物(8)。化合物(6)熔点为 91 ℃,分解温度为 169 ℃,燃烧时少烟,无残渣,且感度较低;化合物(7)的密度为 1.730 g/cm<sup>3</sup>,氧平衡为 +14.9%,分解温度为 153 ℃,感度与 RDX 相当,见图 4。

而化合物(9)与化合物(3)结构类似,可与 TNE 反应,得到化合物(10),该化合物理论单元比冲为 258 s,与 AP 相当<sup>[49]</sup>。见图 5。

并将 2-氟-2,2-二硝基乙基胺与 TNE 进行亲核取代,得到(2-氟-2,2-二硝基乙基)-2,2,2-三硝基乙基硝胺<sup>[50]</sup>,反应路线如图 6。该化合物密度为 1.95 g/cm<sup>3</sup>,氧平衡为 +11.1%,可作为 AP 替代物候选。

Stepanov 等<sup>[51]</sup>以硝基肌氨酸为原料,制备得到了一系列 TNE 的衍生物(13~16),反应路线如图 7。该类化合物密度偏低,均小于 1.72 g/cm<sup>3</sup>,爆速为 6 961~8 415 m/s。

文献[52-54]报道了以L-天冬氨酸和β-丙氨酸为原料合成一系列TNE的氧化剂,以期代替固体推进剂中的 AP。如图 8 所示。对化合物(17~25)的

热性能和感度研究显示,热分解温度均高于 150 ℃,除化合物(18)的分解温度为 65 ℃,摩擦感度和撞击感度均较钝感;化合物(21)的爆速达 9 083 m/s,爆压达到 36.5 GPa。

### 3 TNE 脂肪族类衍生物基础性能及应用前景

#### 3.1 基础性能

如表 2 所示,化合物(1、2、7)的氧平衡较高,均大于 +10%,作为无卤氧化剂具有广阔的应用前景。

#### 3.2 应用探索

为了进一步探究 TNE 衍生物作为氧化剂的应用前景,Axthammer 等<sup>[44]</sup>利用 EXPLO5 V5.05 程序评估了化合物(6、7)与铝粉混合后的比冲,结果如表 3 所示。

从表 3 中可以看出,化合物(6、7)的单元比冲高于 AP,化合物(6)与 20% (质量分数)铝粉混合后的比冲达 249 s,化合物(7)应用于基础配方中的比冲与 AP 相当。

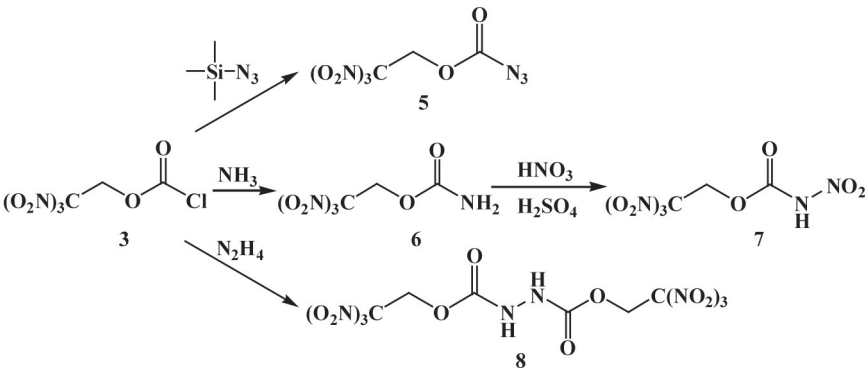


图 4 化合物(3)的反应  
Fig.4 Reaction of Compound (3)

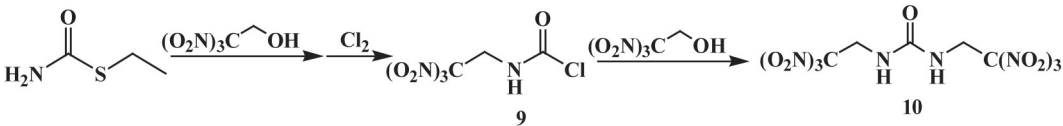


图 5 TNE 与化合物(9)的反应  
Fig.5 Reaction of TNE and Compound (9)

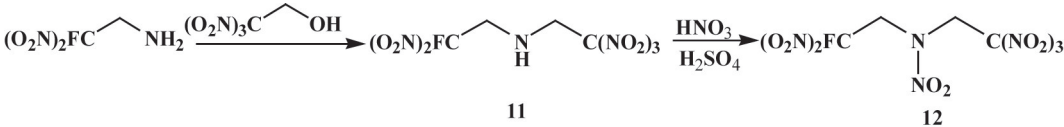


图 6 TNE 与 2-氟-2,2-二硝基乙基胺的反应  
Fig.6 Reaction of TNE and 2-fluorine-2,2-dinitroethylamine

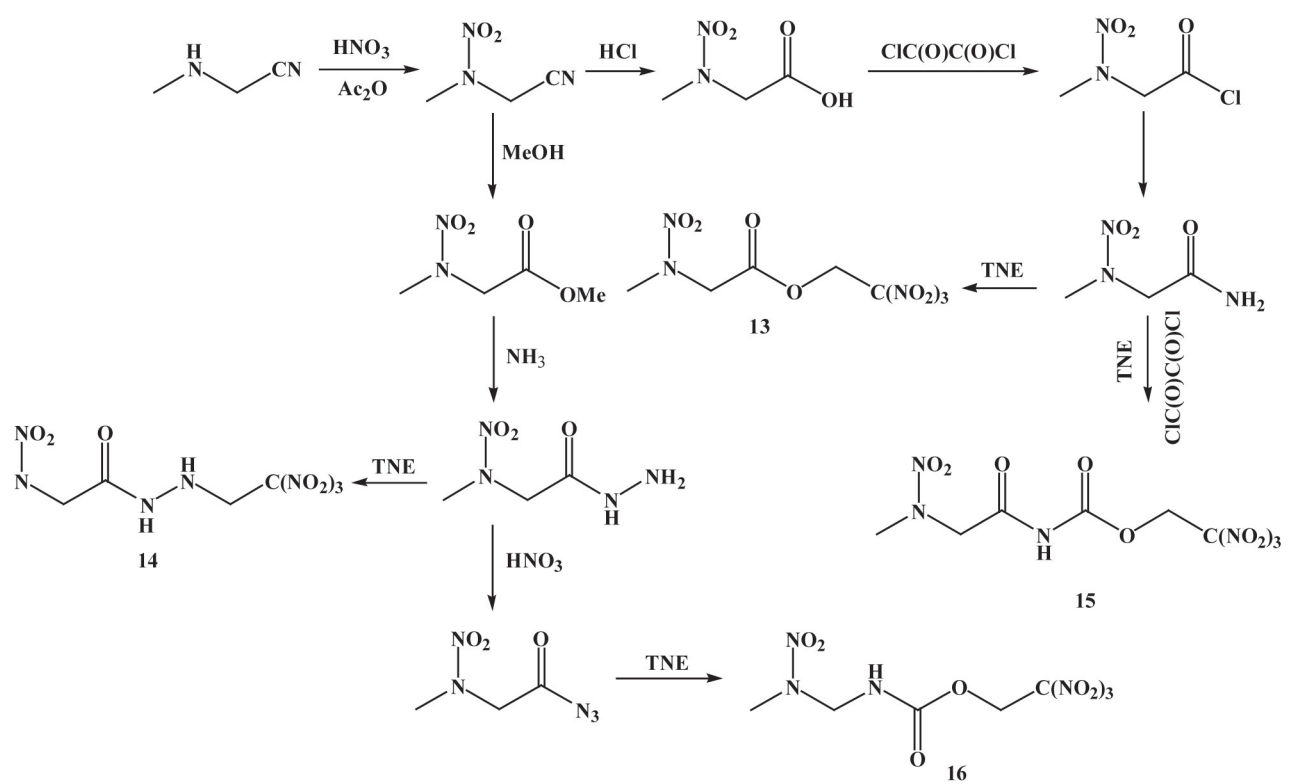


图 7 由硝基肌氨酸制备 TNE 衍生物  
Fig. 7 TNE derivatives prepared by NSAR

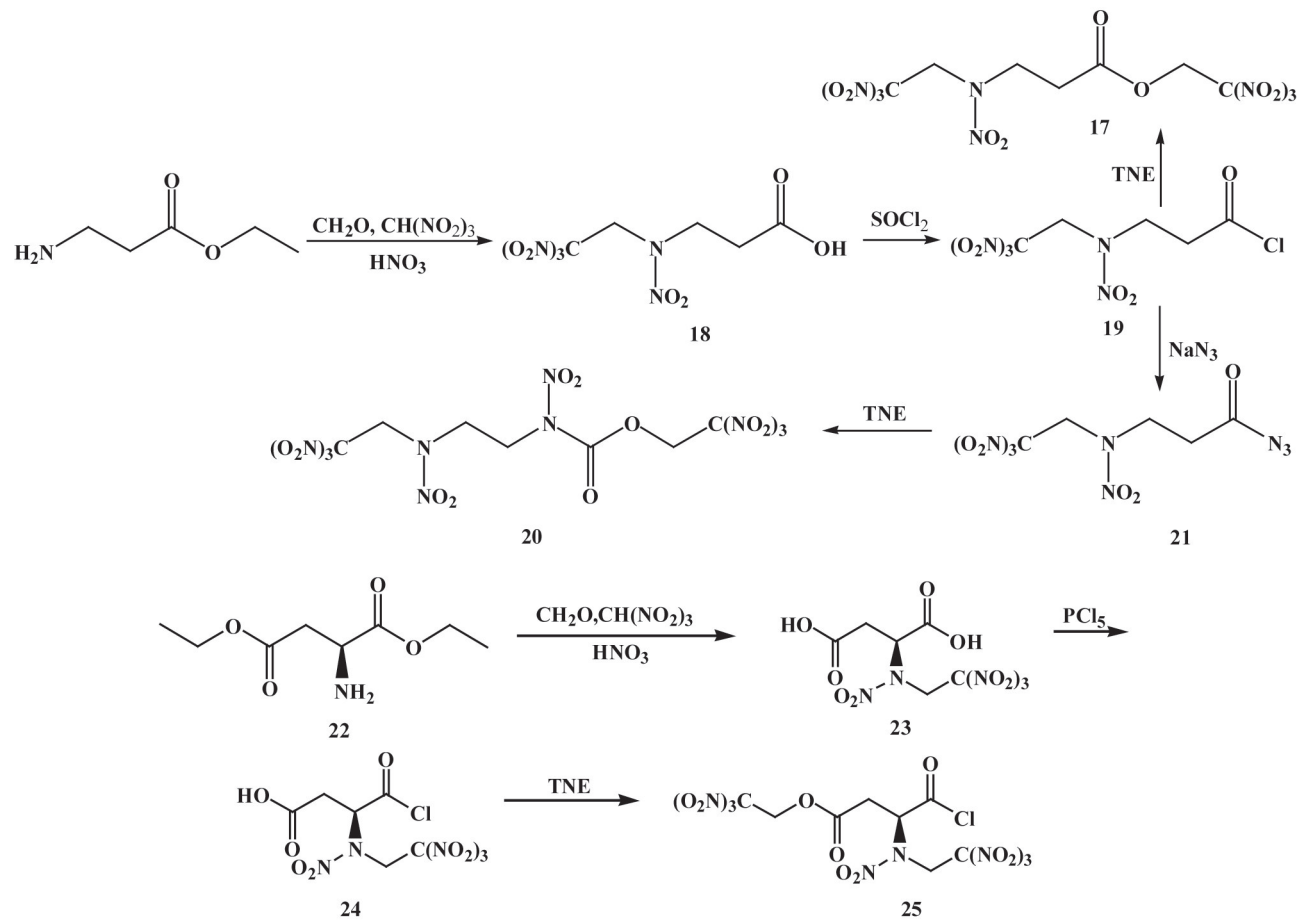


图 8 由  $\beta$ -丙氨酸、L-天冬氨酸制备 TNE 衍生物  
Fig. 8 Preparation of TNE oxidizer by  $\beta$ -alanine and L-ASP

表 2 TNE 脂肪族类衍生物的物理化学性能  
Tab. 2 Physical and chemical properties of TNE aliphatic derivatives

化合物	分子式	氧平衡/%	分解温度/℃	密度/(g·cm <sup>-3</sup> )	爆压/GPa	爆速/(m·s <sup>-1</sup> )
1	C <sub>9</sub> H <sub>8</sub> N <sub>12</sub> O <sub>28</sub>	+13.1	191.0	1.810	31.6	8 419
2	C <sub>7</sub> H <sub>7</sub> N <sub>9</sub> O <sub>21</sub>	+10.1	192.0	1.897	28.4	8 147
4	C <sub>6</sub> H <sub>4</sub> N <sub>6</sub> O <sub>16</sub>	+7.7	162.0	1.840	29.4	8 325
5	C <sub>3</sub> H <sub>2</sub> N <sub>6</sub> O <sub>8</sub>	+6.4	130.4	1.853	30.3	8 359
6	C <sub>3</sub> H <sub>4</sub> N <sub>4</sub> O <sub>8</sub>	0	169.0	1.840	30.9	8 224
7	C <sub>3</sub> H <sub>3</sub> N <sub>5</sub> O <sub>10</sub>	+14.9	153.0	1.730	24.2	7 541
8	C <sub>6</sub> H <sub>6</sub> N <sub>8</sub> O <sub>16</sub>	+3.6	188.3	1.800	28.4	8 188
12	C <sub>4</sub> H <sub>4</sub> FN <sub>7</sub> O <sub>12</sub>	+11.1	162.0	1.950	35.4	8 637
13	C <sub>5</sub> H <sub>7</sub> N <sub>5</sub> O <sub>10</sub>	-8.1	178.0	1.480	20.5	7 286
14	C <sub>5</sub> H <sub>9</sub> N <sub>7</sub> O <sub>9</sub>	-28.3	108.0	1.720	30.5	8 415
15	C <sub>6</sub> H <sub>8</sub> N <sub>6</sub> O <sub>11</sub>	-23.5	150.0	1.710	20.1	7 226
17	C <sub>7</sub> H <sub>8</sub> N <sub>8</sub> O <sub>16</sub>	-7.0	164.0	1.730	29.2	8 300
18	C <sub>5</sub> H <sub>7</sub> N <sub>5</sub> O <sub>10</sub>	-18.8	65.0	1.720	27.7	7 987
21	C <sub>7</sub> H <sub>8</sub> N <sub>10</sub> O <sub>18</sub>	-19.9	157.0	1.890	36.5	9 083
23	C <sub>6</sub> H <sub>7</sub> N <sub>5</sub> O <sub>12</sub>	-16.4	160.0	1.660	23.4	7 515
24	NH <sub>4</sub> ClO <sub>4</sub>	+34.0	240.0	1.950	15.8	6 368

表 3 TNE 衍生物与铝混合后的比冲预估

Tab.3 Predicted specific impulse *I*<sub>s</sub> of TNE derivatives mixed with aluminum

添加物质(质量分数)	化合物(6)	化合物(7)	<i>I</i> <sub>s</sub> /s
	234	223	153
30% 铝	0	244	243
25% 铝	249	247	242
20% 铝	249	247	232
15% 铝	248	247	234
10% 铝	245	239	181
5% 铝	240	233	178
15% 铝 + 14% 黏合剂	0	257	257
10% 铝 + 14% 黏合剂	0	251	253
5% 铝 + 14% 黏合剂	0	244	247

文献[53-54]将化合物(2、4、7)作为氧化剂应用于改性双基推进剂中,结果表明,含有化合物(2、4、7)的推进剂的分解温度分别为 186、193、196 ℃,比常规双基推进剂的热稳定性高;含化合物(4)的推进剂的燃速较低,且火焰较小;含化合物(7)的推进剂的燃速较高,火焰较大,且比较明亮。

4 结论与展望

综上所述,三硝基乙基脂肪族类化合物具有氧

平衡高、密度高、燃烧气体不含氯化氢、环保性好等特点,在炸药、推进剂等领域的应用已展开,具有代替 AP 应用于含能材料领域的前景。但是,大部分三硝基乙基脂肪族类化合物由于多含有羰基、醚基以及硝仿基等基团,影响化合物的稳定性,存在热分解温度低、热稳定性差的问题,所以多集中在应用探索阶段,尚未在型号产品中得到应用。因此,急需开发出热性能优异的三硝基乙基类含能化合物,全面挖掘其在含能材料领域的应用潜力。

参 考 文 献

[1] GÖBEL M, KLAPÖTKE T M. Development and testing of energetic materials; the concept of high densities based on the trinitroethyl functionality [J]. Advanced Functional Materials, 2009, 19(3): 347-365.

[2] KLAPÖTKE T M, KRUMM B, MOLL R. Polynitroethyl- and fluorodinitroethyl substituted boron esters[J]. Chemistry: A European Journal, 2013, 19 (36): 12113-12123.

[3] KLAPÖTKE T M, KRUMM B, REST S F, et al. Polynitro containing energetic materials based on carbonyl-diisocyanate and 2,2-dinitropropane-1,3-diol[J]. Journal of Inorganic and General Chemistry, 2014, 640(1): 84-92.

[4] KLAPÖTKE T M, PIERCEY D G, STIERSTORFER J. Amination of energetic anions: high-performing energetic

- materials [J]. Dalton Transactions, 2012, 41 (31): 9451-9459.
- [5] GIDASPOV A A, BAKHAREV V V, KUKUSHKIN I K. Trinitromethylation reactions of chloro-1, 3, 5-triazines [J]. Russian Chemical Bulletin, 2009, 58(10): 2154-2163.
- [6] TANG Y X, ZHANG J H, MITCHELL L A, et al. Taming of 3,4-di(nitramino)furan [J]. Journal of the American Chemical Society, 2015, 137(51): 15984-15987.
- [7] HUANG H F, SHI Y M, LIU Y F, et al. High-oxygen-balance furazan anions: a good choice for high-performance energetic salts [J]. Chemistry: An Asian Journal, 2016, 11(11): 1688-1696.
- [8] MATHIEU D. Sensitivity of energetic materials: theoretical relationships to detonation performance and molecular structure [J]. Industrial & Engineering Chemistry Research, 2017, 56(29): 8191-8201.
- [9] STARCHENKOV I B, ANDRIANOV V G, MISHNEV A F. The chemistry of furazano-[3,4-*b*]pyrazine. 7: properties of 5,6-diamino- and 5,6-dihydrazino furazano[3,4-*b*]pyrazine [J]. Chemistry of Heterocyclic Compounds, 1999, 35(4): 499-508.
- [10] STARCHENKOV I B, ANDRIANOV V G, MISHNEV A F. The chemistry of furazano-[3,4-*b*]pyrazine. 1: synthesis and thermodynamic appraisal of 4,8-dihydrodifurazano[3,4-*b*,*e*]pyrazine and its derivatives [J]. Chemistry of Heterocyclic Compounds, 1997, 33(2): 216-228.
- [11] ROMANOVA T V, ZELENOV M P, MEL'NIKOVA S F, et al. Esterification of 1,2,5-oxadiazolylacetic acids with polynitro alcohols [J]. Russian Chemical Bulletin, 2009, 58(10): 2188-2190.
- [12] SHEREMETEV A B, YUDIN I L, SUPONITSKY K Y. Ionic liquid-assisted synthesis of trinitroethyl esters [J]. Mendeleev Communications, 2006, 16(5): 264-266.
- [13] CHAVEZ D E, SCHULZE M C, PARRISH D A. Synthesis and characterization of  $N^3$ -(2,2,2-trinitroethyl)-1,2,4-oxadiazole-3,5-diamine [J]. Chemistry of Heterocyclic Compounds, 2017, 53(6/7): 737-739.
- [14] ZHANG Q H, ZHANG J H, PARRISH D A, et al. Energetic *N*-trinitroethyl-substituted mono-, di-, and triaminotetrazoles [J]. Chemistry: A European Journal, 2013, 19(33): 11000-11006.
- [15] KLAPÖTKE T M, KRUMM B, MOLL R, et al. CHNO based molecules containing 2,2,2-trinitroethoxy moieties as possible high energy dense oxidizers [J]. Journal of Inorganic and General Chemistry, 2011, 637(14/15): 2103-2110.
- [16] KLAPÖTKE T M, LEROUX M, SCHMID P C, et al. Energetic materials based on 5,5'-diamino-4,4'-dinitramino-3,3'-bi-1,2,4-triazole [J]. Chemistry: An Asian Journal, 2016, 11(6): 844-851.
- [17] YIN P, ZHANG J H, PARRISH D A, et al. Energetic *N,N'*-ethylene-bridged bis (nitropyrazoles): diversified functionalities and properties [J]. Chemistry: A European Journal, 2014, 20: 16529-16536.
- [18] LI S H, ZHANG W W, WANG Y, et al. 2,4,6-Tris(2,2,2-trinitroethylamino)-1,3,5-triazine: synthesis, characterization, and energetic properties [J]. Journal of Energetic Materials, 2014, 32(suppl. 1): S33-S40.
- [19] EPISHINA M A, FINOGENOV A O, KULIKOV A S, et al. Synthesis and nitration of 3-R-4-(2,2,2-trinitroethyl) aminofuroxans [J]. Russian Chemical Bulletin, 2012, 61(8): 1575-1581.
- [20] YIN P, ZHANG J H, HE C L, et al. Polynitro-substituted pyrazoles and triazoles as potential energetic materials and oxidizers [J]. Journal of Materials Chemistry A, 2014, 2(9): 3200-3208.
- [21] YU Q, YANG H W, JU X H, et al. The synthesis and study of compounds based on 3,4-bis(aminofurazano)furoxan [J]. Chemistry Select, 2017, 2(2): 688-696.
- [22] THOTTEMPUDI V, ZHANG J H, HE C L, et al. Azo substituted 1,2,4-oxadiazoles as insensitive energetic materials [J]. RSC Advances, 2014, 4: 50361-50364.
- [23] TANG Y X, SHREEVE J M. Nitroxy/azido-functionalized triazoles as potential energetic plasticizers [J]. Chemistry: A European Journal, 2015, 21: 7285-7291.
- [24] ZEMAN S, LIU N, JUNGOVÁ M, et al. Crystal lattice free volume in a study of initiation reactivity of nitramines: impact sensitivity [J]. Defence Technology, 2018, 14(2): 93-98.
- [25] FRANKEL M B. Synthesis and reactions of trinitromethyl compounds [J]. Tetrahedron, 1963, 19 (Suppl. 1): 213-217.
- [26] AXTHAMMER Q J, KRUMM B, KLAPÖTKE T M, et al. Synthesis of energetic nitrocarbamates from polynitro alcohols and their potential as high energetic oxidizers [J]. The Journal of Organic Chemistry, 2015, 80(12): 6329-6335.
- [27] MARANS N S, ZELINSIU R P. 2,2,2-Trinitroethanol: preparation and properties [J]. Journal of the American Chemical Society, 1950, 72(11): 5329-5330.
- [28] 刘利钊. 硝仿及其衍生物的合成及工艺优化 [D]. 南京: 南京理工大学, 2016.
- [29] LIU L Z. Synthesis and process optimization of nitroform and its derivatives [D]. Nanjing: Nanjing University of Science & Technology, 2016.
- [29] FEUER H, KUCERA T. Preparation of 2,2,2-trinitro-



- ethanol [J]. The Journal of Organic Chemistry, 1960, 25(11): 2069-2070.
- [30] HARTMAN P F. Process for production of 2,2,2-trinitroethanol:3041383[P]. 1962-06-26.
- [31] EPISHINA M A, OVCHINNIKOV I V, KULIKOV A S, et al. Henry and Mannich reactions of polynitroalkanes in ionic liquids[J]. Mendeleev Communications, 2011, 21(1): 21-23.
- [32] KONKOVA T S, MATYUSHIN Yu N. Combined study of thermochemical properties of nitroform and its salts [J]. Russian Chemical Bulletin, 1998, 47(12): 2371-2374.
- [33] LU H Y, LI J R, YANG D L, et al. A novel synthesis of nitroform by the nitrolysis of cucurbituril[J]. Chinese Chemical Letters, 2015, 26(3): 365-368.
- [34] NAZIN G N, MANELIS G B, DUBOVITSKII F I. Thermal decomposition of nitroform and related compounds in the gas phase[J]. Bulletin of the Academy of Sciences of the USSR, Division of the Chemical Science, 1969, 18(5): 945-948.
- [35] YAN C, DING P, YANG H W, et al. New synthetic route of nitroform (NF) from acetylacetone and study of the reaction mechanism[J]. Industrial & Engineering Chemistry Research, 2016, 55(41): 11029-11034.
- [36] 刘利钊, 靳昕, 王鹏程, 等. N,N-二(三硝基乙基)硝胺 (BTNNA) 的合成工艺优化及热性能[J]. 爆破器材, 2016, 45(3): 47-50.
- LIU L Z, JIN X, WANG P C, et al. Synthesis improvement and thermal properties of bis(2,2,2-trinitroethyl)-nitramine (BTNNA) [J]. Explosive Materials, 2016, 45(3): 47-50.
- [37] 汪惠英, 文亮, 杨红伟, 等. 硝仿肼的合成工艺与晶体结构[J]. 火炸药学报, 2013, 36(6): 43-46, 59.
- WANG H Y, WEN L, YANG H W, et al. Synthesis technique and crystal structure of HNF [J]. Chinese Journal of Explosives and Propellants, 2013, 36(6): 43-46, 59.
- [38] 毕福强, 王伯周, 许诚, 等. 含能材料中间体硝仿的研究进展[J]. 化学试剂, 2012, 34(3): 219-223, 260.
- BI F Q, WANG B Z, XU C, et al. Progress of nitroform (NF), an important intermediate in the preparation of energetic materials [J]. Chemical Reagents, 2012, 34(3): 219-223, 260.
- [39] MURRAY J S, LANE P, GÖBEL M, et al. Intra- and intermolecular electrostatic interactions and their significance for the structure, acidity, and tautomerization behavior of trinitromethane [J]. The Journal of Chemical Physics, 2009, 130(10): 104304.
- [40] GÖBEL M, KLAPÖTKE T M. 2,2,2-Trinitroethanol [J]. Acta Crystallographica Section C: Structural Chemistry, 2007, 63(9): 0562-0564.
- [41] HU R Z, ZHAO F Q, GAO H X, et al. The thermal safety and a density functional theoretical study on N, N'-bis [N-(2,2,2-trinitroethyl)-N-nitro] ethylenediamine (BTNEDA) [J]. Chinese Journal of Energetic Materials, 2012, 20(5): 505-513.
- 胡荣祖, 赵凤起, 高红旭, 等. N,N'-二[2,2,2-三硝基乙基-N-硝基]乙二胺的热安全性和密度泛函理论研究[J]. 含能材料, 2012, 20(5): 505-513.
- [42] HU R Z, YANG D S, GAO S L, et al. Kinetics and mechanism of the exothermic first-stage decomposition reaction of 1,3-bis(2,2,2-trinitroethyl)-1,3-diazacyclopentanone-2 [J]. Journal of Hazardous Materials, 2003, 102(2/3): 147-153.
- [43] ZHAO H A, HU R Z, YANG D S, et al. Kinetics and mechanism of the exothermic first-stage decomposition reaction for 1,5-dimethyl-2,6-bis(2,2,2-trinitroethyl)-4,8-dinitroglycoluril [J]. Thermochimica Acta, 2004, 416(1/2): 1-4.
- [44] AXTHAMMER Q J, KLAPÖTKE T M, KRUMM B, et al. The energetic nitrocarbamate O<sub>2</sub>NN(H)CO[OCH<sub>2</sub>C(NO<sub>2</sub>)<sub>3</sub>] derived from phosgene [J]. Journal of Inorganic and General Chemistry, 2014, 640(1): 76-83.
- [45] ABD-ELGHANY M, KLAPÖTKE T M, ELBEIH A. Thermal behavior and decomposition kinetics of bis(2,2,2-trinitroethyl)-oxalate as a high energy dense oxidizer and its mixture with nitrocellulose [J]. Propellants, Explosives, Pyrotechnics, 2017, 42(12): 1373-1381.
- [46] GÖBEL M, KLAPÖTKE T M. Exceeding the oxygen content of liquid oxygen: bis(2,2,2-trinitroethyl) carbonate [J]. Acta Crystallographica Section C: Structural Chemistry, 2008, 64(2): 058-060.
- [47] KLAPÖTKE T M, KRUMM B, SCHERR M, et al. Facile synthesis and crystal structure of 1,1,1,3-tetranitro-3-azabutane [J]. Journal of Inorganic and General Chemistry, 2008, 634(8): 1244-1246.
- [48] KLAPÖTKE T M, PIERCEY D G, STIERSTORFER J. Amination of energetic anions: high-performing energetic materials [J]. Dalton Transactions, 2012, 41(31): 9451-9459.
- [49] KLAPÖTKE T M, KRUMM B, SCHARF R. Oxalyl chloride and hydrazide based energetic polynitro derivatives [J]. European Journal of Inorganic Chemistry, 2016, 19: 3086-3093.
- [50] ERMAKOV A S, BULATOV P V, VINOGRADOV D B, et al. Synthesis of new polynitro dicarboxylic acid

- Guidance, 2009, 29(2): 117-119.
- [4] 凌荣辉, 钱立新, 唐平, 等. 聚能型鱼雷战斗部对潜艇目标毁伤研究[J]. 弹道学报, 2001, 13(2): 23-27.
- LING R H, QIAN L X, TANG P, et al. Target damage study of shaped-charge warhead of antisubmarine torpedo[J]. Journal of Ballistics, 2001, 13(2): 23-27.
- [5] 罗健. 串联聚能装药在水下弹药中的应用[J]. 弹箭技术, 1996(4): 38-44.
- [6] 步相东, 王团盟. 鱼雷聚能战斗部自锻弹丸水中运动特性仿真研究[J]. 鱼雷技术, 2006, 14(3): 44-47.
- BU X D, WANG T M. Simulation study on kinematic characteristic of explosively formed projectile (EFP) in the water for torpedo shaped charge warhead[J]. Torpedo Technology, 2006, 14(3): 44-47.
- [7] 程素秋, 陈高杰, 赵红光. 聚能战斗部对双层靶板结构毁伤的数值模拟研究[J]. 中国舰船研究, 2013, 8(2): 53-57.
- CHENG S Q, CHEN G J, ZHAO H G. Numerical damage analysis of shaped charge warheads on double-deck target plates[J]. Chinese Journal of Ship Research, 2013, 8(2): 53-57.
- [8] 李向东, 钱建平, 曹兵, 等. 弹药概论[M]. 北京: 国防工业出版社, 2005.
- [9] 杨世昌. EFP 侵彻水介质靶板机理仿真研究[D]. 南京: 南京理工大学, 2009.
- [10] 陈冬梅, 陈智刚, 侯秀成, 等. 三类聚能侵彻体鱼雷战斗部对目标毁伤数值模拟[J]. 弹箭与制导学报, 2012, 32(2): 110-113.
- CHEN D M, CHEN Z G, HOU X C, et al. The simulation on target damage of three shaped-charge penetrators torpedo warheads[J]. Journal of Projectiles, Rockets, Missiles and Guidance, 2012, 32(2): 110-113.
- [11] 王海福, 江增荣, 俞为民, 等. 杆式射流装药水下作用行为研究[J]. 北京理工大学报, 2006, 26(3): 189-192.
- WANG H F, JIANG Z R, YU W M, et al. Behavior of jetting penetrator charge operating underwater[J]. Transactions of Beijing Institute of Technology, 2006, 26(3): 189-192.
- [12] 周方毅, 黄雪峰, 詹发民, 等. 一种双球缺组合药型罩聚能鱼雷战斗部研究[J]. 水下无人系统学报, 2017, 25(3): 278-281, 287.
- ZHOU F Y, HUANG X F, ZHAN F M, et al. A shaped charge warhead with two spherical combined liners for torpedo[J]. Journal of Unmanned Undersea Systems, 2017, 25(3): 278-281, 287.
- [13] 周方毅, 詹发民, 姜涛, 等. 一种组合药型罩聚能战斗部[J]. 鱼雷技术, 2012, 20(5): 380-383, 400.
- ZHOU F Y, ZHAN F M, JIANG T, et al. An idea about shaped charge warhead with combined charge liner for torpedo[J]. Torpedo Technology, 2012, 20(5): 380-383, 400.
- [14] 许世昌, 何多勇, 何源. 射杆分离模式的双层药型罩射流成型仿真[J]. 计算机仿真, 2015, 32(8): 1-5, 72.
- XU S C, HE D Y, HE Y. Research on effective material of double-layered shaped charge liner[J]. Computer Simulation, 2015, 32(8): 1-5, 72.
- [15] 李明星, 王志军, 伊建亚, 等. 不同聚能装药水下作用效果的对比分析[J]. 兵器材料科学与工程, 2017, 40(5): 95-99.
- LI M X, WANG Z J, YI J Y, et al. Comparative analysis of underwater effect for different shaped charge[J]. Ordnance Material Science and Engineering, 2017, 40(5): 95-99.
- [16] 汪玉, 姚耀中. 世界海军潜艇[M]. 北京: 国防工业出版社, 2006: 120-130.

(上接第7页)

- esters [J]. Russian Journal of Organic Chemistry, 2004, 40(7):1062-1063.
- [51] STEPANOV R S, KRUGLYAKOVA L A, ASTAKHOV A M. Effect of the structure of 2,2,2-Trinitroethyl-N-nitroamines on the rate of their thermal decomposition [J]. Russian Journal of Organic Chemistry, 2001, 37 (12):1793.
- [52] KLAPÖTKE T M, KRUMM B, SCHARF R. From amino acids to high-energy dense oxidizers: polynitro materials derived from  $\beta$ -alanine and *L*-aspartic acid [J]. Journal of Inorganic and General Chemistry, 2016, 642
- [53] KLAPÖTKE T M, KRUMM B, SCHARF R. *N*-Nitrosarcosine: an economic precursor for the synthesis of new energetic materials [J]. Chemistry:An Asian Journal, 2016, 11(21): 3134-3144.
- [54] ABD-ELGHANY M, KLAPÖTKE T M, ELBEIH A. Investigation of 2,2,2-trinitroethylnitrocarbamate as a high energy dense oxidizer and its mixture with nitrocellulose (thermal behavior and decomposition kinetics) [J]. Journal of Analytical and Applied Pyrolysis, 2017, 128: 397-404.