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Taming of Tetranitroethane: A Promising Precursor to High Performance Energetic Ingredients

Ping Yin, Qiong Yu, Srinivas Dharavath, and Jean’ne M. Shreeve*

The stabilization of nitrogen-rich or oxygen-rich energetic molecules is an ongoing challenging study in the field of energetic materials. Now we describe the stabilization of tetranitroethylene by various states including metal complexes, nitrogen rich salts, and ionic complexes with ammonium oxide. These newly prepared energetic compounds are characterized by IR and NMR spectroscopy, elemental analysis, and differential scanning calorimetry (DSC). Single-crystal X-ray diffraction analysis was used to obtain further structural confirmation of 10, 11, 12, and 14. The safety parameters associated with impact and friction sensitivities were investigated using BAM (Bundesanstalt für Materialforschung und-prüfung) methods. In addition, detonation performance, e.g., detonation velocity, detonation pressure, and specific impulse were calculated using Explo5 program (version 6.01), which gives rise to a significant assessment for the application potential of tetranitroethylene derivatives as high performance energetic ingredients.

Introduction

The investigation of high energy density materials (HEDMs), e.g., explosives, propellants, and pyrotechnics, has drawn wide attention in both military and civilian engineering science. Major efforts are devoted to the innovation in designing new energetic molecules featuring high performance and low sensitivity. However, it is very challenging to meet various requirements of physicochemical properties. In the design of energetic oxidizers, the increase of oxygen balance and density relies on the introduction of nitrate or perchlorate anions, which can be found in some representative traditional propellants, e.g., ammonium nitrate (AN) and ammonium perchlorate (AP). Although AP is still the primary choice in solid rocket propellants, public concerns have been raised regarding its role in environmental pollution. In comparison, AN is more environmentally-friendly but its relatively low detonation performance is the main obstacle for wide applications in explosives and propellants.

Recently, energetic molecules consisting of organic backbones and explosophores exhibit promising potential as propellant oxidizers because of the high density and good oxygen balance. Furthermore, in contrast to inorganic HEDMs, AP and AN, the high detonation performance and low sensitivity enable them to play another role as primary or secondary explosives. Our recent research interests are focused on expanding the chemistry of 1,1-diamino-2,2-dinitroethene (FOX-7), a star molecule featuring high performance and low sensitivity. A variety of derivatives of FOX-7, e.g., metal complexes, high-oxygen carriers, and hypergolic oxidizers were synthesized and their diversified energetic properties highlight their application potentials as high performance HEDMs. Compared to FOX-7, other C2 based energetic molecules, such as 1,1,2,2-tetranitroethylene (TNEE, 1), 1,1,2,2-tetranitroethane (TNE, 2) and their derivatives, are rarely investigated in the energetic field.

To add to the understanding of the difference of these C2 based analogues, their bond dissociation energies (BDE) were calculated employing the Gaussian 03 suite of programs (Scheme 1). As the first trigger bond, the C-nitro bond of FOX-7 shows a high BDE of 280.3 kJ mol⁻¹, which arises from a pull substituted structure. In comparison with the high molecular stability of FOX-7, neither TNEE nor TNE can be isolated in stable neat forms at room temperature, which is supported by the low C-nitro BDE of 203.6 and 151.3 kJ mol⁻¹, respectively. However, the high oxygen content and positive oxygen balance (OB) of polynitratd frameworks make them...
highly attractive for designing high energy density oxidizers (HEDOs). Now we report the synthesis and properties of tetranitroethane derivatives, which were tamed by metal or nitrogen-rich cations. Compared to the highly unstable tetranitroethane, nitrogen-rich ionic derivatives and metal complexes exhibit greater molecular stabilities that may be suitable for practical applications. Furthermore, some tetranitroethane derivatives show favorable detonation performance and oxygen balance, which enable them to be utilized as potential explosives and propellants.

Results and discussion

As can be seen in Scheme 2a, potassium tetranitroethanide (6) was synthesized from chlorination and nitration of trinitroethanol (4), which was obtained by employing a Mannich reaction of potassium nitroformate (3) with 38% Formalin in the presence of conc. HCl. Preparation of the copper complex 9 was achieved by the reaction of copper (II) nitrate and 6 in aqueous ammonia. Furthermore, when treated with silver (I) nitrate, 6 was converted to silver tetranitroethanide (7) in good yield (Scheme 2a). However, the following attempt to form dihydroxylammonium tetranitroethanide (8) failed in the reaction of 7 with hydroxylammonium chloride. However, the diamminesilver (I) tetranitroethanide (10) was readily prepared from 7 and aqueous ammonia.

When gaseous hydrogen chloride was bubbled into the suspension of 6 in chloroform at ~40 °C, tetranitroethane 2 was prepared in situ and was characterized by 1H and 13C NMR spectra. The reaction of 2 and ammonia in methanol gave rise to diammonium tetranitroethanide [(NH$_4$)$_2$TNE, 11]. However, the reaction of 2 with excess hydroxylamine at room temperature resulted in 12 consisting of dinitroacetaldoxime anion, hydroxylammonium cation and ammonium oxide, as confirmed by single-crystal X-ray diffraction and elemental analysis. In comparison, while the reaction was carried out at -10 °C for few minutes, 13 was precipitated from the mixed solution of chloroform and methanol. In the synthetic attempt to get 8, tetranitroethane was treated with a stoichiometric amount of hydroxylamine but gave rise to an impure hygroscopic product. When 12 was stored in methanol for an extended period, a new ionic complex 14 was crystallized from the mother liquid, which indicated the transformation from the hydroxylammonium cation to the ammonium cation. Additionally, due to the favorable crystalization characteristics of guanidinium derivatives, 15-17 were prepared directly from 6 and the corresponding guanidinium chlorides.

As a useful tool for studying the structural features for solid-state compounds, single crystal X-ray diffraction analyses were carried out for 10, 11, 12, and 14. Crystal 10 crystallizes from an aqueous ammonia solution, whereas crystals of 11 and 12 were obtained from the evaporation of methanol and a mixture of methanol-chloroform, respectively. Crystal 14 was found when the methanol solution of 12 was evaporated very slowly at room temperature. With a good density of 2.705 g cm$^{-3}$ at 173 K, 10 crystallizes in the tetragonal space group I$4/m$ with four molecules in each unit cell (Figure 1). Arising from the steric effect, the adjacent two dinitromethyl groups are twisted with each other, which can be seen from the N(2)-C(1)-C(1A)-N(1A) torsion angle of -74.66°. However, an almost planar structure was observed in each dinitromethyl group (O4-N2-C1-C11, 177.2(16)°). Coordinating with the hydroxylammonium cation to the ammonium cation.

Diammonium tetranitroethanide (11) crystallizes with a calculated density of 1.797 g cm$^{-3}$ (at 130 K) in the monoclinic space group P2$_1$/n. Analogous to 10, the gem-dinitro group is essentially planar, as supported by the torsion angle of O4-N2-
C1-N1, 177.10(9)°. The close contact between ammonium and nitro groups reveals the strong hydrogen-bond interactions, which can be confirmed by short donor-acceptor distance (See electronic supporting information). Both 12 and 14 crystallize in the triclinic space group P-1 with calculated crystal densities of 1.815 and 1.784 g cm\(^{-3}\) at 173(2) K, respectively. The dinitroacetaldoximide anion in 12 and 14 is planar (12, O2-N2-C2-N3, 180.00(14)°; N1-C1-C2-N3, 177.86(16)°; 13, N1-C1-C2-N3, 177.93(2)°, O5-N3-C2-C1, 4.82(3)°) (Figure 3 and 4). The hydrogen bond interactions between ammonium oxide and the hydroxylammonium cation (the donor-acceptor distance) in 12 (d(O...O), 2.453 Å) is shorter than in 14 (d(O...O), 2.559 Å).

These new energetic compounds were fully characterized by FTIR, NMR, differential scanning calorimetry (DSC), and elemental analysis (EA). In the \(^{15}\)C NMR spectra, the characteristic signal for nitro groups is found at -19.25 ppm in the \(^{15}\)N NMR spectrum using D6-DMSO as the solvent. The TNE derivatives exhibit moderate thermal stabilities with decomposition temperatures ranging from 99 to 192 °C, which are comparable to ammonium dinitramide (ADN, \(T_d = 159 \, ^\circ\)C). As a critical index for energetic oxidizers, the oxygen balance (OB) of TNE analogues are significantly enhanced by the dinitromethyl group, which is exemplified by 11, 12, and 13 (OB%, +13.1%, +3.7%, and +18.1%, respectively; OB% is calculated based on the formation of carbon monoxide during the combustion process). Similarly, the oxygen content of 11-13 falls between 52.1% and 56.9%, which exceeds that of hexogen (RDX, O, 43.2%) and is even slightly higher than ADN (O, 51.6%). The other TNE analogues, including the copper and silver complexes (9 and 10), and guanidinium derivatives (15-17), have lower oxygen content and negative oxygen balance, ranging from 26.0% to 39.0% , and from -19.1% to -3.3%, respectively.

The densities of TNE-based energetic salts were measured with a gas pycnometer at 25 °C. Two metal complexes Cu(NH\(_3\))\(_2\)TNE (9) and [Ag(NH\(_3\))\(_2\)]TNE (10) have good densities of 1.933 g cm\(^{-3}\) and 2.586 g cm\(^{-3}\), respectively, which are comparable to those of Cu(NH\(_3\))\(_2\)(FOX)\(_2\) (18, d, 1.973 g cm\(^{-3}\))\(^{8a}\) and Ag(NH\(_3\))FOX (19, d, 2.510 g cm\(^{-3}\)).\(^{8b}\) The CHNO based ionic derivatives exhibit moderate to good densities from 1.653 (17) to 1.805 (13) g cm\(^{-3}\). Heats of formation (\(\Delta H_f\)) were computed using B3LYP function with 6-31+G** basis set with Gaussian 03, Revision E. 01, and the lattice energies were predicted employing Jenkins method.\(^{12}\) Based on the calculated \(\Delta H_f\) and experimental densities, detonation velocity (\(v_d\)), detonation pressure (\(P\)) as well as specific impulse (\(I_{sp}\)) were obtained.
Conclusions

Tetranitroethane-based metal complexes (9 and 10), nitrogen-rich salts (11, 13, and 15-17), and ionic complexes of dinitroacetaldiminate (12 and 14) were synthesized and characterized. Compounds 10, 11, 12, and 14 were further confirmed by single-crystal X-ray diffraction analysis. Ammonium oxide serves as an important building block to stabilize the ionic derivatives 12-14 with enhanced interionic interaction. Of them, 12 exhibits the most favorable integrated detonation performance with acceptable sensitivity parameters ($v_D$, 9264 m s$^{-1}$; $P$, 37.5 Gpa; $I_s$, 8 J; $F_s$, 80 N). In comparison with the unstable precursor of tetranitroethane, these new compounds expand the chemistry of polynitroalkanes and their promising energetic properties highlight the application prospect as high performance secondary explosives and oxygen-carriers.

Experimental section

Safety precautions

All experimental manipulations of TNE derivatives must be carried out by using safety precautions. Eye protection and leather gloves must be worn at all times. Mechanical actions of these energetic materials involving scratching or scraping must be avoided.

General Methods

All chemical reagents were pure ACS grade materials obtained from Aldrich, Oakwood, Acros Organics or AK Scientific and used as received. Decomposition points were recorded on a differential scanning calorimeter (DSC, TA Instruments Q2000) at a scan rate of 5 °C min$^{-1}$. $^1$H, $^{13}$C, $^{15}$N and $^{15}$N NMR spectra were recorded on a 300 MHz (Bruker AVANCE 300) or 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometer. Chemical shifts are reported relative to Me$_4$Si or deuterated solvents. Elemental analyses (C, H, N) were performed on a CHN Elemental Analyzer (Elementar, vario MICRO cube). Impact and friction sensitivity measurements were made using a standard BAM Fallhammer and a BAM friction tester. IR spectra were recorded using KBr pellets with a Thermo Nicolet AVATAR 370 spectrometer. Densities were calculated using Explo5 v6.01.
Synthesis of $\text{K}_2\text{TNE}$ (6) was based on the literature procedure.\textsuperscript{9} Yellow solid, 85% yield. $^{13}$C NMR ($\text{D}_2\text{-DMSO}$): $\delta$ 130.9; IR (KBr pellet): $\nu$ 1464, 1383, 1260, 1214, 1183, 1119, 1007, 791 cm$^{-1}$; elemental analysis (%) calcd for $\text{K}_2\text{Cu(NO}_2\text{)}_4\cdot2.5\text{H}_2\text{O}$, 286 mg, 233 mg was placed in aqueous ammonia (5 mL). The mixture was stirred at 50 °C for 30 min and then was filtered using a Buchner funnel, giving rise to the copper complex 9. Green solid, 75% yield. IR (KBr pellet): $\nu$ 3341, 3352, 1468, 1350, 1194, 1134, 1003, 846, 793, 743 cm$^{-1}$; elemental analysis (%) calcd for $\text{Cu}_2\text{H}_2\text{Cu(NO}_2\text{)}_8$ (339.71), $\delta$ 7.07; C, 3.56; N, 32.99; found: C, 7.09; H, 3.42; N, 32.17.

Synthesis of $[\text{Ag(NH}_3\text{)}_2\text{]}_2\text{TNE}$ (9): Potassium tetrinitroethanide ($\text{K}_2\text{TNE}$, 6, 1 mmol, 286 mg) and copper(II) nitrate hemipentahydrate ($\text{Cu(NO}_2\text{)}_2\cdot2.5\text{H}_2\text{O}$, 1 mmol, 233 mg) was suspended in anhydrous ammonia (5 mL) at room temperature. The slow evaporation of resulting solution gave rise to 9 as a yellow crystalline solid. 51% yield. IR (KBr pellet): $\nu$ 3438, 3317, 1655, 1534, 1467, 1401, 1349, 1220, 1187, 1141, 1116, 1005 cm$^{-1}$; elemental analysis (%) calcd for $\text{Cu}_2\text{H}_2\text{Ag(NO}_2\text{)}_8$ (491.90), C, 4.88; H, 2.46; N, 22.78; found: C, 4.83; H, 2.29; N, 22.15.

Synthesis of $\text{A}_2\text{TNE}$ (7, 1 mmol, 424 mg) was dissolved in aqueous ammonia (5 mL) at room temperature. The slow evaporation of resulting solution gave rise to 7 as a yellow crystalline solid. 41% yield. IR (KBr pellet): $\nu$ 3436, 3399, 3274, 3206, 1654, 1456, 1374, 1333, 1187, 1119, 1008, 849, 793, 539 cm$^{-1}$; elemental analysis (%) calcd for $\text{Cu}_2\text{H}_2\text{N}_2\text{O}_8$ (328.20), C, 14.64; H, 3.69; N, 42.68; found: C, 14.33; H, 3.72; N, 41.88.

General synthetic procedure of 15-17: potassium tetrinitroethanide ($\text{K}_2\text{TNE}$, 6, 1 mmol, 286 mg) was added to a solution of guanidinium hydrochloride (G•HCl, 6 mmol, 573 mg) or aminoguanidinium hydrochloride (AG•HCl, 6 mmol, 663 mg), or trimoguanidinium hydrochloride (TAG•HCl, 6 mmol, 843 mg) in a minium amount of distilled water. The suspension was heated to 50 °C and distilled water was added dropwise until a clear solution was obtained. The resulting solution was placed in an ice bath to cool to ~5 °C, where the crystalline product (15-17) can be collected by filtration and then dried in vacuum.

$\text{G}_2\text{TNE}$ (15): Yellow solid, 69% yield. $^1$H NMR ($\text{D}_2\text{-DMSO}$): $\delta$ 6.91 (br, 12H); $^{13}$C NMR ($\text{D}_2\text{-DMSO}$): $\delta$ 157.9, 130.9; IR (KBr pellet): $\nu$ 3462, 3399, 3274, 3206, 1654, 1456, 1374, 1333, 1187, 1119, 1008, 849, 793, 539 cm$^{-1}$; elemental analysis (%) calcd for $\text{Cu}_2\text{H}_2\text{N}_2\text{O}_8$ (328.20), C, 14.64; H, 3.69; N, 42.68; found: C, 14.33; H, 3.72; N, 41.88.

$\text{AG}_2\text{TNE}$ (16): Yellow solid, 41% yield. $^1$H NMR ($\text{D}_2\text{-DMSO}$): $\delta$ 8.54 (s, 2H), 7.18 (br, 4H), 6.80 (br, 4H), 4.67 (s, 4H); $^{13}$C NMR ($\text{D}_2\text{-DMSO}$): $\delta$ 158.8, 130.9; IR (KBr pellet): $\nu$ 3453, 3356, 3298, 1655, 1578, 1533, 1467, 1420, 1325, 1234, 1186, 1136, 1006, 850, 795, 776, 746, 669, 621, 507, 460 cm$^{-1}$; elemental analysis (%) calcd for $\text{Cu}_2\text{H}_2\text{N}_2\text{O}_8$ (358.23), C, 13.41; H, 3.94; N, 46.92; found: C, 13.21; H, 3.95; N, 46.00.

$\text{TAG}_2\text{TNE}$ (17): Orange crystalline solid, 47% yield. $^1$H NMR ($\text{D}_2\text{-DMSO}$): $\delta$ 8.57 (s, 6H), 4.80 (s, 12H); $^{13}$C NMR ($\text{D}_2\text{-DMSO}$): $\delta$ 159.0, 131.0; IR (KBr pellet): $\nu$ 3319, 3214, 1684, 1615, 1473, 1350, 1188, 1126, 1006, 952, 851, 788, 769, 747, 638, 610 cm$^{-1}$.
1; elemental analysis (%): calculated for C4H14N1O6 (418.29): C, 11.49; H, 4.34; N, 53.58; found: C, 11.08; H, 4.45; N, 51.65.

Conflicts of interest

There are no conflicts to declare.

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Notes and references


Taming of tetranitroethane gives rise to various ionic complexes as new energetic ingredients