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J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/ja5074036 • Publication Date (Web): 08 Aug 2014

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Tetranitroacetimidic acid (TNAA) – A High Oxygen Oxidizer and Potential Replacement for Ammonium Perchlorate

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Supporting Information Placeholder

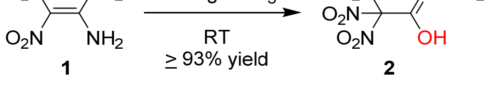
ABSTRACT: Considerable work has been focused on developing replacements for ammonium perchlorate, a primary choice for solid rocket and missile propellants, due to environmental concerns resulting from the release of perchlorate into ground water systems, which have been linked to thyroid cancer. Additionally, the generation of hydrochloric acid contributes to high concentrations of acid rain and to ozone layer depletion. En route to synthesizing salts which contain cationic FOX-7, a novel, high oxygen-containing oxidizer, tetranitroacetimidic acid (TNAA), has been synthesized and fully characterized. The properties of TNAA were found to be exceptional with a calculated specific impulse exceeding that of ammonium perchlorate (AP), leading to its high potential as a replacement for AP. TNAA can be synthesized easily in a one step process by the nitration of FOX-7 in high yield (>93%). The synthesis, properties, and chemical reactivity of TNAA have been examined.

Ammonium perchlorate (AP) has long been the primary choice as an oxidizer in propellants for rockets and missiles.[1,2] However, significant global efforts to replace AP stems from environmental concerns due to the release of perchlorate into ground water systems and the generation of hydrogen chloride during burning – enhancing acid rain and depletion of the ozone layer.[3] The contamination in soil and water has driven major health concerns as perchlorates can affect normal thyroid functions by competing with the binding sites of iodine and is linked to thyroid cancer.[4] In addition, a major disadvantage of AP is that the chlorine content causes a smoke that can be easily detected by radar or when the humidity is high, a white smoke can be seen easily.[5] Therefore, considerable effort has been made to replace AP in propellant formulations. Among the chlorine-free oxidizers developed, ammonium dinitroamide (ADN) and hydrazinium nitroformate (HNF) have risen as potential replacements for AP since their properties are comparable and the reduced introduction of harmful contaminants into the environment make them appealing.[4,6,7] However, both suffer from drawbacks due to their sensitivity towards impact and friction and ADN's high hygroscopic nature.[5,8] Therefore, further research is required to develop oxidizers that are stable, environmentally friendly and readily synthesized (in good yields) to become suitable for replacing AP.

For some time our group has been interested in expanding the chemistry of 1,1-diamino-2,2-dinitroethene (FOX-7),[9] an insensitive energetic material which has attracted considerable attention as a potential replacement for some commonly used sensitive explosives.[1] We recently examined the reactivity of FOX-7 and its hydrazine derivative, 1-amino-1-hydrazino-2,2-dinitroethene (HFOX), with a variety of strong acids which led to the first isolated salts that contain FOX-7 and HFOX cations.[10] This work demonstrated the amphoteric properties of FOX-7 and HFOX and gave rise to new potential building blocks for energetic salts. Among the acids examined, the reaction of FOX-7 with fuming nitric acid led to the formation of the title compound, tetranitroacetimidic acid (TNAA), rather than the anticipated nitrate salt. Few examples of the conversion of gem-dinitro substrates to trinitromethyl complexes have been reported which makes the chemical formation of TNAA of interest.[11] Following characterization of TNAA, this exciting new molecule was found to have applications as an efficient oxidizer with properties exceeding those of AP and comparable to ADN and HNF. Now we describe our contributions to the new chemistry of FOX-7 and to the development of a likely new oxidizer through the synthesis and full characterization of TNAA concomitantly with its potential application as a suitable replacement for AP.

Tetranitroacetimidic acid, TNAA (**2**), was synthesized by the reaction of FOX-7 (**1**) with an excess of fuming nitric acid to leave colorless crystals after removal of the excess acid in vacuo (Scheme 1). Unlike the cationic salts of FOX-7 obtained with other strong acids,[10] compound **2** is stable at room temperature for long periods and is non-hygroscopic.

Scheme 1. Synthesis of **2**.



The colorless crystals may yellow slightly over time. TNAA is only slightly soluble in most organic solvents, but can be partially dissolved in ethyl acetate and dichloromethane. It is unstable in acetonitrile as became evident when dissolved in deuterated acetonitrile for NMR studies. The compound began to decompose, generating heat, and bubbles of a brown gas (nitrogen dioxide). Decomposition also occurs in DMSO.

The structure of **2** was determined by single crystal X-ray analysis (Figure 1). It crystallizes in the monoclinic space group $P2_1/c$ system with four molecules per unit cell. The C-C bond distance (1.53 Å) agrees with the average bond distance for a single C-C bond (1.54 Å). Upon closer examination of the C2-N3 and C2-O16 bond distances, the C-N bond distance of **2** (1.31 Å) is slightly shorter than the average bond distance for a single C-N bond (1.47 Å) and slightly longer than C=N (1.22 Å). Also, the C-O bond distance of 1.29 Å is slightly longer than that of C=O (1.23 Å), suggesting that **2** may exist as an equilibrium between the two forms as shown in Figure 2. Mass spectroscopy (EI) was also used to verify the structure of **2**. The parent peak at 239 amu, a signal at 240 amu assigned to M^++1 and a strong signal at 150 amu assigned to the trinitromethyl group $[-C(NO_2)_3]$ were observed. The amino derivative of **2**, compound **3**, was synthesized earlier by nitrating **1** with a mixture of nitric acid, trifluoroacetic anhydride, and trifluoroacetic acid (Scheme 2).[11] However, **3** was isolated as an oil and found to be very unstable at room temperature. Characterization of **3** has not been reported. Indirect structural deduction of **3** was accomplished by reacting it with ammonia in acetonitrile to obtain the stable products ammonium trinitromethanide and mononitroguanidine.[11]

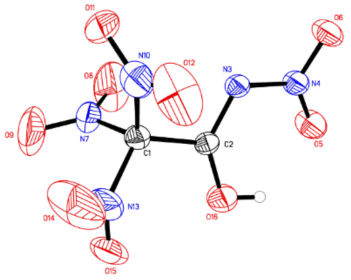


Figure 1. Thermal ellipsoids plot (50%) - single crystal X-ray structure of **2.**

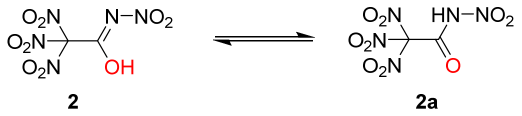
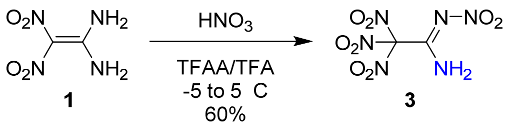


Figure 2. Possible equilibrium between two forms of **2** based on bond lengths.

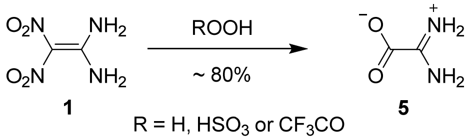
Scheme 2. Reaction of 1 with a mixture of nitric acid, trifluoroacetic anhydride (TFAA), and trifluoroacetic acid (TFA) to form compound 3.



The nitration of 1,1,-diamino-2,2,-dinitroethylene derivatives examined by Baum and co-workers suggested that formation of the trinitromethyl moiety could result from two potential routes: 1) an attack on a nitronium ion by the nitrovinyl carbon with concomitant loss of a proton from the amino nitrogen or 2) nitration of the amine nitrogen; however, the reaction order is unknown.[12]

In our current work, **3** may have formed, but due to the lack of a scavenging agent to take up the resulting water, the latter may react further with the amine intermediate (**3**), leading to **2**. It should be noted that in the preparation of **2**, it is important to use freshly distilled fuming nitric acid and to remove all the excess acid prior to exposing the sample to air. If residual amounts of the acid remain, **2** slowly transforms to nitrourea (**4**) as was confirmed by single crystal X-ray analysis. Surprisingly, no crystal data for nitrourea were found in the records of the Cambridge Crystallographic Data Center. Its crystal structure data is given in the Supporting Information. Formation of **2** is also dependent on the concentration of the nitric acid. When **1** was treated with commercially available 65% nitric acid (~16 M) and allowed to stir overnight, brown gas (nitrogen dioxide) was found over the solution inside the reaction flask. The reaction was quenched with ice and the product was extracted with dichloromethane to yield amidinoformic acid (**5**). The formation of **5** was previously reported by reacting **1** with a variety of organic peroxides such as 30% hydrogen peroxide (H_2O_2), Caro's acid (H_2SO_5) or peroxytrifluoroacetic acid (CF_3CO_3H) (Scheme 3).[13a]

Scheme 3. Synthesis of 5 from 1 with organic peroxides.



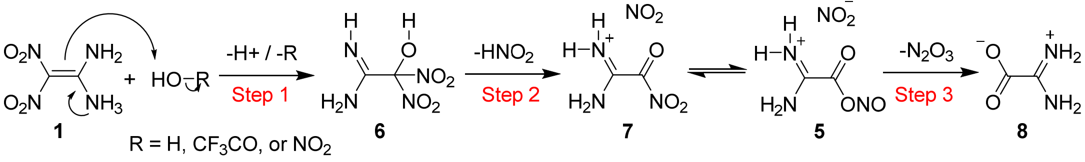
Based on the literature precedence for the formation of **5**, it is likely that the same proposed mechanism is suitable when FOX-7 is reacted with 65% HNO_3 rather than with the peroxide (Scheme 4). The loss of HNO_2 leads to intermediate **7** which can undergo a nitro–nitrito rearrangement[13b] to form **8** in step 3 of Scheme 4. Nucleophilic attack of the nitrite ion with intermediate **8** followed by the displacement of dinitrogen trioxide leads to the formation of product **5** (step

Table 1. Physical properties of AP, ADN and TNAA

	AP	**ADN**[a]	**HNF**[b]	**2**
Formula	NH_4ClO_4	$NH_4N(NO_2)_2$	$N_2H_5C(NO_2)_3$	$C_2HN_5O_8$
Tm[c] (°C)	---	93	129	91
Tdec[d] (°C)	> 200	159	131	137
IS[e] (J)	15[f]	3–5	4	19
FS[g] (N)	> 360[h]	64–72	28	20
N[i]%	11	52	38	29
O[j]%	54	45	52	60
OB[k] %	26	26	13	30
d[l] (gcm^{-3})	1.95	1.81	1.86	1.87[m](1.84)[n]
Isp[o] (s)	156	202[p]	265[q]	209

a) [Ref. 3] b) [Ref. 8]. c) Melting temperature. d) Decomposition temperature [onset]. e) Impact sensitivity. f) Ref. 1. g) Friction sensitivity. h) Measured FS. i) Nitrogen content. j) Oxygen content. k) Oxygen balance. l) Density. m) Measured density. n) Crystal density. o) Specific impulse [values were obtained from Explo5 v6.01 and calculated at an isobaric pressure of 70 bar and initial temperature of 3,300 K]. p) Calculated via Explo 5 v6.01. q) [Ref. 5].

Scheme 4. Proposed mechanism for formation of 5 from 1 with 65% HNO_3.



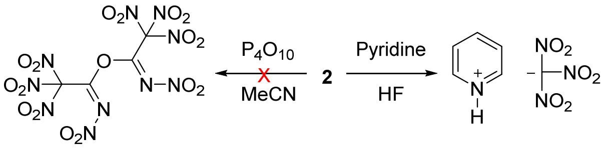
3). The lack of formation of **2** with 65% HNO_3 may be a result of the quenching step with water. When the reaction was attempted without quenching, the excess acid was removed under vacuum to give an unknown white solid. Therefore, the water content present in 65% HNO_3 compared to fuming HNO_3 may play a significant role in the formation of compound **5** versus **2**.

Attempts to extend this acid chemistry to HFOX with fuming nitric acid under neat conditions resulted in combustion of HFOX after the addition of the second drop of nitric acid. Subsequently HFOX was suspended in acetonitrile and cooled in an ice bath before addition of nitric acid. When the excess acid and solvent was removed, white needles were obtained. Upon repeating this reaction several times, the final product exploded at reduced pressure. Because of safety concerns, this chemistry was no longer pursued. Any attempts to study this chemistry should be accomplished with extreme caution keeping in mind that HFOX itself can spontaneously detonate.

Compound **2** is a very attractive and promising stable oxidizer (MP 91°C and $T_{d\ (onset)}$ 137 °C) with a majority of its properties (calculated via Explo5 v6.01) exceeding that of AP (Table 1). It was also found to have properties that were comparable to ADN and HNF. Compared to AP, **2** has a significantly enhanced nitrogen and oxygen content and higher positive oxygen balance due to the trinitromethyl group. The oxygen balance is a measure of the amount of oxygen available for combustion of energetic materials. Positive OBs indicate there is more than enough oxygen to convert all carbon to carbon monoxide and all hydrogen to water whereas negative values indicate that the oxygen content is insufficient for complete oxidation. The specific impulse (Isp) is a measure of a propellant's efficiency. Compared to AP, **2** has a higher specific impulse (209 s) and is slightly more stable towards impact (19 J) with a comparable density. In comparison to ADN, **2** is significantly more stable towards impact with enhanced or comparable properties. It is interesting to note that the calculated ISP value (Explo 5 v6.01) of a fuel mixture comprised of HTPB/TNAA/Al (12/68/20) is 261 s which shows that TNAA is even more effective in a mixed fuel system (HTPB = hydroxyl-terminated polybutadiene). However, the thermal stability and friction sensitivity of **2** are not competitive with AP and is slightly less than that of ADN. Enhancing these two properties may make **2** even more appealing and a better substitute for AP. Therefore we were prompted to study the chemical reactivity of **2** to understand and enhance the molecular structure to obtain the desired properties.

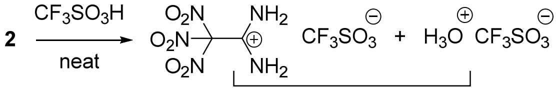
The unique structure of **2** and the likely existence of the two forms (Figure 2) may explain its challenging reaction chemistry. Our initial studies began with examining the reactivity of the hydroxyl group in **2**. Attempts to dimerize compound **2** with P_4O_{10} were unsuccessful (Scheme 5, structure **9**). In an effort to replace the hydroxyl group by fluorine with Olah's reagent (pyridine/HF), no fluorinated product was observed and rather the long known pyridinium trinitromethanide (**10**), first reported in 1920, was isolated.[14] Interestingly the crystal structure of **10** had not been recorded at the Cambridge Crystallographic Data Centre. Suitable crystals of **10** were isolated and single crystal X-ray analysis was obtained to complete the structural analysis (see Supporting Information). The reactivity of **2** with simple bases was then examined. When sodium hydroxide was added to a suspension of **2** in water, sodium carbonate and sodium nitroform were isolated. Similar results were observed when sodium bicarbonate, ammonia or guanidinium carbonate was reacted with **2** where the corresponding trinitromethanide salt was isolated and verified by elemental and crystal structure analysis. These results indicated the highly reactive nature of the amide moiety with bases.

Scheme 5. Reaction of 2 with P_4O_{10} and Olah's reagent.



Compound **2** with acids was also examined. By studying a variety of weak and strong acids [i.e., trifluoroacetic acid (pKa = 0.5), hydrochloric acid (pKa = -7), and perchloric acid (pKa = -10)], it was found that **2** only reacted with triflic acid (CF_3SO_3H; pKa = -15). When **2** was stirred with an excess of triflic acid under neat conditions for 30 minutes at 25 °C, colorless crystals were obtained after the removal of the majority of the acid over an extended period in vacuo. These hygroscopic crystals were identified as the cocrystal salt **11** containing a 1:1 ratio of 1-amino-2,2,2-trinitroethaniminium triflate and triflate hydrate via single crystal X-ray analysis (Scheme 6; Figure 3). They can be stored at room temperature under vacuum for several weeks without decomposition. In addition to X-ray crystal structure, the structure of **11** was also supported by ^{13}C and ^{19}F NMR, elemental analysis. The cocrystal salt (**11**) crystallizes in a triclinic space group P-1 with two molecules per unit cell and has a crystal density of 1.48 gcm^{-3}. The C-C bond distance (C1-C2, 1.53 Å) agrees with the average bond distanc for a

Scheme 6. Reaction of 2 with CF_3SO_3H.



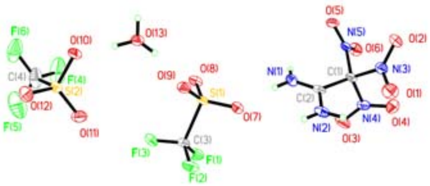


Figure 3. Single crystal X-ray structure of salt **11** - thermal ellipsoids plot (50%).

single C-C (1.54 Å) bond. Examining the bond distance of C2-N1 (1.29) and C2-N2 (1.30), the C-N bond distance is shorter than the average bond distance for a single C-N single bond (1.47 Å) and longer than the average C=N double bond (1.22 Å) suggesting that the positive charge is delocalized over the atoms N1-C2-N2.[10]

The unexpected reduction of the N-NO$_2$ group of **2** in the formation of the trinitroethaniminium cation in **11** is supported by the literature for the unique ability of triflic acid to reduce the nitro group in nitrobenzyl alcohol.[15] However, further investigation is necessary to understand the mechanistic transformation of the 1-amino-2,2,2-trinitroethaniminium cation.

The existence of the 1-amino-2,2,2-trinitroethaniminium cation in **11** is interesting due to its appeal as a precursor for energetic salts. Typical cations used for energetic salts have high nitrogen and low oxygen content; however, the cation of **11** has both high nitrogen and oxygen content, making it an ideal building block for energetic salts. The density of trinitroethaniminium triflate of cocrystal salt **11** was calculated (by literature method)[16] to be 2.09 gcm^{-3} with a detonation pressure (P), detonation velocity (V), and Isp (calcluated via Explo 5 v6.01), of 25 Gpa, 7208 ms^{-1} and 247 s respectively. The low energetic performance is expected as the counter ion is non-energetic. When the 1-amino-2,2,2-trinitroethaniminium cation is parlayed with dinitroamide [N(NO$_2$)$_2^-$] (**12**), the density (calculated)[16] was found to be 2.06 gcm^{-3} with high detonation performances (V = 9053 ms^{-1}; P = 36 Gpa), exceeding the values of FOX-7 (V = 8771 ms^{-1}, P = 35 GPa) and RDX (cyclo-1,3,5-trimethylene-2,4,6-trinitramine; V = 8864 ms^{-1}, P = 36 GPa) (see Supporting Information). Further investigation is required to enhance the stability of **11** with anions that are suitable to stabilize the 1-amino-2,2,2-trinitroethaniminium cation, which may give rise to interesting and powerful energetic salts.

In summary, the chemical reactivity of FOX-7 has been expanded via the synthesis and characterization of a new oxidizer, TNAA (**2**), which results from a simple single step process from FOX-7 in high yield (≥ 93%). This novel molecule has a high potential for replacing AP as an oxidizer for applications in solid rocket propellants and missiles. Compound **2** is more stable towards impact than AP and DNA with enhanced or comparable properties. The reaction chemistry of **2** leads to some interesting insights in its synthesis and reactivity such as the formation of **11**. The 1-amino-2,2,2-trinitroethaniminium cation of **11** represents a very promising energetic precursor for energetic salts due to its high nitrogen and oxygen content. Compound **2** exhibits an interesting molecular structure that adds to the examples of transformation of the gem-dinitro system to trinitromethyl-containing materials. As is the case for FOX-7, the chemical reactivity of **2** needs further investigation in order to fully explore its reaction chemistry.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization data (single crystal X-ray), and heat of formation calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

The authors gratefully acknowledge the support of ONR (N00014-12-1-0536 and N00014-11-AF-0-0002), and the Defense Threat Reduction Agency (HDTRA 1-11-1-0034). We are indebted to Mr. Scott Economu and Dr. Brendan Twamley for considerable assistance with crystal structuring.

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