

Unusual Energetic Periodate, Sulfate and Amino-bistetrazolate Salts of the Trinitropropylammonium Cation

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Abstract. Starting from a nucleophilic Michael addition of nitroform to acrylamide, three synthetic strategies towards 1,1,1-trinitropropyl-1-ammonium salts are described. Due to the high oxygen content and density of one periodate salt, its suitability as high-energy dense oxidizer in energetic formulations was predicted according to its specific impulse and detonation velocity. Furthermore, those properties were compared to the nitrogen-rich amino-bis(5-tetrazolate) salt. The parameters were calculated with the EXPLO5 (V6.03) computer code

and compared to the common solid rocket propellant ammonium perchlorate (AP). Calculations towards the energies of formation were performed using Gaussian 09. Characterization including multinuclear NMR spectroscopy, vibrational analysis (IR, Raman) as well as elemental analysis and a single-crystal X-ray diffraction study was performed. The thermal stability was studied using differential scanning calorimetry and the sensitivities against impact and friction were determined.

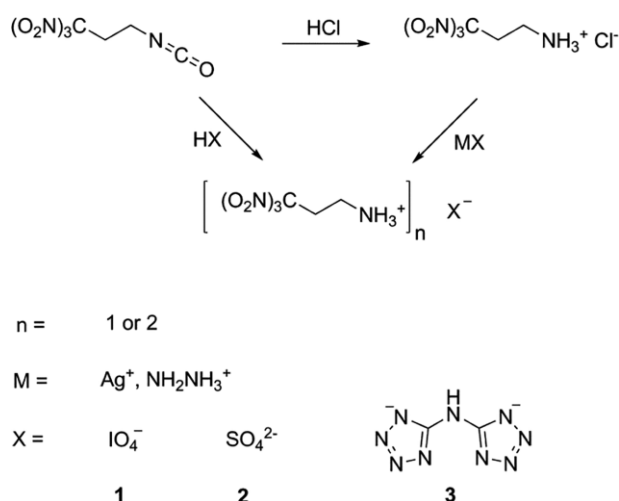
In the area of high-energy dense oxidizers (HEDOs), ammonium perchlorate (AP) still is one of the most popular oxidizers in composite propellants. While the ammonium cation acts as a reducing agent, the perchlorate anion is the important oxidizer during the combustion.^[1] The formed oxygen reacts with the aluminum and binder, which are present in the composite, and in consequence leads to a very high heat of combustion and high burning temperature.^[2] Nevertheless, toxic gases such as hydrogen chloride are also released, as well as the own toxicity of perchlorate anion, as it competes with iodine in the thyroid gland.^[3]

An interesting building block for designing new perchlorate free HEDOs is the trinitromethyl unit, due to its high oxygen content. Whereas the more oxygen-rich but chemically less stable 2,2,2-trinitroethyl moiety has been studied exhaustively, the 3,3,3-trinitropropyl moiety gained more attention lately. Our initial study concerning the 3,3,3-trinitropropyl unit as promising energetic building block showed, that compounds carrying the propyl moiety, although not exhibiting higher thermal stabilities, in general were less sensitive, compared to the corresponding ethyl salts.^[4]

Until now, no salts are known containing the 2,2,2-trinitroethyl-1-ammonium unit. However, with the 3,3,3-trinitropropyl-1-ammonium cation, it is possible to study salts containing this particular cation. The first exemplary salts showed

excellent performance data, but increased sensitivities towards impact and friction. Furthermore, only the 3,3,3-trinitropropyl-1-ammonium perchlorate displayed a thermal stability up to 164 °C.^[5] In this contribution, we tested two oxygen-rich and one nitrogen-rich counterions, namely the periodate, sulfate and amino-bis(5-tetrazolate) salts of the 3,3,3-trinitropropyl-1-ammonium moiety.

The central precursors are the reactive isocyanate 1,1,1-trinitropropan-3-isocyanate and the 3,3,3-trinitropropyl-1-ammonium chloride, which are available by a route starting from a Michael addition of nitroform with acrylamide.^[5] Reaction of the isocyanate with periodic acid resulted in the corresponding periodate salt **1**, similar to the chloride (Scheme 1) and nitrate salts. The sulfate and amino-bis(5-tetrazolate) salts **2** and **3** were obtained via metathesis reactions of 3,3,3-trinitropropyl-1-ammonium chloride with the corresponding silver or hydrazinium salts.



Scheme 1. Synthesis of the 3,3,3-trinitropropyl-1-ammonium salts **1–3**.

Identification and characterization is performed as usual with multinuclear NMR spectroscopy. Since the resonances in

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the ^1H , ^{13}C , and ^{14}N NMR spectra are as to be expected in the same ranges as already described salts with this cation, they are not discussed in detail. For the periodate salt **1** the ^{127}I NMR resonance was obtained at $\delta = 4103$ ppm, for the sulfate salt **2** the ^{33}S resonance at -1.5 ppm, both as relatively sharp singlets.

Low-temperature X-ray diffraction analysis was possible for the sulfate salt **2** after recrystallization from water. However, in the second 3,3,3-trinitropropyl-1-ammonium unit a disorder is observed and omitted in Figure 1. Due to the steric repulsion from the three relatively large nitro groups around one carbon atom, the C–N bond lengths in the trinitromethyl moiety are in the range of 1.51–1.54 Å, which is longer than a regular C–N bond (1.47 Å).^[6] The structure shows also the typical propeller-like arrangement of the trinitromethyl moieties, which optimizes the non-bonded N \cdots O attractions. These attractions are considerably shorter (2.55–2.56 Å) than the sum of the van der Waals radii of nitrogen and oxygen (3.07 Å).^[7]

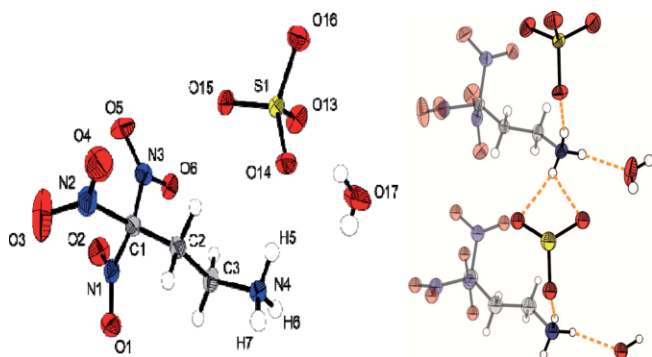


Figure 1. Crystal structure of bis(3,3,3-trinitropropyl-1-ammonium) sulfate (**2**). Selected distances /Å and angles /°: O2–N1 1.221(4), O3–N2 1.200(6), N3–C1 1.524(4), C1–C2 1.504(3), C2–C3 1.522(8), C1–N4 1.477(5), S1–O16 1.463(9), S1–O14 1.482(8), O1–N1–O2 127.3(9), C3–C2–C1 116.8(3), N3–C1–N2 106.4(8), O13–S1–O15 108.6(9), O14–S1–O16 107.9(8).

Strong hydrogen bonds (image at right in Figure 1) are observed between the hydrogen atoms of the ammonium moiety and the oxygen of the sulfate ion [DHA N4–H7 \cdots O14, bond angle DHA 166.9°, $d(\text{D–A}) = 2.73$ Å, $d(\text{H–A}) = 1.84$ Å, DHA N4–H5 \cdots O15, bond angle DHA 153.2°, $d(\text{D–A}) = 3.11$ Å, $d(\text{H–A}) = 2.27$ Å, DHA N4–H5 \cdots O13, bond angle DHA 122.0°, $d(\text{D–A}) = 2.90$ Å, $d(\text{H–A}) = 2.31$ Å] as well as the hydrate water [DHA N4–H6 \cdots O17, bond angle DHA 146.6°, $d(\text{D–A}) = 2.84$ Å, $d(\text{H–A}) = 2.03$ Å].

The periodate **1** was obtained hydrate-water free and has a relatively high oxygen content, in contrast to the amino-bis(5-tetrazolate) **3** which owns the nitrogen-rich amino-bis(tetrazole) moiety. Their energetic potential and physical properties were determined as outlined in Table 1 (the sulfate salt **2** is not considered here due to its water content, sensitivities see Experimental Section). Both salts **1** and **3** are stable for over a year under standard conditions, though **1** should be stored under the exclusion of light. Compared to the other already published 3,3,3-trinitropropyl-ammonium salts, **3** showed most moderate impact and friction sensitivities. Furthermore, its room temperature density and thermal stability are most com-

parable to the 5,5'-azobistetrazolate salt (1.67 g·cm $^{-3}$, 120 °C).^[5] In contrast, the periodate salt **1** is the most sensitive salt so far, having the highest decomposition temperature amongst the energetic, perchlorate-free 3,3,3-trinitropropyl-ammonium salts. In addition, due to the relatively heavy iodine atom, its density exceeds clearly 2.00 g·cm $^{-3}$ and also, that from all salts of this cation.

Table 1. Physical properties, calculated heat of formation and predicted detonation and combustion parameters of salts **1** and **3**, as well as ammonium perchlorate (AP).^[8]

	1	3	AP
Formula	C ₃ H ₇ N ₄ O ₁₀ I	C ₈ H ₁₅ N ₁₇ O ₁₂	NH ₄ ClO ₄
FW /g·mol $^{-1}$	386.01	541.32	117.49
T_m /°C ^{a)}	105	–	–
T_{dec} /°C ^{b)}	138	118	240
IS /J ^{c)}	2	15	20
FS /N ^{d)}	6	360	360
ρ /g·cm $^{-3}$ ^{e)}	2.12	1.66	1.95
N /% ^{f)}	14.5	44.0	11.9
O /% ^{g)}	41.5	35.5	54.5
Ω_{CO_2} /% ^{h)}	2.1*	–34.0	34.0
ΔH_f° /kJ·mol $^{-1}$ ⁱ⁾	35	833	–296
ΔU_f° /kJ·kg $^{-1}$ ^{j)}	63	1640	–2433
Q_v /kJ·kg $^{-1}$ ^{k)}	–4902	–5924	–1421
T_{ex} /K ^{l)}	4663	3953	1725
V_0 /L·kg $^{-1}$ ^{m)}	619	825	884
p_{CJ} /kbar ⁿ⁾	258	293	183
V_{det} /m·s $^{-1}$ ^{o)}	7074	8486	6810
I_{sp} /s ^{p)}	225	267	155
I_{sp} /s (Al) ^{q)}	240	275	233
I_{sp} /s (Al and 14% binder) ^{r)}	236	239	256

a) Onset melting and b) Onset decomposition point from DSC measurement, heating rate of 5 K·min $^{-1}$. c) Impact sensitivity. d) Friction sensitivity. e) Room temperature densities are measured by gas pycnometer. f) Nitrogen content. g) Oxygen content. h) Oxygen balance assuming the formation of CO₂ according to the Springall–Roberts-Rules (*as calculated by EXPLO5 (V6.03) computer code^[9]). [i] Enthalpy and j) Energy of formation calculated by the CBS-4M method using Gaussian 09.^[10] k) Heat of detonation. l) Detonation temperature. m) Volume of gaseous products. n) Detonation pressure, and o) Detonation velocity calculated by using the EXPLO5 (V6.03) code.^[9] p) Specific impulse for the neat compound, q) for optimized compositions with aluminum and, r) for three component compositions with oxidizer, aluminum and 14% binder (6% polybutadiene acrylic acid, 6% polybutadiene acrylonitrile and 2% bisphenol A ether) at 70.0 bar chamber pressure, isobaric combustion conditions (1 bar) and equilibrium to throat and frozen to exit (see Supporting Information).

The specific impulses I_{sp} of **1** and **3** were calculated for the neat compounds, for compositions with different amounts of aluminum as fuel, and additionally with binder. These impulses were compared with the calculated impulses of ammonium perchlorate (AP) as neat compound, as mixture with 15% aluminum, and as mixture with 15% aluminum and 14% binder. The amino-bis(5-tetrazolate) **3** has high specific impulses as neat compound and in mixtures with aluminum, but in composites containing oxidizer, fuel and binder the specific impulse decreases. The optimized composites of salts **1** and **3** are in appropriate ranges, but are neither superior to the former trinitropropyl-ammonium salts, nor to the optimized composites of ammonium perchlorate. Optimization plots can be found in the Supporting Information.

Experimental Section

General experimental details are described in the Supporting Information.

CAUTION! The 1,1,1-trinitropropyl-1-ammonium salts show increased sensitivities towards heat, impact and friction. No hazards occurred during the preparation and manipulation of those salts, but they should be handled with caution, especially the periodate salt. Protective equipment, such as leather jacket, face shield, ear protection, Kevlar® gloves, is strongly recommended.

3,3,3-Trinitropropyl-1-ammonium Periodate (1): Periodic acid (H_5IO_6 , 308 mg, 1.4 mmol) was dissolved in small amounts of water and immediately added to freshly prepared 1,1,1-trinitropropan-3-isocyanate (269 mg, 1.2 mmol). The reaction mixture was stirred at 50 °C for 5 h under exclusion of light. The solvent was removed in vacuo, the resulting crude product was suspended in 1,2-dichloroethane and filtered. The periodate salt **1** was obtained as colorless solid in 53 % yield (250 mg). **¹H NMR** (D_2O): $\delta = 8.27$ (br., 3 H, NH_3), 3.80 (m, 2 H, CH_2), 3.56 (m, 2 H, CH_2). **¹³C NMR** (D_2O): $\delta = 127.8$ ($\text{C}(\text{NO}_2)_3$), 34.0 (CH_2), 30.8 (CH_2). **¹⁴N NMR** (D_2O): $\delta = -32$ (NO_2) -351 (NH_3^+). **¹²⁷I NMR** (D_2O): $\delta = 4103$ (IO_4^-). **EA:** $\text{C}_3\text{H}_7\text{N}_4\text{O}_{10}\text{I}$ (386.01): calcd. C 9.33, H 1.83, N 14.51%; found C 9.27, H 1.80, N 14.26%. **IR** (ATR): $\tilde{\nu} = 3208$ (w), 3103 (w), 2972 (w), 2937 (w), 2361 (w), 2339 (w), 1586 (vs), 1495 (m), 1469 (m), 1431 (w), 1361 (w), 1314 (m), 1297 (m), 1158 (m), 1143 (m), 1015 (w), 994 (w), 906 (w), 844 (s), 832 (s), 797 (w), 739 (w) 680 (w) cm^{-1} . **Raman** (500 mW): $\tilde{\nu} = 3007$ (3), 2974 (6), 2939 (7), 1618 (4), 1601 (5), 1470 (2), 1432 (4), 1375 (5), 1298 (4), 1167 (2), 1016 (4), 907 (2), 858 (22), 852 (20), 841 (20), 792 (100), 625 (2), 567 (3), 424 (8), 400 (10), 384 (11), 361 (6), 341 (7), 325 (14), 313 (9), 269 (18) cm^{-1} . **Sensitivities** (BAM): impact: 2 J; friction: 9 N; (grain size: <100 μm) **DSC** (5 $\text{K}\cdot\text{min}^{-1}$): 105 °C (mp.), 138 °C (dec.).

Bis(3,3,3-trinitropropyl-1-ammonium) Sulfate Hydrate (2): A solution of silver sulfate (156 mg, 0.5 mmol) in water (25 mL) was poured to a solution of 3,3,3-trinitropropyl-1-ammonium chloride (231 mg, 1.00 mmol) in water (10 mL). After stirring for 1 h under exclusion of light, the filtrate was evaporated to dryness and a yellowish solid was obtained (210 mg, 86%). **¹H NMR** (D_2O): $\delta = 8.26$ (br., 3 H, NH_3), 3.76 (m, 2 H, CH_2), 3.52 (m, 2 H, CH_2). **¹³C NMR** (D_2O): $\delta = 128.0$ ($\text{C}(\text{NO}_2)_3$), 34.0 (CH_2), 30.9 (CH_2). **¹⁴N NMR** (D_2O): $\delta = -26$ (NO_2) -346 (NH_3^+). **³³S NMR** (D_2O): $\delta = -1.5$ (SO_4^{2-}). **EA:** $\text{C}_6\text{H}_{14}\text{N}_8\text{O}_{16}\text{S}\cdot\text{H}_2\text{O}$ (504.29): calcd. C 14.29, H 3.20, N 22.22, S 6.36%; found C 14.05, H 3.57, N 21.34, S 6.69%. **IR** (ATR): $\tilde{\nu} = 2987$ (w), 2940 (w), 2883 (w), 2777 (w), 2695 (w), 2637 (w), 2526 (w), 2360 (w), 2339 (w), 1589 (vs), 1532 (m), 1473 (w), 1425 (w), 1369 (w), 1300 (m), 1197 (w), 1172 (w), 1154 (w), 1099 (s), 1052 (s), 971 (w), 856 (w), 801 (s), 756 (w) cm^{-1} . **Raman** (500 mW): $\tilde{\nu} = 3100$ (4), 3041 (6), 2991 (24), 2948 (29), 2847 (4), 2808 (5), 2730 (4), 1613 (20), 1473 (12), 1427 (11), 1371 (32), 1337 (12), 1303 (25), 1187 (4), 1171 (7), 1158 (9), 1044 (9), 1030 (10), 1004 (10), 973 (67), 932 (4), 910 (12), 859 (102), 802 (7), 757 (4), 742 (4), 636 (9), 563 (10), 469 (7), 416 (39), 404 (44), 380 (40), 362 (27), 346 (30), 295 (12) cm^{-1} . **Sensitivities** (BAM): impact: 6 J, friction: 252 N (grain size: <100 μm) **DSC** (5 $\text{K}\cdot\text{min}^{-1}$): 120 °C (dec.).

Bis(3,3,3-trinitropropyl-1-ammonium) Amino-bis(5-tetrazolate) (3): Dihydrazinium amino-bis(5-tetrazolate) (109 mg, 0.5 mmol) was dissolved in H_2O (5 mL) and cooled to 0 °C. A pre-cooled solution

of 3,3,3-trinitropropyl-1-ammonium chloride (231 mg, 1.0 mmol) and water (1 mL) was added slowly. After 5 minutes an orange precipitate was formed, which was filtered and air dried. The amino-bis(5-tetrazolate) salt **3** was obtained as an orange powder in 31 % yield (85 mg). **¹H NMR** (CD_3OD): $\delta = 8.63$ (br., 3 H, NH_3), 3.70 (m, 2 H, CH_2), 3.41 (m, 2 H, CH_2). **¹³C NMR** (CD_3OD): $\delta = 157.5$ (CN_4^-), 35.5 (CH_2), 32.7 (CH_2). **¹⁴N NMR** (CD_3OD): $\delta = -30$ (NO_2), -355 (NH_3^+). **EA:** $\text{C}_8\text{H}_{15}\text{N}_{17}\text{O}_{12}$ (541.31): calcd. C 17.75, H 2.79, N 43.99%; found C 17.66, H 2.97, N 42.05%. **IR** (ATR): $\tilde{\nu} = 3213$ (w), 3023 (w), 2982 (w), 2941 (w), 2874 (w), 2826 (w), 2510 (w), 2366 (w), 2136 (w), 1733 (w), 1717 (w), 1645 (m), 1586 (vs), 1540 (m), 1506 (s), 1464 (w), 1442 (w), 1421 (w), 1363 (m), 1322 (m), 1295 (m), 1230 (w), 1176 (m), 1154 (w), 1131 (w), 1109 (w) 1050 (m), 1032 (m), 1020 (m), 1006 (m), 909 (w), 854 (w) 797 (s), 736 (m), 693 (w) cm^{-1} . **Raman** (500 mW): $\tilde{\nu} = 3080$ (9), 3039 (11), 2980 (40), 2946 (48), 2900 (13), 2832 (10), 2797 (9), 2103 (6), 1912 (6), 1712 (5), 1664 (10), 1631 (18), 1606 (43), 1581 (54), 1540 (18), 1511 (66), 1473 (16), 1464 (46), 1424 (26), 1366 (71), 1302 (37), 1226 (22), 1204 (5), 1178 (6), 1156 (7), 1148 (6), 1130 (17), 1122 (15), 1069 (68), 1034 (30), 1012 (19), 931 (8), 912 (9), 876 (10) 857 (100), 836 (4), 801 (9), 785 (8), 745 (8), 627 (7), 560 (8), 505 (5), 481 (5), 458 (7), 417 (40), 406 (50) cm^{-1} . **Sensitivities** (BAM): impact: 15 J, friction: 360 N (grain size: <100 μm) **DSC** (5 $\text{K}\cdot\text{min}^{-1}$): 118 °C (dec.).

Supporting Information (see footnote on the first page of this article): General experimental details; NMR and Vibrational spectroscopy details; Crystallographic data; Calculation details.

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