High-nitrogen energetic materials derived from azotetrazolate

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ABSTRACT

The preparation and properties of three unique high-nitrogen materials based on the anion azotetrazolate are described. Cations examined were the ammonium, guanidinium and triaminoguanidinium. These compounds are unique in their gas generating ability with little or no smoke or residue produced. These materials have possible applications as explosives, pyrotechnics, gas generants and low signature propellants.

INTRODUCTION AND RESULTS

Conventional organic energetic materials almost exclusively contain the nitro-group. The nitro-group oxidizes the carbon and hydrogen in the backbone of the molecule to water and oxides of carbon, all of which have very negative heats of formation. Nitro-based explosives typically have heats of formation of approximately zero and therefore all of the energy is derived by the formation of the product gases. Unfortunately, even for highly nitrated molecules, rarely is there enough oxygen to completely oxidize the carbon in the backbone to carbon dioxide. As a result these materials typically produce significant quantities of soot, residue and

smoke from the solid carbon and unoxidized organics produced during detonation or combustion.

High-nitrogen materials, on the other hand, typically have few or no nitro groups and rely on their efficient gas production and also on their high heats of formation for energy release since elemental nitrogen, which has a zero heat of formation, is the major product of decomposition. The limited amounts of carbon and hydrogen in these materials mainly form methane[1] upon decomposition especially when the compounds only contain the elements of carbon, hydrogen and nitrogen. High-nitrogen compounds also produce more gas per gram than most high explosives and; since nitrogen is the major decomposition gas the products are inherently cooler. As a result of these properties high-nitrogen materials offer distinct advantages over conventional energetic materials and may be used as ingredients in pyrotechnics, gas generants and low-signature propellants.

An initial literature survey on high-nitrogen materials showed that some previous work had been done on the azotetrazolate dianion[2] (1). This material was easily made from 5-aminotetrazole as either the sodium or potassium salt. These salts crystallized from aqueous solution as pentahydrates and are completely
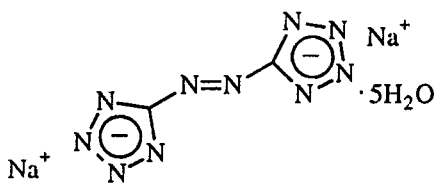
FIGURE 1
Sodium Azotetrazolate pentahydrate

insensitive to impact as hydrates; when dry they are extremely sensitive and dangerous materials. The alkali metal salts were readily converted to the ammonium salt in ammonium hydroxide by salting out the product (2) with ammonium chloride.
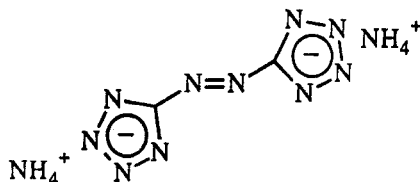
FIGURE 2

Ammonium Azotetrazolate

The ammonium azotetrazolate is not a hydrate and is not hygroscopic. The impact sensitivity is similar to that of RDX. The structure was deduced by x-ray crystallography.[3] This material is capable of producing 979 ml of gas per gram under standard temperature and pressure assuming nitrogen and methane as the products. The properties of ammonium azotetrazolate are given in Table 1.

Table 1: Properties of Ammonium Azotetrazolate

Density (g/cm^3)	1.53
Heat of Formation (kcal/mol)	+106.1
Spark Sensitivity (J)	0.18
Impact Sensitivity (cm, Type 12) (HMX=25)	21.4
Vacuum Stability (ml/g for 48h at 100°C)	0.54
Friction Sensitivity (BAM, kg)	4.4
DTA Exotherm (°C)	190
Detonation Velocity (km/s) (calc.)	7.6
Detonation Pressure (GPa) (calc.)	187

Since the ammonium salt has no oxygen, mixtures with oxidizing agents may enhance performance as an explosive. The only oxidizing agent investigated thoroughly was ammonium nitrate, offering low cost, minimal smoke production and insensitivity. Mixtures of ammonium nitrate and ammonium azotetrazolate were prepared by intimate grinding to give a perfect oxygen balance to carbon dioxide:

$$C_2H_8N_{12} + 8NH_4NO_3 \longrightarrow 2CO_2 + 20H_2O + 14N_2$$
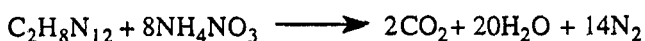
Remarkably, this mixture was less sensitive to impact than pure ammonium azotetrazolate and was calculated (by Tiger) to perform better (see Table 2).

Table 2: Properties of Ammonium Azotetrazolate Mixed with Ammonium Nitrate

Spark Sensitivity (J)	0.25
Impact Sensitivity (cm, Type 12) (HMX=28)	39.5
Vacuum Stability (ml/g for 48h at 100°C)	0.2
Friction Sensitivity (BAM, kg)	Not sensitive at 36 kg
DTA Exotherm (°C)	175
Detonation Velocity (km/s) (calc.)	8.98
Detonation Pressure (GPa) (calc.)	312

The ammonium or sodium salts of azotetrazolate were easily converted to two other high-nitrogen energetic salts, the triaminoguanidinium, and guanidinium. Triaminoguanidinium azotetrazolate (3) was prepared by treating the ammonium salt (2) with triaminoguanidine hydrochloride in aqueous solution. The triaminoguanidinium salt is not a hydrate nor is it hygroscopic.
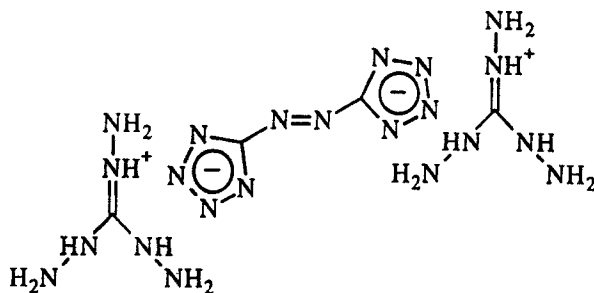
FIGURE 3

Triaminoguanidinium Azotetrazolate

Its thermal and sensitivity properties are very similar to (2) except that the heat of formation was measured to be +257 kcal/mol. The triaminoguanidinium salt is a powerful yet smokeless gas generant, making 981 ml of gas per gram under standard conditions, assuming nitrogen, methane and hydrogen as products. Both (2) and (3) have distinct trigger temperatures at which the conversion of solid to gas is very rapid. This trigger temperature is at the DTA exotherm listed in the tables. The properties of (3) are given in Table 3.

Table 3: Properties of Triaminoguanidinium Azotetrazolate

Density(g/cm^3)	1.602
Heat of Formation (kcal/mol)	+257
Impact Sensitivity (cm, Type 12) (HMX=26)	25
Vacuum Stability (ml/g for 48h at 100°C)	0.25
Friction Sensitivity (BAM, kg)	8.4
DTA Exotherm ($^\circ$C)	195
Detonation Velocity (km/s) (calc.)	9.05
Detonation Pressure (GPa) (calc.)	292

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The guanidinium salt of azotetrazolate (4) was found to be much different from the other salts prepared. In fact (4) has no distinct trigger temperature, burns with smoke, leaves some residue and is more thermally stable, see Table 4. Remarkably it is also completely insensitive to impact. These differences are thought to be caused by two complementary effects. First, the heat of formation is much lower especially considering a normalized value where the molar heat of
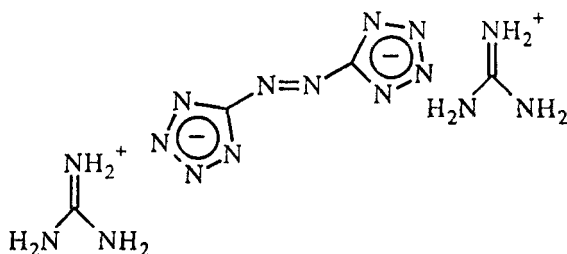
FIGURE 4

Guanidinium Azotetrazolate

formation is divided by the number of atoms in the molecule. Second, the crystal structure revealed that there was some hydrogen bonding between the guanidinium cation and the nitrogen in the azo-linkage. This hydrogen bonding is not present in the other salts.

Table 4: Properties of Guanidinium Azotetrazolate

Density (g/cm^3)	1.538
Heat of Formation (kcal/mol)	+98
Impact Sensitivity (cm, Type 12) (HMX=26)	>320
Vacuum Stability (ml/g for 48h at 100°C)	0.21
Friction Sensitivity (BAM, kg)	Not Sensitive at 36 kg
DTA Exotherm (°C)	240
Detonation Velocity (km/s) (calc.)	7.1
Detonation Pressure (GPa) (calc.)	155

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Mixtures of (4) with ammonium nitrate to make a carbon monoxide balanced mixture (1:10) were prepared and also found to be quite insensitive to impact with a measured value of 252 cm determined (Type 12, HMX=26 cm). This mixture burned smoothly with no smoke or residue produced.

SUMMARY

High-nitrogen energetic materials represent a new and relatively unexplored class of energetic materials. The unique properties of these materials allow their use as gas generants, low signature propellants and pyrotechnics. The ammonium and triaminoguanidinium salts, (2) and (3) seem to be especially suited for use in propellants. As a direct replacement for HMX in composite propellants these materials should give comparable performance and cooler, less reactive and less visible gases. The guanidinium salt (4) has been explored as a replacement for sodium azide in safety equipment.[4] The gases produced would be cool and inert. The material has excellent impact and thermal stability, and the problems associated with toxicity and sodium hydroxide production from sodium azide could be avoided.

EXPERIMENTAL

All reagents were purchased from commercial sources, except where noted. All nmr spectra were obtained on a JEOL GSX-270 spectrometer. Chemical shifts are relative to internal tetramethylsilane for ^{1}H and ^{13}C spectra. The structures of all compounds were verified by x-ray crystallography.[3]

Sodium azotetrazolate pentahydrate (1)

This procedure is based on the original preparation of Thiele[2]. To 300 ml of 2 M sodium hydroxide was added aminotetrazole monohydrate (10.3 g, 0.1

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mol). The temperature was brought to 60°-70°C with stirring and potassium

permanganate (12 g, 0.076 mol) was added slowly, portionwise over 1h. Excess

permanganate was destroyed by slow addition of sodium sulfite with vigorous

stirring. The endpoint of sulfite addition was determined by a color change from an

initial green solution to a yellow solution. The suspended brown solid was

removed by hot filtration and the filter cake washed with boiling water until the

washings were a very light yellow. The bright yellow solution of product was

reduced in volume to 300 ml (reduced pressure) and allowed to crystallize in the

refrigerator overnight. The long yellow needles were then filtered and carefully air

dried to yield 22.5-24 g (75-80%) of pure (1). ^{13}C nmr (deuteriomethyl sulfoxide):

∂ 173.2.

Ammonium azotetrazolate (2)

To 300 ml of concentrated ammonium hydroxide was added sodium

azotetrazolate pentahydrate (20 g, 0.066 mol) with stirring. The temperature was

brought to 30°-35°C and stirring was continued until dissolution was complete.

Ammonium chloride (25 g, 0.467 mol) was added over a 10 min. period with

vigorous stirring. Towards the end of the addition the ammonium azotetrazolate

began to precipitate. The suspension was cooled to 5°C, filtered and air dried to

yield 12.6 g (95%) of pure (2) as a yellow powder. This material does not melt but

rather begins to decompose over 200°C. ^{1}H nmr (deuteriomethyl sulfoxide): ∂

7.35 (bs, 4H); ^{13}C (deuterium oxide): ∂ 171.6.

Triaminoguanidinium azotetrazolate (3)

Ammonium azotetrazolate (5 g, 0.025 mol) was dissolved in the minimum

amount of 80°-90°C water (approximately 60 ml). To this solution was added

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triaminoguanidinium chloride[5] (7.03 g, 0.05 mol) with stirring. The yellow solution was allowed to cool to room temperature and the yellow crystalline solid was filtered and air dried to yield 7.7 g (83%) of (3) mp 196°-197°C (dec.). ^{1}H nmr (deuteriomethyl sulfoxide): ∂ 4.45 (bs, 12H), 8.61 (s, 6H); ^{13}C (deuteriomethyl sulfoxide): ∂ 159.1, 173.4.

Guanidinium azotetrazolate (4)

Sodium azotetrazolate pentahydrate (5 g, 0.0166 mol) was dissolved in the minimum amount of 80°-90°C water (approximately 70 ml) with stirring. To this solution was added guanidine hydrochloride (3.18 g, 0.033 mol). A yellow precipitate formed immediately. The precipitate was digested by boiling the suspension for 2 minutes and then allowed to cool to room temperature. The solid was filtered, washed with water and air dried to give 4.51 g (95%). This material does not melt but rather decomposes over 240°C. ^{1}H nmr (deuteriomethyl sulfoxide): ∂ 7.24 (bs, 12H); ^{13}C (deuteriomethyl sulfoxide): ∂ 158.1, 172.9.

REFERENCES

(1) M. Cowperthwaite and H. H. Zwisler, Tiger Computer Program, NWC IOP-3518, (1973).

(2) J. Thiele, Ann. 303, 57 (1898).

(3) Unpublished Data, R. Gilardi, Office of Naval Research, Washington D.C.

(4) K. M. Bucerius, F.-W. Wasmann and K. Menke, U. S. Patent 5, 198, 046 (1993).

(5) M.D. Coburn, G.A. Buntain, B.W. Harris, M.A. Hiskey, K.-Y. Lee and D.G. Ott, Heterocyclic Chem. 28, 2049 (1991).