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Preparation and Properties of 3-Amino-5-Nitro-1,2,4-Triazole

Los Alamos

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Preparation and Properties of 3-Amino-5-Nitro-1,2,4-Triazole

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PREPARATION AND PROPERTIES OF 3-AMINO-5-NITRO-1,2,4-TRIAZOLE

by

Kien-Yin Lee and Carlyle B. Storm

ABSTRACT

A novel method for the preparation of 3-amino-5-nitro-1,2,4-triazole (ANTA) has been invented. The yield of ANTA by selective reduction of the ammonium salt of 3,5-dinitro-1,2,4-triazole with hydrazine hydrate is 94% to 96% under mild reaction conditions. There is no volatile hydrazine present at the end of the reaction as it is isolated as hydrazine hydrochloride. ANTA, a potential insensitive explosive, has a crystal density of 1.82 g/cm^3, and a positive heat of formation (ΔH_f) of 21.0 kcal/mol, and is thermally stable. The detonation velocity of ANTA, calculated at crystal density, is higher than that of triaminotrinitrobenzene. In addition to the preparation of ANTA, we have also synthesized a new hydrazinium salt of ANTA.

I. INTRODUCTION

In the past, the common explosives RDX, HMX, and TNT were considered adequate for all weapons applications. Because of the many catastrophic explosions resulting from unintentional initiation of munitions, by either impact or shock, aboard ships, aircraft carriers, and ammunition trains, these explosives have become less attractive.

Triaminotrinitrobenzene (TATB), an explosive developed at Los Alamos, is noted for its insensitivity and is currently employed for insensitive high-explosive (IHE) applications in nuclear weapons. Another explosive developed at Los Alamos, 3-nitro-1,2,4-triazol-5-one (NTO)[1], is being evaluated as an insensitive substitute for RDX in bomb fills by the Navy. Unfortunately, neither TATB nor NTO produces sufficient performance to replace HMX in some applications. Therefore, the search for other new, powerful insensitive explosives continues.

ANTA (3-amino-5-nitro-1,2,4-triazole) was first described by workers in the USSR as an end product from the nitration of acetamidotriazole with acetyl nitrate, followed by acid hydrolysis.[2] No properties or use as an explosive was reported. We have prepared a sufficient amount of ANTA for preliminary characterization and sensitivity tests. It was found that ANTA is thermally stable and insensitive in the drop-weight impact test. Because the yield of ANTA from the Soviet procedure is too low to be economically feasible for large-scale production, we have studied alternative methods of preparing ANTA for performance testing.

In this report, a novel method of preparing ANTA will be described. The physical and explosive properties of ANTA obtained from characterization and small-scale sensitivity tests will also be listed.

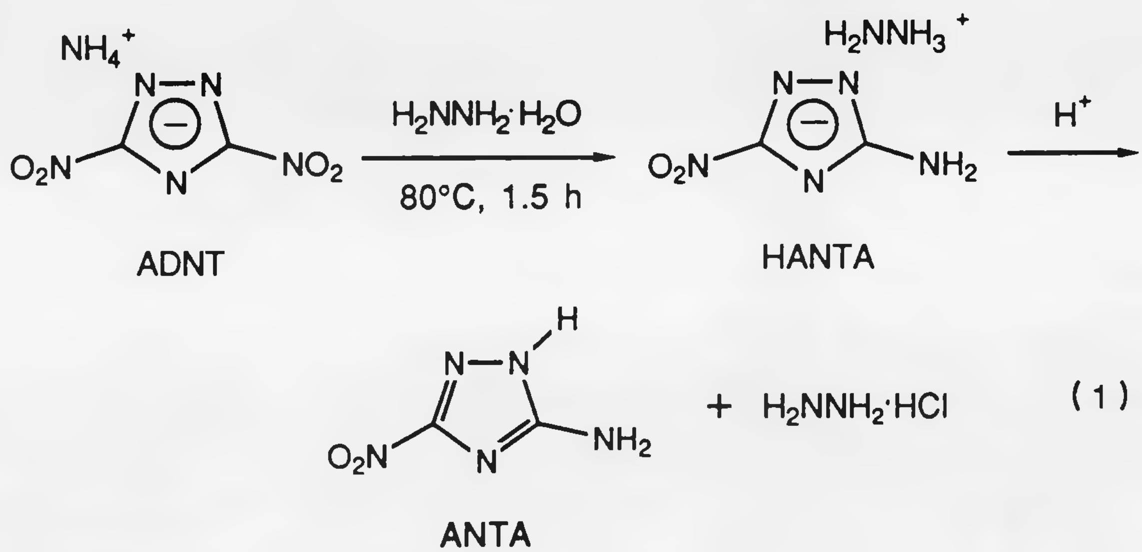
II. SYNTHESES

Sodium sulfide was reported to be employed in the selective reduction of nitro-to-amino compounds.[3-4] We have investigated the preparation of ANTA by reacting the ammonium salt of 3,5-dinitro-1,2,4-triazole (ADNT)[5] and sodium sulfide in an aqueous solution. The yield of ANTA by this approach was only 60% or less, and the separation of ANTA from other sulfide by-products was tedious.

In an attempt to improve the yield of ANTA, the reduction of ADNT with hydrazine hydrate was studied.[6] It was found that ANTA can be prepared in greater than 94% yield under moderate reaction conditions.

A. Preparation of ANTA

To a stirred solution of hydrazine hydrate (1.87 ml, 0.0385 mol) is added ADNT (1.45 g, 0.0082 mol) at room temperature. After the mixture is stirred for 10 minutes, the temperature of the reaction mixture is raised to 78-80°C over an oil bath, and the reaction continues for 1.5 hours. After cooling to room temperature, the resulting mixture is diluted with water and adjusted to pH 4.0 with 10% hydrochloric acid. The precipitated ANTA is filtered and dried at high vacuum to yield 0.99g (94%). (Reaction 1)



(1)

The completion of the reaction is monitored by silica gel TLC (thin-layer chromatograph) analysis. The solvent system used for ANTA spot development is methylene chloride:ethanol/5:1 (v/v) and a few drops of acetic acid. The TLC spots are observed with UV light. The ANTA is determined by both ^{13}C and ^{15}N NMR analysis to be free of impurities.

B. Preparation of HANTA

If the reaction product in Reaction 1 was isolated before it was adjusted to pH 4.0, the compound thus obtained is identified to be the hydrazinium salt of ANTA (HANTA).

III. PROPERTIES

A. Properties of ANTA

ANTA is a lemon-colored crystalline compound, has little solubility in water, and is not hygroscopic. The result of small-scale screening tests of ANTA, together with its physical properties, are tabulated in Table 1. Those of TATB are also listed for comparison.

Table 1 Physical and Explosive Properties

	ANTA	TATB
Molecular Formula	$C_2H_3N_5O_2$	$C_6H_6N_6O_6$
Crystal Density (g/cm^3)	1.82	1.94
Melting Point (°C)	244	448-449
Thermal Stability (°C) DTA	>240	>350
Vacuum Stability (ml/g/48 h/120°C)	0.3	0.2
Impact Sensitivity (cm), Type 12	>320	>320
Spark Sensitivity (J) (3-mil foil)	>0.1	4.25
Heat of Formation (ΔH_f) (kcal/mol)	21.0 ± 2.5	-36.85
D (km/s) (at crystal density)	8.46 (calc.)	7.98 (calc.)
Pcj (kbar) (at crystal density)	314 (calc.)	315 (calc.)

B. Properties of HANTA

HANTA is not stable. When left in the hood at room temperature for a few days or heated at 100°C for 10 minutes, it loses the hydrazine molecule, and ANTA is recovered. Some of the physical and explosive properties of HANTA are listed in Table 2.

Table 2 Physical and Explosive Properties of HANTA

Molecular Formula	$C_2H_7N_7O_2$
Crystal Density (g/cm^3)	1.62
DTA Stability (Endotherm) (°C)	130
Impact Sensitivity (cm), Type 12	>320
Preliminary Spark Sensitivity (J) (3-mil foil)	>0.1

IV. DISCUSSION AND FUTURE WORK

A novel method for the preparation of ANTA by selective reduction of ADNT with hydrazine hydrate has been achieved. The reaction proceeds at moderate reaction conditions, no special apparatus is required, and large-scale production is feasible. Another unique feature of this reaction is that no volatile hydrazine is present at the end of the reaction. The excess hydrazine exists as hydrazinium hydrochloride salt in the final solution. Therefore, it is conceivable that this procedure will be safe for the environment, even though hydrazine hydrate is involved in the reduction reaction (see Reaction 1).

Although the crystal density of ANTA is lower than TATB, the detonation velocity of ANTA, calculated at crystal density, is greater than that of TATB (see Table 1). It appears that ANTA could be substituted for TATB in some applications in which a higher detonation velocity is required.

We plan to carry out performance and large-scale sensitivity tests on ANTA, and to prepare new ANTA derivatives that might have desirable explosive properties for military and industrial applications. A nitro-pyrimidine derivative of ANTA, patented by CEA of France, was reported to have a detonation velocity of 8.6 km/s.

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