High-Nitrogen Pyrotechnic Compositions[1]

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ABSTRACT

Pyrotechnics produce irritating and obscuring smoke. High-nitrogen materials have been investigated for use in pyrotechnic compositions to reduce smoke production. Compositions containing dihydrazino-tetrazine have been found to produce brilliantly colored flames with little or no smoke or ash production. The preparation of dihydrazino-tetrazine is also discussed.

Keywords: low smoke pyrotechnics,
high-nitrogen energetic materials,
dihydrazino-tetrazine

Introduction

Almost all pyrotechnic compositions produce smoke. The smoke is derived from two main sources. Partial combustion of fuels accounts for a certain amount of the smoke, as rarely is the mixture's oxygen balance sufficient for complete combustion. Metals account for most smoke. Metal compounds are used in pyrotechnics as both oxidizers [e.g., $KClO_4$, KNO_3] and as coloring agents [e.g., $Sr(NO_3)_2$, $Ba(NO_3)_2$, Na_3AlF_6, CuS]. Except in instances where smoke is specifically required, it is generally a nuisance. Spectators typically find smoke to be irritating to the nose and eyes, and smoke also obscures the display.

Metal compounds in pyrotechnics cannot be avoided. Fortunately, lead, mercury and arsenic compounds are typically not used in modern compositions, but metal salts as flame colorants are widely used in concentrations of 20% to 60% by weight. Drastic reduction of metal-salt, flame-coloring agents would result in a much cleaner burning composition but is usually not possible, as depth of color would suffer. Thus, pyrotechnic formulators are faced with a dilemma, as they are required to strike a delicate balance between color quality and excessive smoke. Indoor displays are further complicated by the simple fact that the smoke is contained in the room. Reduction of metal compounds in pyrotechnics for indoor displays would reduce exposure of cast, crew and audience to such toxic metals as copper, strontium, barium and antimony.[2]

Results

At Los Alamos National Laboratory, we have been involved with the preparation of high-nitrogen energetic materials for use as explosives[3] and gas generants[4] as well as pyrotechnic ingredients. When ignited, high-nitrogen fuels typically exhibit an almost colorless flame and produce no smoke or ash. For use as a pyrotechnic ingredient, a high-nitrogen material must have the proper ratio of carbon, hydrogen and nitrogen as well as an appropriate ambient pressure burn rate.

After examination of a large number of materials, including nitroguanidine, guanidine nitrate, aminoguanidine nitrate, and 3,6-diamino-1,2,4,5-tetrazine, we found that 3,6-dihydrazino-1,2,4,5-tetrazine (Figure 1) (abbreviated Hz_2Tz) gave easily ignited, brilliantly colored flames when mixed in the proper proportions with oxidant and coloring agent. More importantly, these mixtures produced no smoke and little or no ash.

It was found that two equivalents of available oxygen from the oxidant were required for

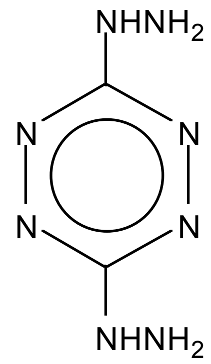

Figure 1. Hz_2Tz.

sustained burning of Hz_2Tz. The only oxidants examined were ammonium perchlorate (NH_4ClO_4, AP) and ammonium nitrate (NH_4NO_3, AN). These oxidants were examined as they contain no metals.

Flame coloring agents were the commonly used metal salts with the exception of blue (copper) where it was noticed that water soluble copper salts were powerful burn rate accelerants for Hz_2Tz. Copper(II) sulfide (CuS) was found to give an acceptable blue-colored flame with only a slight increase in burning rate. The levels of colorant were 5 weight percent for AP formulations and 8 weight percent for AN formulations. A small amount of AP is added to the AN formulations as a source of chloride to deepen flame colors.

The mixtures contain no binder. The AP formulations were simply wet with water, pressed to shape in a simple hand press and air-dried. The consolidated material appeared to be strong enough for use as stars in aerial shells. It was not possible to use water in the AN formulations due to the hygroscopic nature of this oxidant. These mixtures were wet with ethanol or isopropanol before being hand pressed to shape, and air dried. AN pieces were much more fragile than AP pieces and more difficult to ignite; thus, they were primed, strengthened, and waterproofed by dipping in nitrocellulose lacquer of the type used to coat Visco® safety fuse. AN formulations which contained strontium exhibited strobing at about 2–3 Hz. Two rarely seen pyrotechnic colors are easily achievable using Hz_2Tz as fuel. One is a deep red-purple strobe with AN as oxidant and strontium nitrate and copper(II) sulfide as colorants. A deep turquoise is also made using AP as oxidant and copper(II) sulfide and barium nitrate as colorants.

Synthesis of Hz_2Tz

Hz_2Tz has been known in the literature since 1963.[5] Its preparation was somewhat tedious in that it involved hydrazinolysis of diaminotetrazine at elevated temperature.[6] We have a much simplified procedure utilizing the readily available 3,6-bis(3,5-dimethylpyrazol-l-yl)-1,2-dihydro-1,2,4,5-tetrazine (abbreviated BDDT) which is made from triaminoguanidine hydrochloride and 2,4-pentanedione.[7]

Stirring the BDDT with 2 equivalents of hydrazine hydrate at room temperature with exposure to atmospheric oxygen results in both aromatization and nucleophilic displacement to yield Hz_2Tz in a 92% yield (Figure 2). Hz_2Tz is a very insoluble bright red powder that has a fifty percent drop height of 65 cm (Type 12). Black Powder has a drop height of 32 cm. Hz_2Tz has a heat of formation of +128 kcal/mol as determined by combustion calorimetry. A flotation density of 1.69 g/cm^3 and differential thermal analysis (DTA) exotherm at 160 ºC were also measured.

Experimental

The following procedure should only be attempted by those experienced and equipped in energetic materials synthesis with proper laboratory facilities. Materials used are toxic and flammable. Hydrazine and its derivatives should be regarded as possible carcinogens. All reagents were purchased from commercial sources except where noted. Nuclear magnetic resonance (nmr) spectra were obtained on a JEOL GSX-270. Chemical shifts are relative to internal tetramethylsilane for ^1H and ^{13}C spectra.

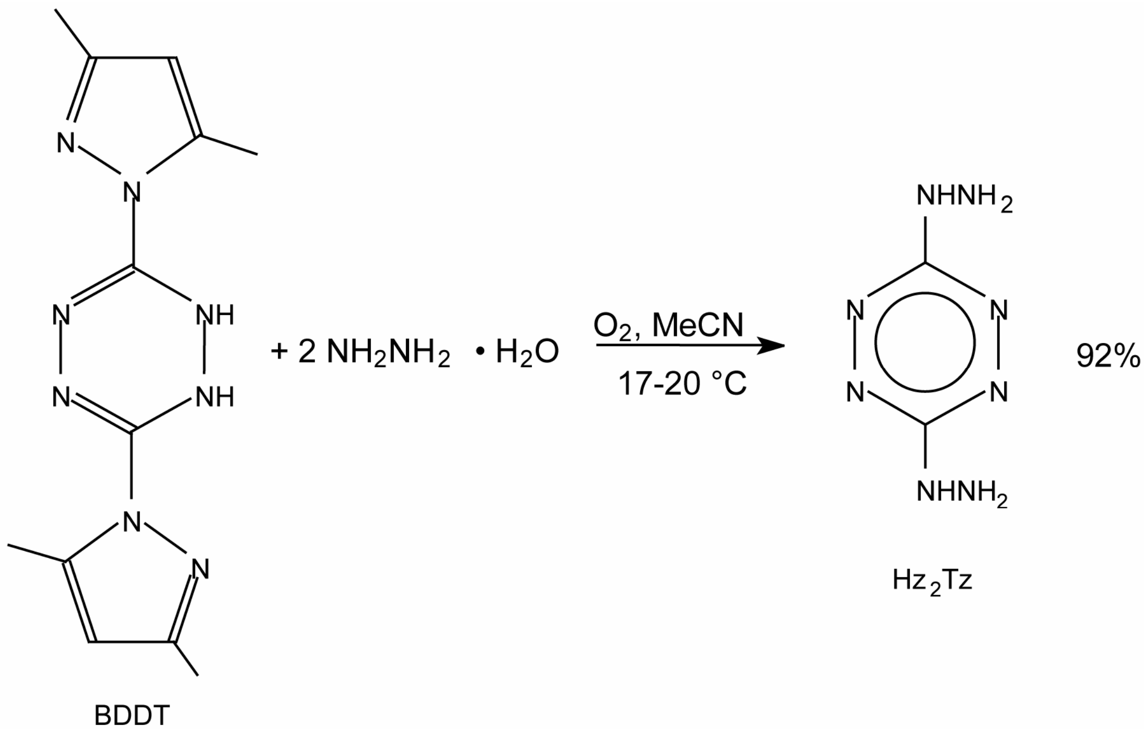

Figure 2. Preparation of Hz_2Tz.

3,6-Dihydrazino-1,2,4,5-tetrazine

The following procedure should be only attempted by those experienced in the synthesis of energetic materials. Proper laboratory facilities are essential. To a 500 ml three-necked jacketed flask equipped with a mechanical stirrer is added 54.5 g of 3,6-bis(3,5-dimethyl-pyrazol-l-yl)-1,2-dihydro-1,2,4,5-tetrazine (0.2 mol) and 300 ml acetonitrile. The temperature of the bath is reduced to 12 ºC and 21 g hydrazine hydrate (0.42 mol) is added dropwise with stirring. After the addition, the funnel is removed and the mixture is stirred 48 h at 17–20 ºC with exposure to air in which time a maroon red precipitate forms. This is filtered off on a glass frit, washed with acetonitrile and air dried yielding 26.1 g (92 %). This material is identical in all respects to that previously reported.[6,7] ^{1}H nmr (deuteriomethylsulfoxide) δ 4.26 (bs, 4H), 8.39 (s, 2H). ^{13}C nmr (deuteriomethylsulfoxide) δ 164.0

Warning: The long term stability of Hz_2Tz and Hz_2Tz mixed with oxidants is excellent. However, the stability of Hz_2Tz with transition metals is suspected to be somewhat less but has not yet been proven. A blue AN-based star was reported to have spontaneously ignited.[8]

Ammonium Perchlorate Compositions

The ammonium perchlorate formulations had the following compositions by weight:

AP	47.5 %
Hz_2Tz	47.5 %
colorant	5.0 %

Colorants:

Red		$Sr(NO_3)_2$ or $CaCl_2$
Yellow		$NaNO_3$
Green		$Ba(NO_3)_2$
Blue		CuS
Blue-Green	8:1	$Ba(NO_3)_2$:CuS
Purple	2:1	CuS:$Sr(NO_3)_2$
Red Purple	1:1:3	CuS:$Ba(NO_3)_2$:$Sr(NO_3)_2$
White		Sb_2S_3

All ingredients were thoroughly ground together, dampened with water, pressed to shape and air-dried. The only exceptions to the above AP compositions were the white and blue.

White stars doubled the Sb_2S_3 concentration to 10% while blue had the following composition: 50% Hz_2Tz, 41% AP, 9% CuS.

Ammonium Nitrate Compositions

The ammonium nitrate formulations had the following compositions by weight:

Hz_2Tz	45%
AN	38%
AP	8%
colorant	8%

All ingredients were thoroughly ground together, wet with alcohol, pressed to shape, air dried, dipped in nitrocellulose lacquer and redried. Blue stars utilized CuO rather than CuS as a somewhat deeper color was obtained.

Conclusion

Pyrotechnic compositions containing Hz_2Tz have been shown to burn with little or no smoke. The formulations have comparable or deeper coloration with a lower concentration of metals. Novel colors are also possible using Hz_2Tz as fuel. The preparation of Hz_2Tz has been simplified and improved over previous methods.

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