



Factors affecting the intramolecular decomposition of hexamethylene triperoxide diamine and implications for detection



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ABSTRACT

Hexamethylene triperoxide diamine (HMTD) is an easily synthesized and highly sensitive organic peroxide frequently used as a primary explosive. The vapor pressure of HMTD is very low, impeding vapor detection, especially when compared to other peroxide explosives, such as triacetone triperoxide (TATP) or diacetone diperoxide (DADP). Despite this fact, HMTD has a perceptible odor that could be utilized in the indirect detection of HMTD vapor. Headspace measurements above solid HMTD samples confirm that HMTD readily decomposes under ambient conditions to form highly volatile products that include formic acid, ammonia, trimethylamine and formamides. The presence and quantity of these compounds are affected by storage condition, time, and synthetic method, with synthetic method having the most significant effect on the content of the headspace. A kinetic study of HMTD decomposition in solution indicated a correlation between degradation rate and the presence of decomposition species identified in the headspace, and provided further insight into the mechanism of decomposition. The study provided evidence for a proton assisted decomposition reaction with water, as well as an intramolecular decomposition process facilitated by the presence of water.

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1. Introduction

Improvised explosives can be comprised of any of a number of different chemical compounds and mixtures, resulting in an extremely diverse range of associated physical and chemical properties. Energetic compounds generally have extremely low vapor pressures that push the limits of state-of-the-art detection capabilities. Due in part to their high sensitivity, ion mobility spectrometers (IMS) have been successfully deployed for the detection of low-volatility explosive analytes, and research to improve this technology is still ongoing. IMS instruments in the field, however, require the collection of explosives particulates from contaminated surfaces, typically through the use of swipes, prior to introduction to the unit for desorption and analysis [1,2]. The detection of vapors would be a much more attractive approach, if feasible, since it eliminates contact sampling and is more amenable to

detecting packaged or buried explosives. New sensing technologies are emerging that can sensitively detect low volatility analytes while still being selective towards the specific functional groups accompanying the various types of explosives and/or contaminants or decomposition products that comprise a characteristic vapor signature [3–7]. Regardless of the detector technology used, it is imperative that sensor developers fully understand the complex vapor mixtures arising from specific explosive compounds in order to optimally develop appropriate transducers.

Hexamethylene triperoxide diamine (HMTD) is an example of a low-volatility explosive compound that has a distinct odor, perceptible even to the human nose. HMTD is similar to triacetone triperoxide (TATP) in that it is a primary peroxide explosive that is easily synthesized from readily available precursor materials, but the two compounds otherwise demonstrate divergent properties. TATP has a moderately high vapor pressure (2.4×10^{-4} at. to 8.7×10^{-5} at.) [8] and is thermally stable when compared to HMTD [9], making sample collection, thermal desorption and direct detection by conventional analytical instrumentation or vapor sensors straightforward. Direct detection of HMTD is much more challenging due to its exceedingly low vapor pressure (estimated to be near 3×10^{-7} at. [10,11]), the actual value of which is still somewhat

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Table 1
Estimated vapor pressures, reported in the literature, of selected explosives compounds [8].

Explosive	Estimated vapor pressure (atm, 25 °C)
Nitromethane	4.8×10^{-2}
TATP	2.4×10^{-4} to 8.7×10^{-5}
Trinitrotoluene (TNT)	2.1×10^{-7} to 4.0×10^{-9}
HMTD	3×10^{-7}
1,3-trinitroperhydro-1,3,5-triazine (RDX)	8.0×10^{-10} to 3.1×10^{-12}

disputed, owing to the difficulty of measuring the vapor pressure of this compound. For comparison, the vapor pressures of several explosive compounds are listed in Table 1 [8]. HMTD was not observed in the gas phase by thermolysis experiments, apparently due to its low volatility, but also potentially because of intramolecular reactions that occur in the condensed phase [12]. Due to its thermal instability and the ease by which HMTD decomposes into smaller, more volatile compounds, the indirect detection of HMTD vapor is plausible as an alternative to detection of gas-phase HMTD.

The vapor signature, or mixture of volatile decomposition products found in the headspace of HMTD at elevated temperatures, has been reported to contain *N,N*-dimethylformamide, *N,N'*-methylenbisformamide and hexamine, but the presence of trimethylamine gives HMTD a very distinct “fishy” odor [13]. It is unknown what factors affect the decomposition of HMTD into these volatile components, and the mechanisms responsible for formation and decomposition have, thus far, only been postulated [9,14]. HMTD is a unique and interesting molecule with two parallel bridgehead nitrogens that are sp^2 hybridized and, thus, planar [15]. The geometry of HMTD creates a high degree of internal strain in the molecule, contributing to its overall sensitivity. The strain is also responsible for a low-temperature decomposition mechanism that seems to favor an ionic pathway, resulting in C–N bond cleavage rather than O–O bond hemolysis, which is frequently observed in peroxide molecules [9,12].

The study discussed here has been conducted to satisfy two primary objectives. First, a headspace monitoring experiment was designed to identify and quantify the volatile species encountered in the headspace above solid HMTD. This information is critical in identifying target analytes for detection by sensors. Secondly, the decomposition of HMTD dissolved in acetonitrile was monitored to provide further insight into the mechanisms and conditions necessary for volatile decomposition product evolution. A fundamental understanding of HMTD decomposition will permit optimal targeting of characteristic vapor components comprising an HMTD source, in addition to providing characterization laboratories with accurate methodologies for generating vapor sources that properly mimic the fingerprint volatile profile emanating from an HMTD source.

2. Materials and methods

2.1. Bulk HMTD

The decomposition of HMTD was considered both as a solid material and dissolved in solution. Solid HMTD samples were provided by Tripwire Operations Group, LLC (Gettysburg, PA) and the Federal Bureau of Investigation, Explosives Unit (FBI-EU, Quantico, VA). Two batches were obtained from Tripwire: the first was synthesized from laboratory-grade materials, and the second from commercially available materials, mimicking clandestine synthesis. The clandestine material was catalytically prepared using citric acid, while the laboratory-grade material used HCl. Following synthesis, the material was simply rinsed with water until the pH was neutralized. Additional material obtained from the FBI-EU was also

Table 2
Selected synthesis parameters for bulk HMTD batches used in headspace and solution analysis.

Batch	Manufacturer	Material source	Catalyzing acid	Rinse
1	Tripwire	Commercial/clandestine	Citric acid	Water
2	Tripwire	Laboratory-grade	HCl	Water
3	FBI-EU	Laboratory-grade	Citric acid	Water/methanol

made from laboratory-grade starting components with citric acid as the catalyst, though this batch was rinsed with both water and methanol. These synthetic parameters are summarized in Table 2.

2.2. HMTD safety and handling

WARNING! HMTD is a primary explosive that is sensitive to external stimuli, such as heat, friction, and electrostatic discharge. Standard operating procedures were developed for the handling of HMTD during this work. Upon receipt, all solid HMTD samples (250 mg, each in separate vials) were stored in 28.71 mL polypropylene, static dissipative vials (ESD Plastic Containers, Yorba Linda, CA), held within a Department of Transportation (DOT) approved container (MK 663), and placed in an explosion-proof safe at ambient temperature. When removing HMTD from storage for experimentation, a second certified person was always present in addition to the certified explosives handler. All experiments were carried out from behind an Explosives Personnel Shield (certified to net explosive weight of 3.0 g). Confirmation of the absence of lightning within 30 nautical miles was ensured prior to and during all operations.

2.3. Experimental method

2.3.1. Headspace analysis

The accumulation of volatile decomposition products in the headspace of solid HMTD was monitored biweekly, over a three month period, using solid phase microextraction (SPME) with gas chromatography/mass spectrometry (GC/MS). Bulk material was divided into 250 mg aliquots and stored in polypropylene vials at ambient temperatures. The bulk materials were prepared in triplicate. Samples were categorized by their synthetic ingredients and preparation methods (i.e. clandestine with water rinse; laboratory-grade with water rinse; or laboratory-grade with water/methanol rinse).

During headspace extraction, each sample was held separately within a custom-built stainless steel sampling chamber previously developed for headspace sampling of explosives [16]. Samples were enclosed in the chamber for 1 h prior to sampling. At the time of sampling, a small orifice (1/16”) was opened for insertion of the SPME fiber. Divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) fibers (24 Ga, 50/30 μ m, Sigma-Aldrich, St. Louis, MO) were used with headspace extraction times of 1 h. Equilibration and headspace extraction were performed under ambient conditions with no airflow. Following the completion of the headspace extraction, each sample was flushed with either clean dried air or clean humidified (~80% RH) air. After flushing, the samples were immediately closed, wrapped with parafilm, and stored at ambient conditions until the next sampling.

Triplicates of all samples were prepared and sampled consecutively. Blank vials were sampled in the same manner for comparison. Data is reported as mass (ng) detected, and was determined by comparison to an external calibration curve. Calibration curves were prepared by dilution of analytical-grade chemicals (Sigma-Aldrich) in the appropriate solvent at five calibrant concentrations. Calibrants were injected as liquid solutions into the GC/MS using the same method as used for SPME analysis, discussed below.

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