

**CYCLIC ORGANIC PEROXIDES IDENTIFICATION AND TRACE
ANALYSIS BY RAMAN MICROSCOPY AND OPEN-AIR
CHEMICAL IONIZATION MASS SPECTROMETRY**

By

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Abstract

The persistent use of cyclic organic peroxides in explosive devices has increased the interest in study these compounds. Development of methodologies for the detection of triacetone triperoxide (TATP) and hexamethylene triperoxide diamine (HMTD) has become an urgent priority. However, differences in physical properties between cyclic organic peroxides make difficult the development of a general method for peroxide analysis and detection.

Following this urgency, the first general technique for the analysis of any peroxide, regarding its structural differences is reported. Characterization and detection of TATP and HMTD was performed using an Open-Air Chemical Ionization High-Resolution Time-of-Flight Mass Spectrometer. The first spectrometric analysis for tetramethylene diperoxide dicarbamide (TMDD) and other nitrogen based peroxides using Raman Microscopy and Mass Spectrometry is reported. Analysis of cyclic peroxides by GC-MS was also conducted to compare results with OACI-HRTOF data.

In the OACI mass spectrum, HMTD showed a clear signal at m/z 209 MH^+ and a small adduct peak at m/z 226 $[M+NH_4]^+$ that allowed its detection in commercial standard solutions and lab made standards. TMDD presented a molecular peak of m/z 237 MH^+ and an adduct peak of m/z 254 $[M+NH_4]^+$. TATP showed a single peak at m/z 240 $[M+NH_4]^+$, while the peak of m/z 223 or 222 was completely absent. This evidence suggests that triperoxides are stabilized

by the ammonium ion. TATP samples with deuterium enrichment were analyzed to compare results that could differentiate from HMTD.

Raman microscopy was used as a complementary characterization method and was an essential tool for cyclic peroxides identification, particularly for those which could not be extensively purified. All samples were characterized by Raman spectroscopy to confirm the Mass Spectrometry results. Peroxide O-O vibrations were observed around 750-970 cm^{-1} . D₁₈-TATP studies had identified ketone triperoxide $\nu(\text{O-O})$ vibration around 875 cm^{-1} in Raman. HMTD and TMDD shared $\nu(\text{O-O})$ vibration around 912 cm^{-1} (HMTD: 910 cm^{-1} ; TMDD: 914 cm^{-1}). Some of the vibrations identified were $\nu(\text{CH})$ {3000-2930 cm^{-1} }, $\nu(\text{C-O})$ {1000-1100 cm^{-1} }, $\delta(\text{CH-C})$ {1470-1400 cm^{-1} }, $\nu(\text{N-C})$ {1370 cm^{-1} }, and $\nu(\text{N-H})$ {3340 cm^{-1} }. Both Raman microscopy and OACI-mass spectrometry represent excellent alternatives to be used sensitive checkpoints and forensic laboratories.

Resumen

El uso persistente de peróxidos orgánicos cíclicos en artefactos explosivos ha aumentado el interés en estudiar estos compuestos. Desarrollo de metodologías para detectar triperóxido de triacetona (TATP) y triperóxido diamina de hexametileno (HMTD) se ha convertido en una prioridad urgente. Sin embargo, diferencias en propiedades físicas entre los peróxidos orgánicos cíclicos dificultan el desarrollo de un método generalizado para el análisis y detección de peróxidos.

Siguiendo esta urgencia, se presenta la primera técnica general para el análisis de cualquier peróxido sin importar sus diferencias estructurales. La caracterización y detección de TATP y HMTD se realizó usando Espectrometría de Masas de Tiempo-de-Vuelo de Alta Resolución (HR-TOF) con Ionización Química al Aire-Libre (OACI). Se informa también sobre el primer análisis espectrométrico de diperóxido dicarbamida de tetrametileno (TMDD) y otros peróxidos basados en nitrógeno mediante microscopia Raman y espectrometría de masas. El análisis de peróxidos cíclicos fue también llevado a cabo por GC-MS para comparar los resultados obtenidos con OACI-HRTOF.

En el espectro de masas con OACI, HMTD mostró una señal clara a m/z 209 MH^+ y un pequeño pico de un aducto de m/z 226 $[M+NH_4]^+$ que permitió su detección en soluciones comerciales estándar y soluciones estándar hechas en el laboratorio. TMDD presentó un pico molecular de m/z 237 correspondiente a $[M+H]^+$ acompañado de su aducto a m/z 254 $[M+NH_4]^+$. TATP evidencio un solo

pico a m/z 240 $[M+NH_4]^+$. Los picos de m/z 223 o 222 estaban completamente ausentes. Esta evidencia apunta al hecho de que los triperóxidos se estabilizan con el ión de amonio. Muestras de TATP enriquecidas con deuterio fueron analizadas y comparadas con HMTD para poder diferenciar los resultados.

Usado como un método complementario, la microscopía Raman fue esencial para la identificación de peróxidos orgánicos. Todas las muestras fueron caracterizadas por espectroscopía Raman para confirmar los resultados de espectrometría de masas. Las vibraciones peróxido O-O fueron observadas alrededor de los $750-970\text{ cm}^{-1}$. Los estudios con D_{18} -TATP pudieron identificar la vibración $\nu(O-O)$ de los triperóxido de cetona cerca de los 875 cm^{-1} en Raman. HTMD y TMDD comparten ésta $\nu(O-O)$ vibración alrededor de 912 cm^{-1} (HMTD: 910 cm^{-1} ; TMDD: 914 cm^{-1}). Otras de las vibraciones observadas fueron $\nu(CH)\{3000-2930\text{ cm}^{-1}\}$, $\nu(C-O)\{1000-1100\text{ cm}^{-1}\}$, $\delta(CH-C)\{1470-1400\text{ cm}^{-1}\}$, $\nu(N-C)\{1370\text{ cm}^{-1}\}$, y $\nu(N-H)\{3340\text{ cm}^{-1}\}$. Juntos microscopía Raman y espectrometría de masas con OACI representan alternativas excelentes para ser usadas en centros de cotejo sensitivos y laboratorios forenses.

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*This work is dedicated to my wife Maly and her family, to my father Álvaro and to my mother Doralba.
For your unconditional love, help and support even at difficult times*

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CHAPTER I

Introduction

Interest in cyclic organic peroxides has increased in recent years, due to their constant use in improvised explosive devices (IED) ^{1,2}. Since their early preparations, their instability and sensitivity has been documented ³. However, their multiple applications, such as in medicine ⁴⁻⁶ and in polymer synthesis ^{7,8}, has increased the interest in the development of new peroxides. One of the oldest cyclic peroxides known is hexamethylene triperoxide diamine (HMTD) ^{9,10}. Since it was first synthesized by Legler ⁹ in 1882, it has become one of the most studied cyclic peroxides due to its interesting cage structure ^{10,11}, potential as antimalarials ^{4, 12}, and recently by its strong explosive power ¹³⁻¹⁸. Other well known cyclic peroxides are triacetone triperoxide (TATP) and diacetone diperoxide (DADP) ¹⁹. After their first syntheses by Wolffenstein ¹⁹ in 1895, their simple method of preparation was evident ³. This characteristic of acetone peroxides, along with their high explosive power, became a major problem for security agencies ²⁰⁻²².

In the last decade, cyclic peroxyacetones began to appear in several terrorist cases in Israel, Europe, and United States ^{20,21,23}. National Security agencies discovered that peroxides such as TATP and HMTD have been used by terrorist movements ²⁴⁻²⁶ and current explosive detection technology have certain limitations for their detection ^{18,27-34}. Most explosive detection equipment available at airport check points, such as ion mobility spectrometers (IMS) and gas chromatography-chemiluminescence detectors are designed to detect nitro

groups (NO_x) in explosives^{30,35}. IMS allows fast, highly sensitive and specific detection, and it has been shown to detect TATP and hexamethylene triperoxide diamine (HMTD) by analyzing their decomposition products formed at the high temperature of the sample inlet port^{30,36-39}. TATP can only be detected in positive mode using IMS, however most nitroexplosives are analyzed in negative mode^{30,36-38}. HPLC is an excellent technique for forensic analysis in post blast detection, with plenty of time to analyze the explosives, but it is too slow for explosives detection at security check-points, especially when used for the confirmation of the peroxides, which may require the use of MS/MS as Xu demonstrated¹⁵. GC/MS offers high sensitivity and structural information; however, previous works have reported that TATP and HMTD analysis by GC/MS presented problems with polar columns, which became deactivated, limiting the selectivity due to other compounds showing similar fragmentation patterns^{18,27}. Use of non-polar columns reported relatively high detection limits, but the methods have been adapted to avoid thermal decomposition and are slow for fast screening^{35,40-42}.

Open-Air Chemical Ionization (OACI) is one of the most novel methods of atmospheric pressure ionization mass spectrometry^{1,3}. With substantial simplicity, metastable helium or nitrogen atoms are used to generate ionic water clusters that produce the reactions that ionize molecules before entering the mass spectrometer orifice^{4,5}. The recent advances in time of flight (TOF) mass spectrometry allow identifying any organic compound by its high resolution and sensitivity. This combination of these equipments permits to detect organic

compounds with immediate results and little sample preparation⁶⁻⁸. The following work presents the development of Open-Air Mass Spectrometry methodology for the analysis and trace detection of energetic organic peroxides. This research also shows a complementary technique for peroxide characterization and identification by Raman microscopy. Ionization mechanism for OACI are proposed and compared with common electron ionization (EI). The work also was focused on the study of common cyclic peroxides, such as benzoyl peroxide, TATP, and HMTD, and uncommon peroxides like tricyclopentylidene triperoxide and tetramethylene diperoxide dicarbamide (TMDD). Figure 1 shows the structures of the most relevant cyclic peroxides during this research.

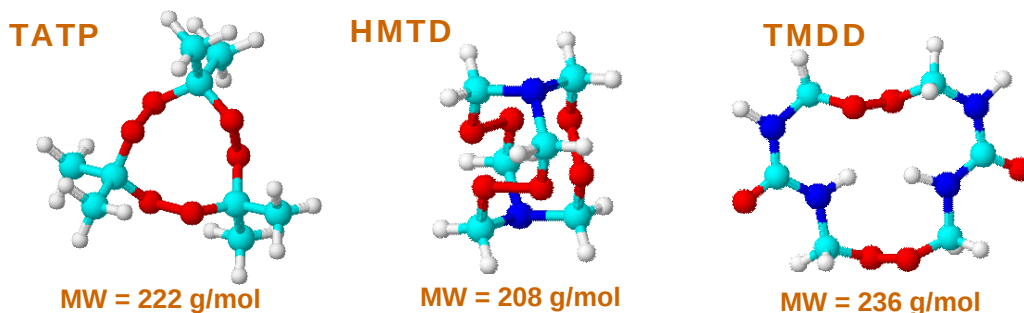


Figure 1-1. Structure of common cyclic organic peroxides: TATP, HMTD and TMDD. The molecular mass of TATP is 222.11 g/mol; the molecular mass of HMTD is 208.07; the molecular mass of TMDD is 236.08.

CHAPTER II

Previous Works

Many studies have focused in developing reliable trace detection methods for explosive compounds. New technologies have brought improvements in several instruments, such as fast neutron activation analysis (FNA)^{8,12}, ion mobility spectrometry (IMS)⁸ coupled to a portable hand-held GC⁹ and GC with Chemiluminescent detection (GC-TEA)^{8,10}. These have aided the detection of illegal drugs and bombs in baggage^{1,12}. Several of the methods for detection of TATP and DADP are focused in the spectroscopic analysis of tetraoxanes and hexaoxanonanes. Researchers that worked with these organic peroxides warned about the precautions necessary since they are extremely sensitive to impact or heat and therefore extremely dangerous¹⁹.

In 1995, Kolla described the advantages and limitations in methodologies utilized to detect bombs⁸. He concluded that detecting hidden explosives required a combination of radiation-based and vapor-based procedures. These methods are complementary approaches and no single technique can be used to detect all possible explosives, because the target chemicals have different properties depending on their functional groups and chemical structures.

As new explosives are used in terrorist activities, new equipment is needed to counter-act and prevent disasters. The cyclic organic peroxides cannot be detected by the IMS Negative Mode (Barringer Ionscan 400) or by GC-TEA (Thermedics Egis 3000). As stated earlier, compounds such as TATP and DADP can be easily prepared from ketones and strong acids in cold solutions at

improvised laboratories^{4,6,7,14,17}. Synthetic methods for TATP and DADP have been reported since early in the twentieth century⁴. However, these compounds are now being used by terrorists to avoid detection by conventional techniques referenced in reports, presented in seminars or federal agency symposiums, such as the Federal Bureau of Investigation^{5,12}. Several studies on peroxides were conducted before the 1970's in Europe^{4,18,20}. However, it has only been since 1983 that TATP and DADP have been identified as dangerous compounds by U.S. Federal Agencies^{5,7}.

In December 1958, Milas and Golubović²¹ published a study of organic peroxide mixtures prepared by mineral acids and hydrogen peroxide. They separated the peroxide mixtures by paper chromatography and cellulose columns impregnated with dimethylformamide. The mobile phase, a saturated hexane solution of dimethylformamide and hydrogen iodide-glacial acetic acid, was used as the detecting agent. Mixtures containing various hydroperoxides as well as some hexaoxonanes and tetraoxanes were separated and analyzed by infrared spectroscopy, resulting in several important spectroscopic signatures. They also documented the use of sublimation to separate and purify some of the peroxides. In May 1959, the same group presented a continuation of this research²², which revealed development of the capacity to clearly identify cyclononatriperoxane and other hydroperoxides. Most of the identified hydroperoxides revealed a polymeric arrangement.

In October 1968, Ward and Mair²³ presented an application of Nuclear Magnetic Resonance for the analysis of organic peroxide mixtures. In their article

they presented many specific chemical shifts for hydroperoxides and organic peroxides diluted in different solvents. They used alcohols to compare chemical shifts. The carbon chemical shifts of interest included the following: $(\text{CH}_3)_3\text{C}$ -detected at 73.0 Hz, ROOR detected at 76.3 Hz and ROOH detected at 75.2 Hz. Most of the characterization techniques and principal spectrometric studies were reviewed in the collection of Organic Peroxides of Swern¹⁸.

In more recent studies, Cafferata and co-workers (1989)¹⁷ analyzed the thermal decomposition of DADP and other substituted tetraoxanes in benzene. In an earlier work, they reported that DADP decomposes thermally into oxygen, acetone, and isopropyl methyl ether²⁴. In subsequent studies they proposed a free radical decomposition process for DADP and other tetraoxanes that also yields CO_2 .^{25, 26} In these articles, the thermal sensitivity of DADP is evident above 150°C.

In 1992, Matsuyama and Kumura²⁷ analyzed the decomposition of peroxy-cycloalkanes and their substituent effect. They demonstrated that these peroxides reacted in a free-radical process and produced traces of acetone and alcohols.

In 1984, Evans⁷ reported the first forensic case in which TATP was used as a homemade explosive (HME). This investigation presented IR and mass spectrometry (MS) data for TATP. The data revealed electron impact mass spectra with the following mass to charge ratio (m/z) for the ions observed: 43, 58, 75, 89, 101, 117 and 223 m/z . The electron impact ionization source induced extensive fragmentation of the TATP molecule. It is worth pointing out that the

nominal molecular weight of TATP is 222. The electron impact mass spectra showed the protonated molecular ion at 223 m/z. This paper also described a rudimentary way to analyze for TATP after impact detonations.

DADP analysis began almost at the same time as for TATP. In 1994, Cafferata published a kinetics analysis of DADP in gas phase²⁵. Hong performed a thermolysis study of DADP in 1996²⁸. Many other have found that DADP is formed in mixtures with TATP as was verified by our research in 2000^{1,2}.

In 1999, Jiang and collaborators reported on the synthesis of a tetramer compound of peroxyacetones using $\text{SnCl}_4 \cdot \text{H}_2\text{O}$ ²⁹. They reported the production of the peroxyacetone during the selective oxidation of olefins catalyzed by metals. They performed the synthesis at different proportions revealing different amounts of the tetramer. This is one of few articles available that address the synthesis of the compound.

Recently, many researchers have focused their efforts on detecting TATP. Crowson used LC/MS and improved the detection and performed post blast analysis¹⁴. In 2003, Kolla and Karst presented a method for TATP detection using HPLC¹⁵. They performed the detection by degradation of TATP and derivatizing the products to fluorescence active compounds. In 2003, Buttiege studied the possibility of analyzing TATP by Ion Mobility Spectrometry¹³. Recently, Xu and collaborators performed a complete method development for TATP and HTMD detection using a HPLC-Atmospheric Pressure Chemical Ionization¹⁶.

Zeiri and collaborators presented a computer simulation for detection techniques for TATP by forming metal complexes³⁰. This paper suggests that triperoxides are more stable if a metallic cation is added to the structure. In 2005, Keinan and Zeiri presented a complete study of TATP, DADP and HMTD calculating their thermal properties⁶. This paper presented organic peroxides as entropic compounds during their decomposition and detonation. The paper also included crystallographic calculations and possible products of TATP explosions.

CHAPTER III

Equipment

Different techniques were used for the characterization of prepared organic peroxides. Among these are Gas Chromatography-Mass Spectrometry (GC/MS), Attenuated Total Reflectance (ATR) - Fourier Transform-Infrared (FT-IR), Thermal Gravimetric Analysis (TGA), Fourier Transform-Nuclear Magnetic Resonance (FT-NMR) and Raman Spectroscopy. These techniques were used to confirm purity and for positive identification of the synthesized compounds. Some compounds were analyzed by X-Ray powder diffraction in substitution of NMR analysis, due very low solubility in common NMR solvents.

The Fourier Transform Infrared (FTIR) spectrometer used was Nicolet FT-IR spectrometer 8700 Nexus E.S.P with Attenuated Total Reflectance (ATR). For preliminary peroxide identification a Jobin-Yvon model T64000 triple spectrograph coupled to a Microscope was used for the Raman spectroscopic analysis. Only a few crystals were necessary for the analysis. Other Raman instrumentation used included Renishaw RM2000 Raman Microscope equipped with Coherent, Inc. high power solid state diode laser model VERDI-6W, operating at 532 nm and Coherent, Inc. INNOVA 308 Ar⁺ laser system wavelength selected for 514.5 nm (green line) and 488 nm (blue line). All spectrometers were equipped with polarization analyzers and de-scramblers. Schematic of the Renishaw Raman equipment is shown in Figure 3-1.

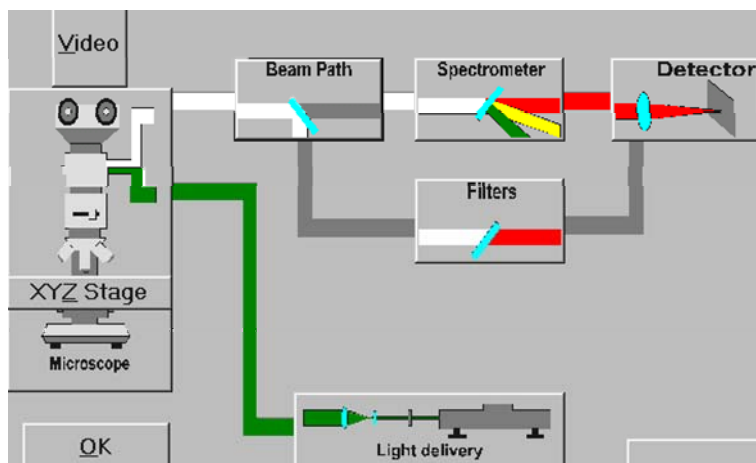


Figure 3-1. Schematic of the Renishaw Raman Equipment.

A Hewlett Packard HP 5890 GC system coupled to a HP 5790 mass selective detector (GC/MS) was also used to characterize the DADP and TATP and to determine the level of purity of the products. Figure 3-2 presents a schematic of the GC/MS interface to the mass selective detector. In an electron impact source the compounds are bombarded by electrons of 70 eV energy, ionized and sent to the quadrupole (analyzer) that separate the ion masses and send them to the ion detector.

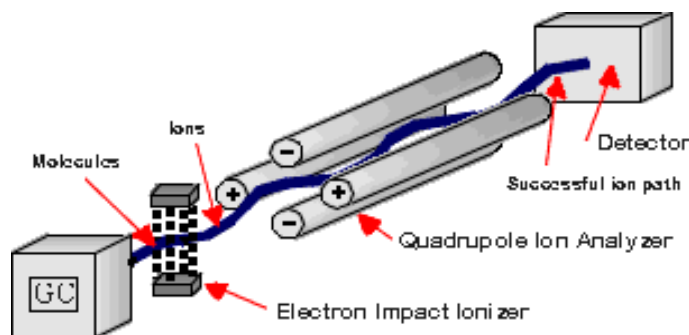


Figure 3-2. Schematic of the GC/Mass Selective Detector.

Open-Air Mass spectrometry analysis was performed by a using a JEOL-USA DART™ ion source coupled to high resolution Time of Flight Mass

Spectrometer (AccuTOF). DART is an acronym for Direct Analysis in Real Time. Helium flow rate was set at 2 L/min, the needle voltage was 3500 V, electrode 1 used 150 V and electrode 2 was set at 250 V. AccuTOF is a reflectron Time-of-Flight mass spectrometer that has a resolution of 5000. Figure 4 shows a schematic of the system.

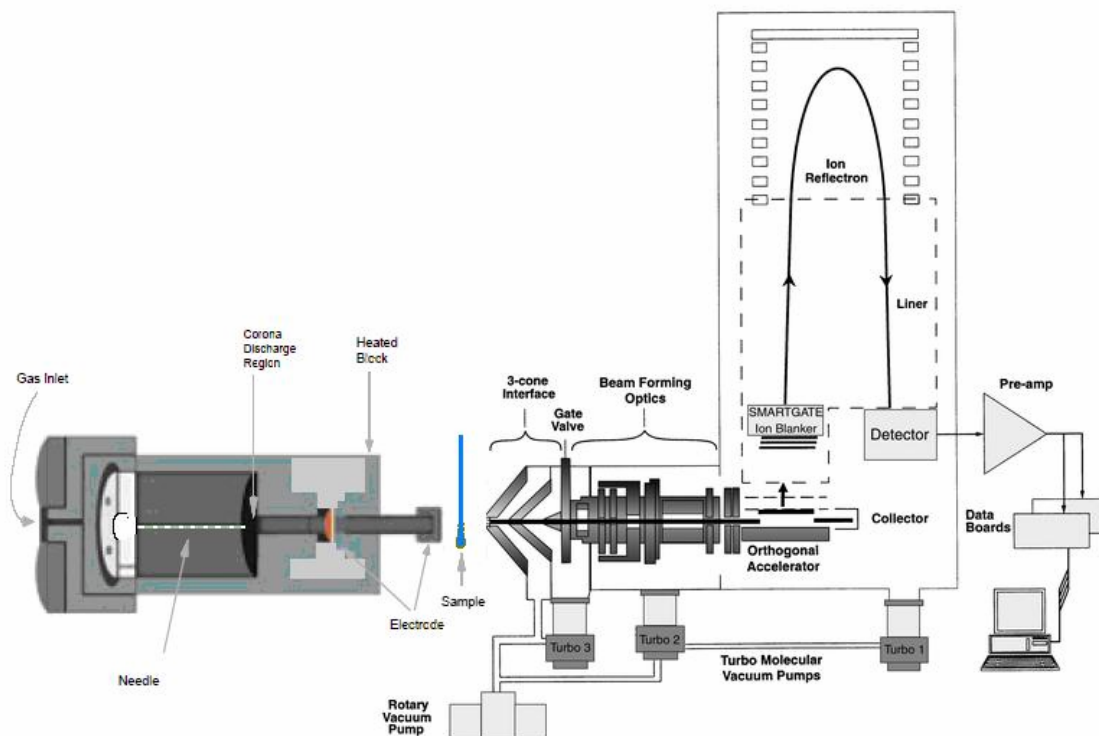


Figure 3-3. Direct Analysis in Real Time (DART) – High Resolution Time of Flight.

CHAPTER IV

Experimental Procedures

1. Synthesis and purification of Cycloalkane Triperoxides

Synthesis of TATP and its deuterated analog D₁₈-TATP was relatively simple but not free of hazards. This synthetic method was reported by Swern⁶. Equal portions of acetone and hydrogen peroxide were mixed in a cold system catalyzed by a strong acid such as HCl or H₂SO₄. After a few minutes the liquid solidified to a crystalline mass, which was recrystallized with dichloromethane or ether to give the trimeric ketone peroxide (mp 97°C).

To purify TATP and its analog crystals, sublimation was performed by heating in warm plate at 70 to 80°C for approximately 10 min. Using a weighting bottle, the sample was placed on the bottom of the flask and the purified crystals were recovered at the top. The original method recovered crystals in a cold finger that works as follows: a large test tube will hold the crude triperoxide (TP) product and another smaller test tube will work as the finger collector. The finger collector is filled with ice and fitted into the mouth of the larger test tube. This sublimation system is then submerged in mineral oil and heated. The temperature must never be allowed to increase over 100°C since TP will not be collected in the finger and will remain in the gaseous form. If the temperature was allowed to increase over 150°C TP could ignite and explode. The white crystals were recovered as tiny feather-like spikes. Figure 4-1 shows a diagram of the sublimation setup.

Approximately 5-10 mg of TATP can be collected in a single sublimation process from 30 mg. But if 100 mg of TATP are sublimed it will require two, three or even four processes to recollect 30 to 50 mg since the rest of the product decomposes into a yellow liquid that was not characterized.

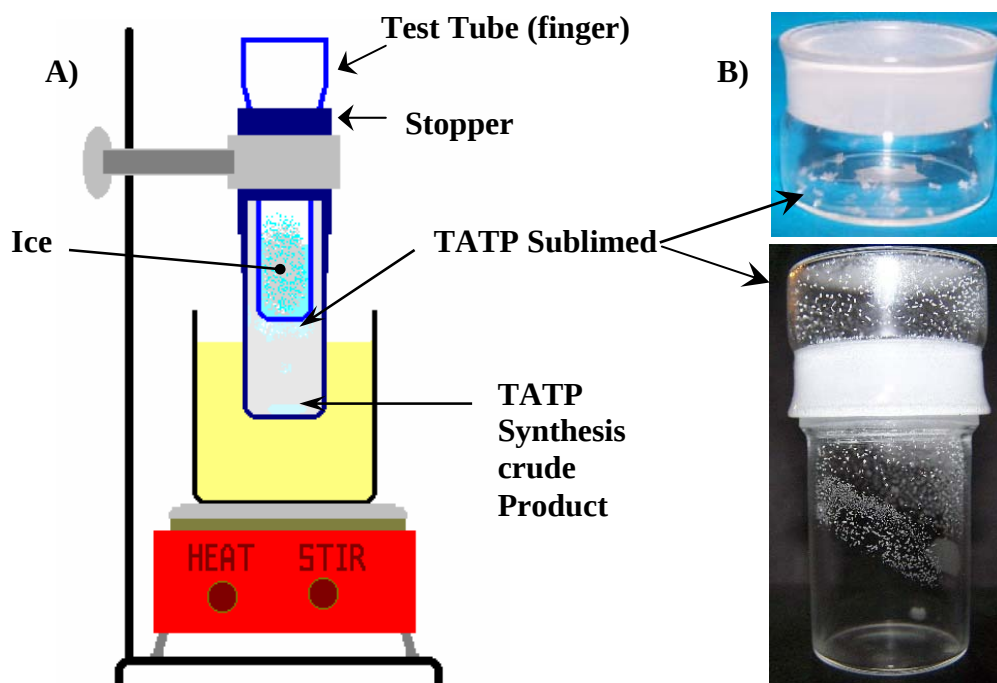


Figure 4-1. Sublimation Equipment for ketone peroxide purification: A) Our original sublimation system heating with mineral oil; B) Latest method of sublimation using a cup warmer and a weighting bottle. TATP, D₁₈-TATP and cyclopentanone triperoxide were purified by this method.

TATP and its analogs samples were dissolved in chloroform or dichloromethane and analyzed by GC-MS using the total ion chromatogram (TIC) mode. Raman microscopy was also used to confirm the structure of triperoxides (TP). Detailed description of the processes will be presented in next chapters.

2. Synthesis of HMTD

For HMTD synthesis, two different methods were used, one that was provided by Sheaffer²⁷ using citric acid and the other one provided by von Girssewald²⁶ using diluted HCl. Both methods used hexamethylene tetramine (Hexamine) and hydrogen peroxide ~25%. Hexamine and hydrogen peroxide were mixed in a cooling solution below 5°C. This solution was stirred until all solid dissolved. To catalyze the reaction, dissolved citric acid or a diluted solution of HCl was added. The solution was stirred for three hours until a white precipitate was observed. The product was washed with water and kept in a freezer. These crystals are HMTD and cannot be stored at room temperature and samples needed to be used a few days after the preparation before HMTD began to decompose. Accompanying this degradation process, an unpleasant smell could be detected emerging from the crystals.

3. Synthesis of TMDD

TMDD was simple to prepare, but the synthesis was not as fast as the other peroxides. For the preparation, the basic method provided by von Girssewald and Siegens³² was used in diluted HCl or H₂SO₄. A solution of formaldehyde and hydrogen peroxide was prepared and cooled below 10°C. Then, powdered urea was added and stirred until all the solid was dissolved. The solution was cooled below 0°C, before the addition of the diluted acid. The solution was stirred again, and then was placed in the refrigerator for at least three days. After the first day, it was possible to observe the formation of some

crystals, however the highest yield of precipitated product was observed after three days. The product was filtered and washed with water and kept in the refrigerator.

4. Sample Preparation of TATP and HMTD

Standard preparation required sample purification. HMTD preparation produce a considerable pure compound, however it must be kept in a freezer before it began to degrade. TATP and D₁₈-TATP produced small contaminants and required purification. TATP and D₁₈-TATP crude products were sublimated and the crystals collected. Crystal samples of HMTD, TATP and D₁₈-TATP weight between 1-3 mg. Then, 1 mL of the solvent was added. For typical GC-MS analysis, chloroform and dichloromethane was used. To store the standards and make mixtures with other peroxides, acetonitrile was chosen. After the 1000 ppm standards are prepared, aliquot solutions are prepared to prepared for calibration curves or to determine detection limits.

5. Instrumentation, column and parameters used for quantification

Chromatographic separations were performed on a Agilent HP 5890 GC system with a 15 m long, 0.25 mm i.d., 0.25 μ m film thickness capillary column (ZB35). The detector was a HP 5790 mass selective detector using the TIC analysis, a mass range between 30-550 m/z and in the SIM mode monitoring the m/z fragment ions located at 43, 59, 75, 101, and 222, which are characteristic of TATP. Helium carrier gas was used at a rate flow of $\approx$ 0.789 mL/min. The

injector temperature was 120°C and the optimum detector temperature was 200°C. The GC temperature program was started at 80°C for 1 min in the splitless mode followed by a ramp of 40°C/min rate to 90°C for 2 min, where the TATP eluted from the column and was detected. Finally, column temperature was increased at a 50°C/min rate to 190°C for column cleaning purposes.

CHAPTER V

Characterization and Differentiation of High Energy Amine and

Amide Peroxides by

Direct Analysis in Real Time-TOF Mass Spectrometry

Characterization of hexamethelene triperoxide diamine (HMTD), tetramethylene diperoxide dicarbamide (TMDD) and tetramethylene diperoxide acetamide (TMDA) was carried out using Open Air Chemical Ionization/Time of Flight Mass Spectrometry (OACI-TOF/MS). The study also centered in the detection of their precursors such as hexamine and formaldehyde. Analysis of the compounds by GC-MS was also conducted. HMTD showed a clear peak at 209 m/z that allowed its detection in standard solutions and lab made standards. TATP was detected by ammonium adduct addition at m/z 240. Commercially available standards were compared with laboratory made standards. Phthalate contamination was observed in commercial standards at m/z 223. Sublimated sample produced single ammonium molecular adduct peaks. All samples were characterized by Raman and FT-IR to confirm the MS characterization results. Some of the vibrations observed were in the $\nu(\text{O-O})$, $\nu(\text{N-C})$, $\nu(\text{N-H})$, $\nu(\text{C-O})$, $\delta(\text{CH}_3\text{-C})$ and $\delta(\text{C-O})$. Peroxide O-O vibrations were observed around 750-970 cm^{-1} . Peroxide C-O vibrations were observed at 1000-1100 cm^{-1} . Amine peroxides showed N-C vibration at 1370 cm^{-1} . Development methodology for

trace detection was compared with GC/MS and HPLC-MS results previously presented for HMTD and TATP.

1. Introduction

Recent advancements in mass spectrometry (MS) have generated new potential methodologies for detection of energetic materials and other threat agents. Among these recent improvements in MS such as the fact that Time-of-Flight (TOF) technology has become more reliable and sensitive technique that can even be used to discriminate mass fractions¹ the design and development of a tunable electron energy monochromator; atmospheric pressure interfaces as the recently described by the JEOL device that addresses Direct Analysis in Real Time (DART)¹⁻³ and the desorption electrospray ionization (DESI) by Prof. Cooks in Purdue University⁴, have significantly advanced real time, atmospheric pressure MS analysis. Equipments such as JEOL-USA DART-AccuTOF and DESI-QI/TMS are being used for the explosives and illegal compounds detection⁵.

Widespread use of organic peroxides in terrorist acts has forced government security agencies to find and promote new technologies for the detection of these compounds. Triacetone triperoxide (TATP) and hexamethylene triperoxide diamine (HMTD) are the more commonly used cyclic peroxides in terrorist acts such as the London bombing⁶. Several new methods have been developed for their detection. In 2006, Mullen and colleagues

analyzed TATP, DNT and TNT by laser desorption TOF with detection limits of 40 ppb for nitro explosives⁷. In the same year, Wilson used selected-ion tube flow mass spectrometry for TATP detection at 10 ppb level⁸. In 2006, our research group presented a methodology for TATP, HMTD and TMDD detection using Raman microscopy and direct probe mass spectrometry⁹⁻¹⁰. Buttigieg presented an Ion Mobility Spectroscopy study for the detection of TATP in 2003¹¹. Karst and coworkers developed several methods for detection of peroxides by an ingenious method of UV degradation and post column derivatization for HPLC analysis¹²⁻¹³. Widmer also presented a HPLC/MS method for TATP¹⁴. Stambouli discussed a method for TATP detection by head space GC-MS¹⁵. Recently, Sigman developed a methodology for GC/MS and GC/FID detection of TATP using chemical ionization in which ammonium ion was used to generate an adduct of 240 m/z and allowing picogram detection¹⁶. In 2002, Zeiri proposed a method for the detection using metal cations¹⁷, and Lu presented in 2007 a method using this property¹⁸. In 2000, our research group developed a methodology for TATP and DADP detection using GC/MS at picograms levels and then these results revised and presented in 2005¹⁹⁻²⁰. In 1992, White discussed a case in which TATP was analyzed by a forensic laboratory²¹. Fast technology throughput technology is required for airport screening at checkpoints in which the analysis is required in seconds to minutes. This is the reason to present new technologies that can be used for real time analysis with high sensitivity and selectivity: DART-TOF-MS, is an excellent tool for analysis of traces of organic compounds deposited on any kind of surface or liquid. DART

system uses a metastable inert gas (He or N₂) to produce reactive charged water clusters that will ionize any molecule at ambient pressure.

TATP was first synthesized by Wolffstein in 1895²². Swern published its simple synthesis method in his classical books on Organic Peroxides, 1972²³. Hexamethelene triperoxide diamine (HMTD) is one of the most common amine peroxides. This explosive compound has been known longer than triacetone triperoxide (TATP). It was synthesized by Legler in 1885 from ammonia and bishydroxymethyl peroxide²⁴. Many other investigators have tried to synthesize HMTD by easier routes and seeking to obtain higher overall yield. Among these were Baeyer and Villiger, Von Girssewald, and Shaefer²⁵⁻²⁷. HMTD is not only more sensitive and unstable than TATP, but also the compound can be synthesized easier and it is more difficult to detect due to its lower vapor pressure. The first step in the characterization of HMTD was the determination of its structure using x-ray crystallography²⁸. The vibrational spectra and NMR analysis demonstrated that HMTD forms a cage compound as other cyclic peroxides²⁹. In 2000, Oxley and Smith determined the mass fragmentation by isotopically labeled HMTD and then in 2002, presented its thermal decomposition²⁹⁻³⁰. In 1999, Edward and his colleagues synthesized other cage amine peroxides³¹. Tetramethylene diperoxide dicarbamide (TMDD) was synthesized by von Girssewald and Siegens in 1914³². This study presents the characterization and differentiation of TATP, HMTD, TMDD and other amine peroxides by Raman spectroscopy and AccuTOF-DART. Also included is a mass spectrometry method development for trace analysis of TATP, HMTD and TMDD.

2. Methods

2.1. Reagents

The reagents used in this research were: acetone, urea, aniline, acetamide, hexamethylene tetraamine (98% w/w, Acros-Organics, Fairlawn, NJ), formaldehyde (CH_2O , 37% wt, Acros-Organics N.V., Fairlawn, NJ), hydrogen peroxide (H_2O_2 , 50% in water, Fisher Scientific International, Fairlawn, NJ), and hydrochloric acid (HCl , 12 M, Merck, VWR International, Inc., West Chester, PA 19380), and sulfuric acid (H_2SO_4 , Sigma-Aldrich Chemical Co., Milwaukee, WI).

2.2. Instrumentation

Fourier Transform Infrared (FT-IR) spectrometer used was a Thermo-Nicolet FT-IR spectrometer Nexus E.S.P with Attenuated Total Reflectance (ATR) accessory and Bruker Optics model IFS 66v/S FT-IR microscope. Raman instrumentation used included Renishaw RM2000 Raman Microscope equipped with Coherent, Inc. high power solid state diode laser model VERDI-6W, operating at 532 nm and Coherent, Inc. INNOVA 308 Ar^+ laser system wavelength selected for 514.5 nm (green line) and 488 nm (blue line). Dispersive Raman equipment was operated in confocal mode. A Hewlett-Packard gas chromatograph model GC-MS HP 5890 GC system coupled to a HP 5790 mass selective detector was used for the mass spectroscopy experiments. A JEOL DART-AccuTOF mass spectrometer was used for the analysis of all samples. Schematic of the Direct Analysis in Real Time probe is shown in Figure 5-1¹.

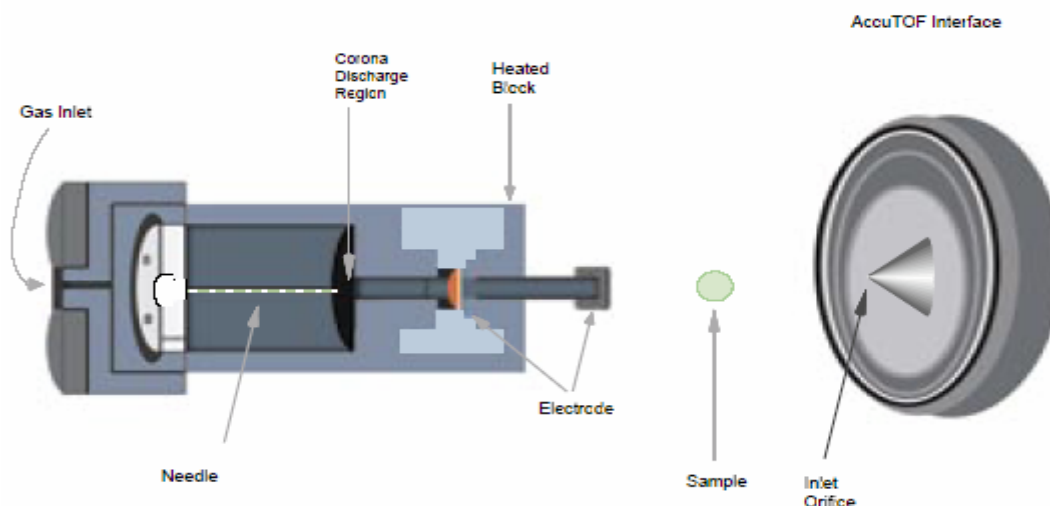


Figure 5-1. Schematic diagram of Direct Analysis in Real Time probe components.

2.3. Method of analysis

TATP was purified by sublimation in a small weighting bottle by heating slightly in a hot water bath. Characterization was performed by GC-MS and Raman Microscopy. Amine peroxides are sensitive to heat. Some offer low synthetic yields and present very low solubility in most organic solvents, for this reason purification was not performed. To determine purity grade, high yield samples were analyzed by melting point in an Electrothermal Melt-Temp, Barnstead International, Dubuque, IA. Characterization of amine peroxides was made by Raman Microscopy. Confirmation of TATP, HMTD and TMDD by infrared absorption studies were performed with a FTIR Attenuated Total Reflectance equipped with germanium crystal optics, interfaced to a Thermo-Nicolet spectrometer, model Nexus E.S.P. Samples were dried and clear crystals

of approximately 2 mg were analyzed. For Raman microanalysis, the samples were studied at 20x and 50x magnification. Commercially available HMTD diluted in acetonitrile was analyzed in a direct insertion probe of a JEOL GC-Mate II.

Synthesized HMTD was analyzed by FTIR and Raman Microscopy. All samples were insoluble in the solvents tested: water, ethanol, chloroform and acetonitrile. TATP, HMTD and TMDD were dissolved (suspended) in acetonitrile; aniline peroxide and acetamide peroxide were analyzed in solid state due to low synthesis yield. All samples were analyzed in the AccuTOF by adding ammonium hydroxide in a cotton swab after the ion source and then placing a capillary tube before MS inlet. Ammonium cations helped to detect peroxides in the TOF-MS. Electron impact mass spectra of the organic peroxides (TATP, HMTD) were performed in the HP GC/MS injecting 0.1 μ L of a slightly diluted solution (suspension). The GC parameters were adapted to prevent thermal decomposition.

3. Results

3.1. Synthesis

Synthesis of TATP was done following the Swern method²³. HMTD was made by dissolving hexamethylene tetramine in hydrogen peroxide at low temperature. Then a diluted solution of a strong acid (HCl) was added. Figure 5-2 b shows the synthesis of HMTD developed by Von Girsewald²⁶. The mixture was cooled in the refrigerator for 24 h and the solution was then filtered. Since HMTD is not soluble in typical solvents purification by crystallization cannot be

easily performed. Crystals obtained were powder like, but in the microscope they can be easily recognized as in Figure 5-2 with a 50x of magnification objective.

Synthesis of amine peroxides was specific for each compound. Most of them followed a similar preparation to that for TATP, but required the addition of formaldehyde. For security reasons, the syntheses will be only presented without the amounts. Figure 5-3 presents a schematic synthesis of most of the amine peroxides. In a cold flask between 0°C and -5°C, formaldehyde and hydrogen peroxide were mixed and then urea or the desired amine was added and dissolved in the mixture. After totally dissolving, a small portion of strong acid was added.

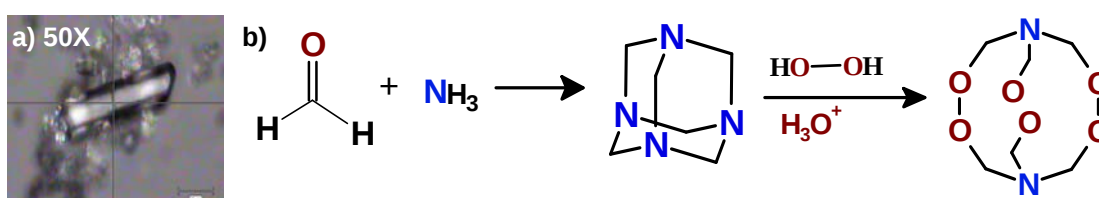


Figure 5-2. Preparation of HMTD. (a) White light micrographs of HMTD crystals at 50X; (b) general synthetic scheme for HMTD reported by Baeyer, Villiger²⁵ and Von Girsewald²⁶.

The solution was cooled in a refrigerator for 3 to 5 days and a white precipitate was formed. TMDD was difficult to dissolve. The purification with organic solvents only served to remove soluble impurities. Figure 5-3 shows the generally accepted mechanism for this synthesis. Preparation of other cyclic amine peroxides was tried using m-nitroaniline and acetamide. The compound with acetamide was successfully synthesized with low yield. Small crystals were analyzed by Raman spectroscopy. M-nitroaniline based amine peroxide was synthesized but the exciting laser damaged the sample.

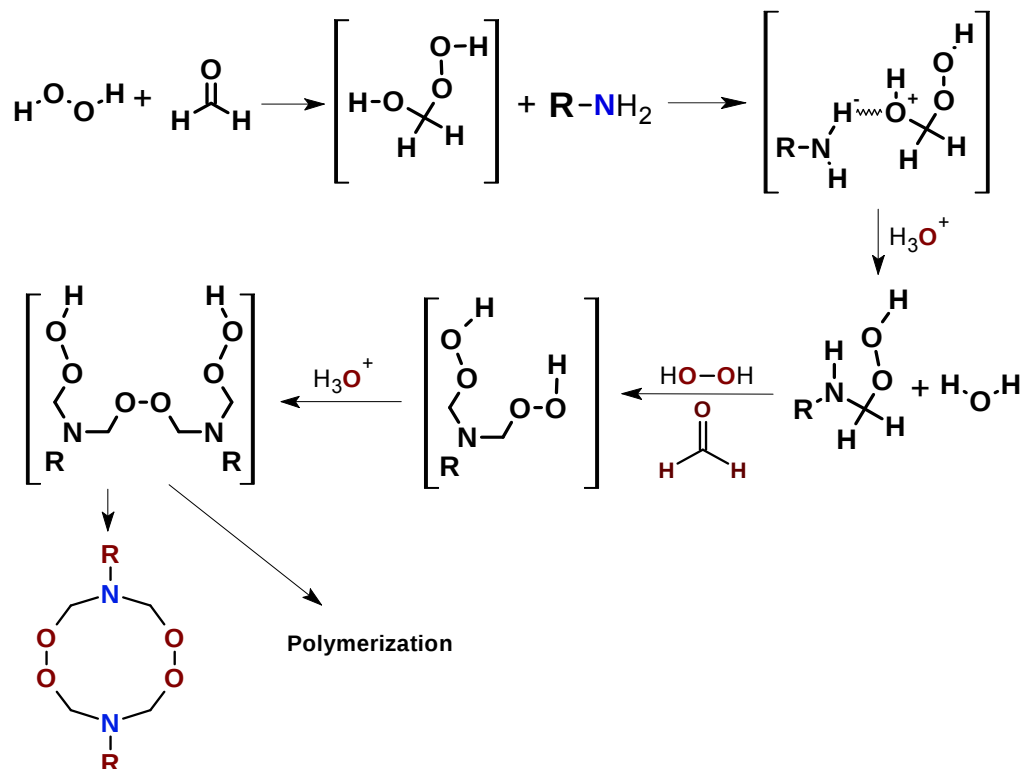


Figure 5-3. Schematic of synthesis of amine and amide peroxides.

3.2 Vibrational spectroscopic characterization

Infrared and Raman spectroscopies were useful tools in the characterization of the target compounds in this investigation, particularly in the fingerprint region. Figure 5-4 presents the full vibrational spectra of HMTD by Raman and FT-IR microscopy. Both techniques show bands about 2965 cm^{-1} and 2925 cm^{-1} that belong to CH_2 stretching: symmetric and asymmetric vibrations of the six-methylene groups. Amine N-C vibrations observed at $1398\text{--}1310\text{ cm}^{-1}$ belong to the tertiary amine stretchings $\{\nu(\text{N-C})\}$. C-O vibrations were detected at 1066 and 1039 cm^{-1} (Raman), and 1055 and 1031 cm^{-1} (IR). The characteristic intensity pattern of the peroxide bands (e.g., TATP) between 950

cm^{-1} and 750 cm^{-1} are inverted in both techniques³³⁻³⁴: the 777 cm^{-1} symmetric vibration is stronger in Raman and the asymmetric stretches at 870 cm^{-1} and 945 cm^{-1} are stronger in IR. These results are consistent with the symmetric structure of HMTD. All these bands are consistent with the work of Sülzle and Klaeboe²⁸. These results characterized and confirmed the synthesis of HMTD.

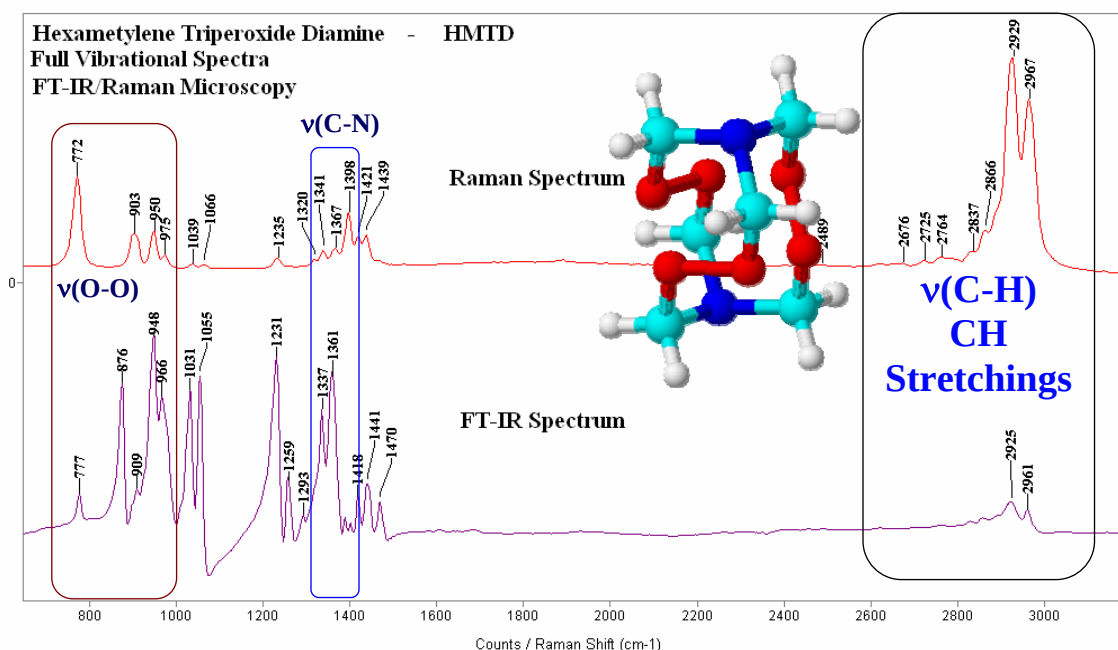


Figure 5-4. Vibrational spectra of HMTD by FT-IR Microscope and Raman at 532 nm.

Figure 5-5 presents full vibrational spectral characterization of TATP by Raman and FTIR microscopy. Vibrational data showed a doublet band at 3010 cm^{-1} and 2996 cm^{-1} that belongs to asymmetric and symmetric stretching of the CH_3 due to the six-methyl groups moving at different phases. Characteristic peroxide O-O bands appeared between 950 cm^{-1} and 750 cm^{-1} , these bands were also present in FT-IR spectra, but with stronger intensities.

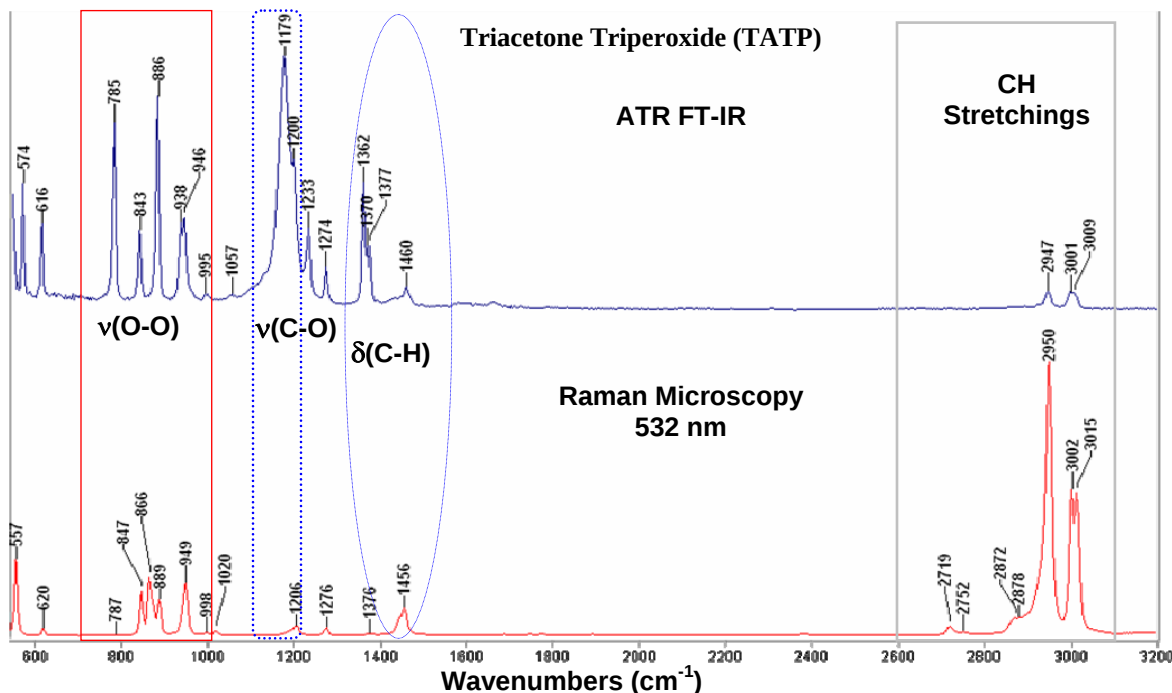


Figure 5-5. Vibrational spectra of TATP by FT-IR ATR and Raman at 532 nm.

There are no previous reports in the literature for spectroscopic characterization of TMDD that could be used to confirm or compare the spectra. However, the simplicity of the spectra obtained allowed its characterization. Figure 5-6 shows the vibrational spectra of TMDD. The principal evidence of the synthesis of the carbamide compound, TMDD, is the strong absorption of the N-H stretching at 3336 cm^{-1} in FT-IR and 3346 cm^{-1} in Raman¹⁹⁻²⁰. Then the CH_2 stretches observed at 2946 and 3045 cm^{-1} in IR (2993 cm^{-1} and 2949 cm^{-1} in Raman) are similar to those found in HMTD, which indicated that the molecule has methylene groups. Urea has strong carbonyl absorption in the range of $1700\text{--}1600\text{ cm}^{-1}$; TMDD should share this absorption (Raman scattering). In the IR spectra, strong absorptions in the range of $1500\text{--}1660\text{ cm}^{-1}$ demonstrate the

presence of a carbonyl group. In Raman the corresponding signal can be observed about 1650-1770 cm^{-1} . The characterization of the N-C present in amides can be observed at 1253, 1296 and 1127 cm^{-1} $\{\nu(\text{N-C})\}$. Finally, the most relevant evidence of the synthesis of the peroxide is the typical vibrations of the O-O bond $\{\nu(\text{O-O})\}$. The white crystalline solid has absorptions between 980-700 cm^{-1} . In FT-IR, the asymmetrical peroxide stretching at 943 cm^{-1} and 910 cm^{-1} are very strong; in Raman, these peroxide stretches are weak at 974 cm^{-1} and 914 cm^{-1} , but the symmetrical peroxide stretches vibrations at 776 and 756 cm^{-1} are more intense than in IR. A doublet band at 2359 and 2340 cm^{-1} due the presence of CO_2 can be observed in the FT-IR spectrum. This band is absent in Raman.

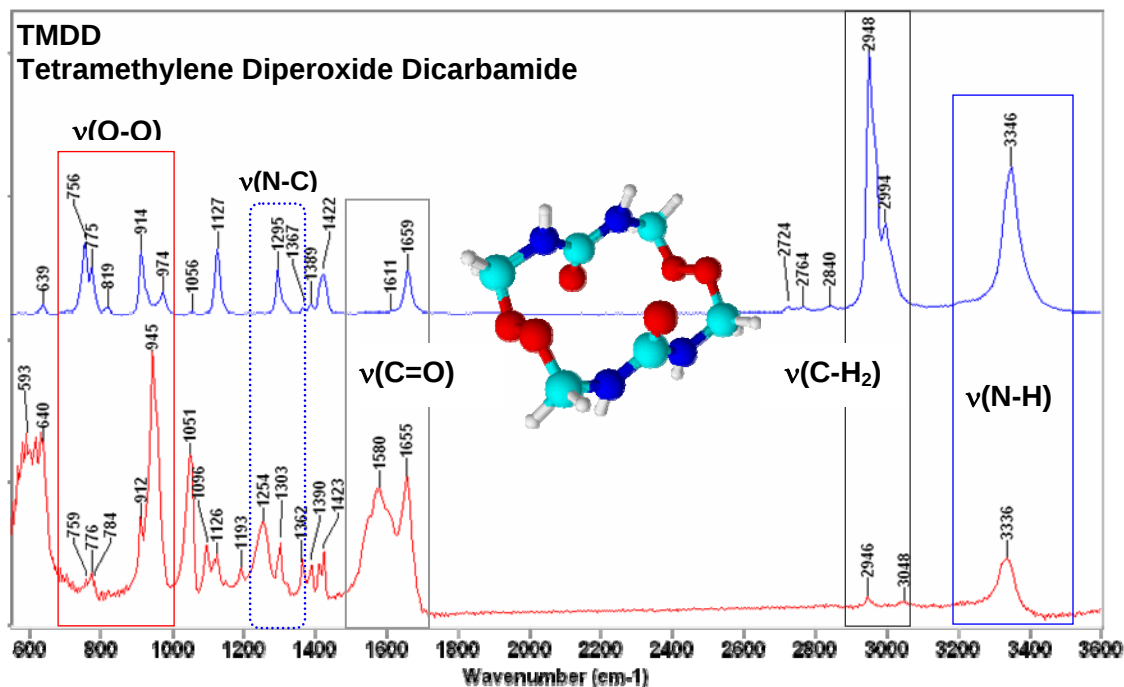


Figure 5-6. Vibrational spectra of TMDD by FT-IR-ATR and Raman at 532 nm.

3.3 Vibrational Spectroscopic Analysis of other Cyclic Amine Peroxides

Other cyclic amine and amide peroxides synthesized also showed the $\nu(\text{O-O})$ region bands and peroxyacetones and HMTD as well nitro-aniline peroxides were decomposing with laser and results will be not shown. Acetamide peroxide is one example of the compounds that were analyzed by Raman Microscopy, because only a small grain could be obtained from the mother liquors by precipitation. Figure 5-7 shows the obtained Raman spectrum of the amide peroxide made from acetamide. The spectrum revealed that the most prominent absorptions in the range $2960\text{--}2650\text{ cm}^{-1}$ were methylene groups of the compound and methyl groups of the acetamide. Amine absorptions, $\nu(\text{N-C})$, can be observed at 1330 and 1296 cm^{-1} . Also, the bands assigned to $\nu(\text{O-O})$ are

present in the minute crystalline sample. As can be noticed, there are bands between $1000\text{--}750\text{ cm}^{-1}$ which are consistent with other peroxides (HMTD and DADP). There are other bands that are consistent with the presence of nitrogen bonds in the sample.

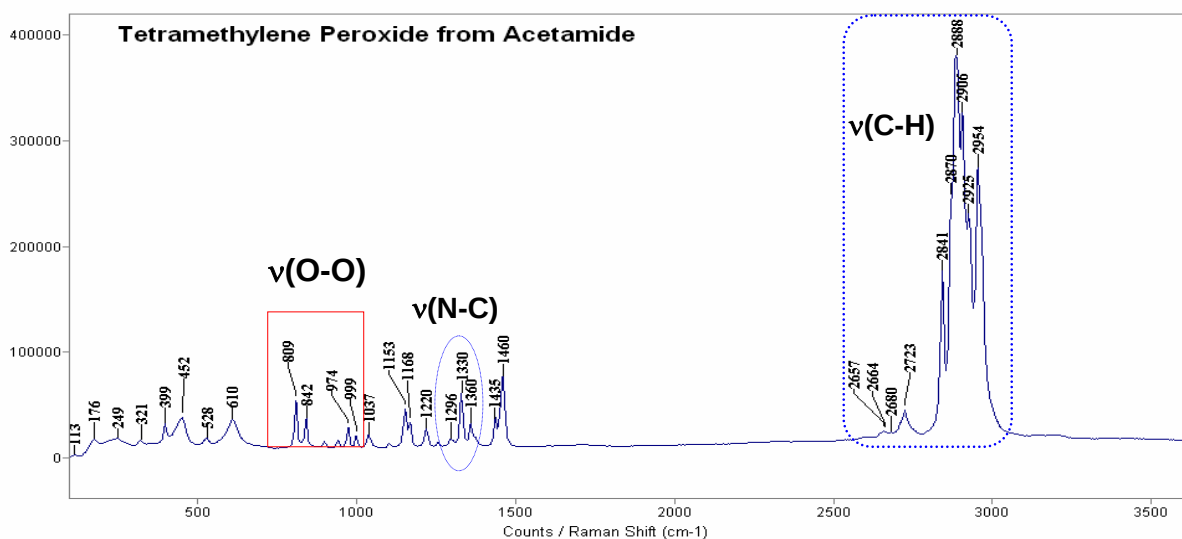


Figure 5-7. Raman spectrum of acetamide peroxide.

3.4 Mass spectral analysis

Figure 5-8 a shows the mass spectrum of HMTD developed by Direct Insertion Mass Spectroscopy (DI-MS). As shown, the molecular peak stands out very clearly at m/z 208 in contrast with TATP where the molecular peak of m/z 222 is slightly seen in the fragmentation pattern (Figure 5.8 b). The base peak of HMTD EI spectrum is m/z 30 which is a fragment of $[\text{CH}_4\text{N}]^+$. This fragmentation pattern could change depending on the temperature of the direct insertion probe. Other mass spectra experiments showed the based peaks at m/z : 42 $[\text{CH}_2\text{NCH}_2]^+$ and 45 $[\text{CH}_2\text{NO}]^+$. Other fragments of HMTD are m/z 58, 69, 73, 81, 88, 117 and 176. This fragmentation can help to differentiate from acetone

peroxides that showed the following fragmentation pattern: base peak of m/z 43, peaks at m/z 58, 59, 75, 101 and 117.

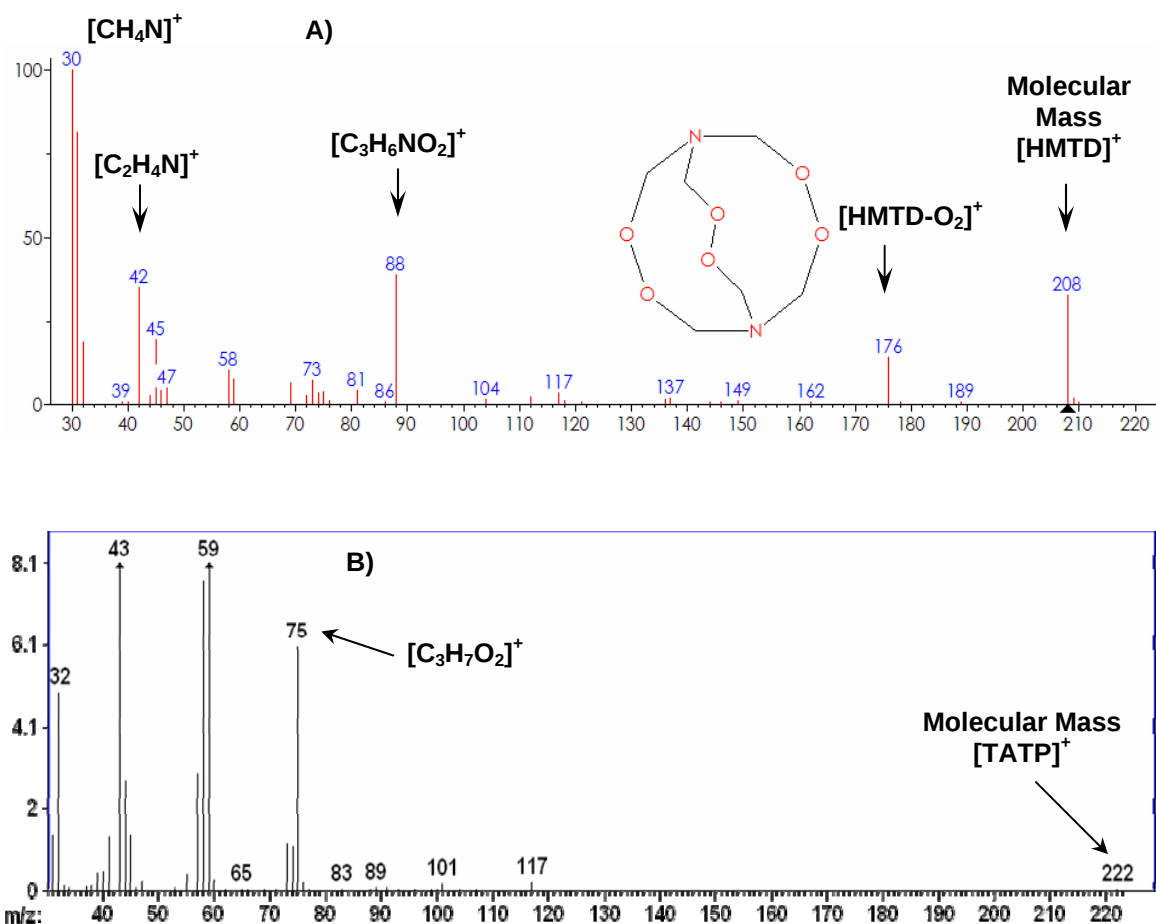


Figure 5-8. Electron Ionization mass spectra of cyclic peroxides: A) Mass spectrum of HMTD by Direct Insertion analysis; B) Mass Spectrum of TATP by GC-MS analysis.

3.5 DART-HRTOF Analysis of Cyclic Organic Peroxides

HMTD has low solubility and low vapor pressure, which limits its analysis by gas chromatographic methods and techniques. HMTD is slightly soluble in chloroform, dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF). TMDD, on the other hand, is insoluble in most organic solvents and thus represents a challenge for chromatographic analysis. TATP and other acetone peroxides are highly volatile, but also are sensitive to high temperature. OACI-HR-TOF-MS

provided a new methodology for explosive detection with considerably low detection limits. By adding ammonium hydroxide, positive adducts of ammonium ion are promoted and help to identify these peroxide compounds similarly to chemical ionization.

Figure 5-9a presents HMTD mass spectra by OACI-MS. Molecular ion mass can be easily identified as m/z 209.0781 $[M+H]^+$. Other significant mass fragments can also be observed in lower relative abundance: m/z 226 $[M+NH_4]^+$; 179 $[C_5H_{11}O_5N_2]^+$; 145 $[C_5H_9O_3N_2]^+$; and 88 $[C_2H_6O_2N]^+$. TATP mass spectrum by OACI-TOF is clearly different as can be seen in Figure 5-9b. A peak at 240.1438 m/z is assigned to molecular ion adduct with one unit of ammonium ion $[TATP+NH_4]^+$. TATP sample was sublimated for purification and its purity was verified by GC-MS. The absence of any fragmentation pattern and even the molecular mass of m/z 222 seen in GC/MS, suggest that TATP is stabilized by the presence of the ammonium ion. This results were confirmed by deuterated form of TATP in which DART-MS $^{2}D_{18}$ substituted molecular ion adduct with NH_4^+ is located at m/z 258.2579 $[D_{18}TATP+NH_4]^+$.

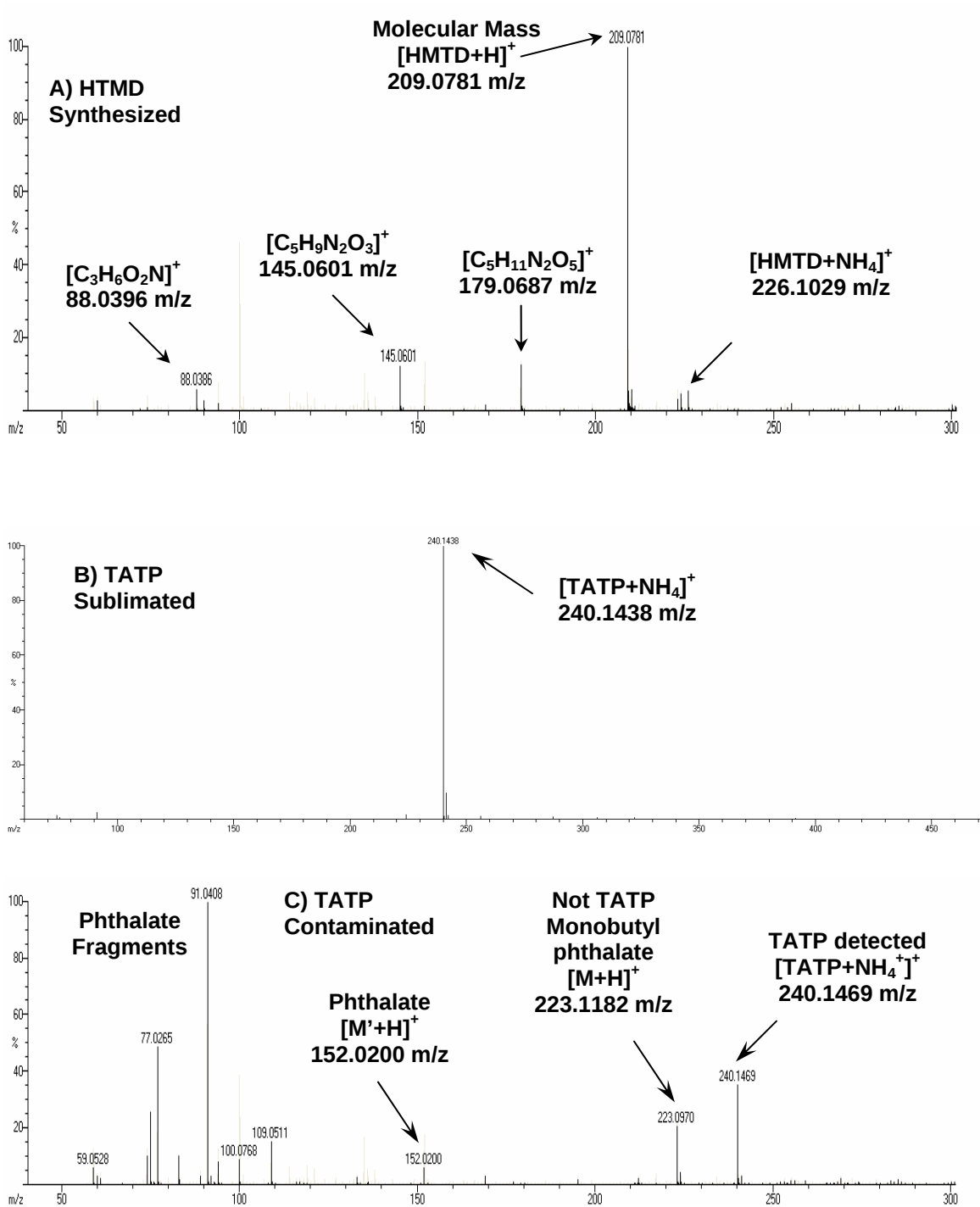


Figure 5-9. DART-TOF Mass Spectra of HTMD and TATP: A) HMTD synthesized; B) TATP sublimated; and C) TATP contaminated.

Figure 5-9c shows the importance of employing high resolution TOF/MS: the m/z 223 peak is not the $[M+H]^+$ which would be expected at 223.1182 m/z , but it is a contaminant with the composition $C_{12}H_{15}O_4$, most likely $[M+H]^+$ for diethyl phthalate or monobutyl phthalate. These results are confirmed by the presence of a signal at m/z 152.0200 (phthalate, $[M+H]^+$).

TMDD presented a challenge in mass spectra analysis (Figure 5-10). The melting point of TMDD is approximately 180°C, and at lower temperatures, OACI analysis was very difficult to perform. TMDD was analyzed at 175°C, but mass spectra were considerably different to TATP and HMTD. Similar to TATP, TMDD showed the $[M+NH_4]^+$ at m/z 252.1112, in presence of ammonium ion, but also the m/z 237 $[M+H]^+$, molecular peak of the molecule. These peaks demonstrate the presence of TMDD proposed molecular structure in Figure 5-11. The other fragmentation suggests that TMDD is unstable at high temperatures or simply that the synthesis products were not pure enough. Mass fragments of m/z 189.0625, 161.0659, 146.0563, 134.0563, 119.0457, and 101.0333 are common to previous TMDD analysis at lower temperatures in the ionization zone. Molecular mass fragments were visible at 175°C and in presence of a relatively high concentration of ammonium ion. These results represent the first methodology available for TMDD characterization and detection. Other methods of mass analysis were tried such as electrospray, but results were limited by TMDD solubility. The OACI-TOF analysis suggest the presence of a different mass isomer with $[M+NH_4]^+$ at 252 m/z and molecular mass of 235 m/z , but further analysis required to confirm these observations.

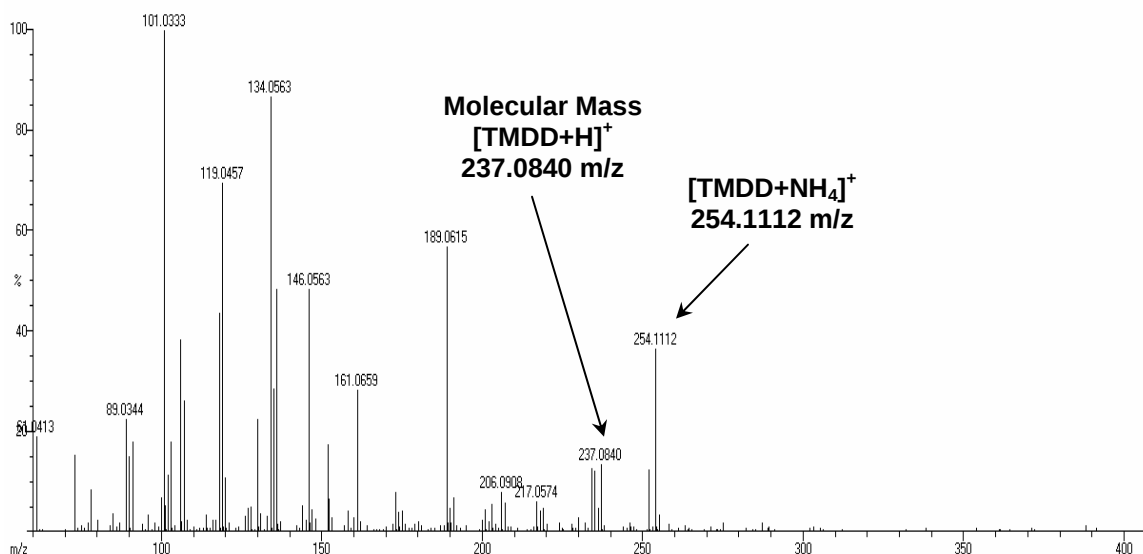


Figure 5-10. DART-Mass Spectrum of TMDD at 175 °C. TMDD was treated like TATP by adding ammonium vapor in the ionization stream to produce adduct ions.

4. Discussion

TATP, HMTD, TMDD and other amine peroxides have been characterized by vibrational methods. IR and Raman spectroscopy revealed common signals between 990 to 700 cm^{-1} in TATP, HMTD and TMDD. Raman was able to distinguish HMTD from other amine peroxides using very small sample amounts. Results also indicate that Raman can help in the identification of amine peroxides and acetone peroxides in forensic analysis. OACI-TOF has proven that MS information of HMTD is equivalent to electron ionization mass spectrometry analysis due its clear m/z 209 that helps to identify this compound. Also TATP can be analyzed with high accuracy, even in complex mixtures because TATP generates and adduct peak at m/z 240. A simple addition of ammonium ion could enhance the signal of organic peroxides. Tetramethylene triperoxide

dicarbamide (TMDD) has been characterized by vibrational and mass spectrometry techniques. Raman has proven essential to the characterization of TMDD, but along with OACI-TOF, any compound could be analyzed. Raman also proved to be an excellent technique along with ATR FT-IR for the characterization of less known peroxides. Raman microscopy can show morphological information of the sample and Attenuated Total Reflectance FT-IR can be used as complementary technique.

5. Conclusions

As part of the objective of this work of developing methods for detection of energetic organic peroxides, triacetone triperoxide (TATP), hexamethylene triperoxide diamine (HMTD) and tetramethylene diperoxide dicarbamide (TMDD) were synthesized and characterized using vibrational spectroscopy. The results presented indicate that FT-IR and Raman Microscopy can be used as useful tools for the characterization and identification amine peroxides. Due the low vapor pressure of amine cyclic peroxides, DART-TOF is an ideal technique to analyze this kind of compounds, due its soft ionization at ambient pressure. OACI-HR-TOF has proven to be useful in the characterization of insoluble compounds and has been validated against common mass spectrometry equipment such as GC-MS and direct insertion MS. The accuracy of HR-TOF was decisive determining TATP in mixtures with other compounds almost instantaneously, in contrast to chromatographic techniques that require at least minutes to make a single analysis. OACI-TOF-MS proved to be robust technique for analysis and trace detection for cyclic organic peroxides and complementary technique to well known characterization methods of FTIR and Raman spectroscopy. This research presents the potential of the OACI-HR-TOF as forensic equipment and useful tool for airport and government checkpoints, because it can analyze samples with no preparation, in any phase (gas, liquid or solid) and with high mass accuracy.

6. References

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CHAPTER VI

Synthesis, Characterization and Differentiation of High Energy

Amine Peroxides by Vibrational Microscopy

Synthesis and characterization of hexamethylene triperoxide diamine (HMTD), tetramethylene diperoxide dicarbamide (TMDD) and tetramethylene diperoxide acetamide (TMDA) using FT-IR and Raman Microscopy has been carried out. The study also centered in the synthesis and characterization of other cyclic amine peroxides, including and different forms of caged peroxides from other diaminoalkanes. Interest also was given to the secondary products of all syntheses and the effect of temperature in the composition mixtures of the preparations. Differentiation spectroscopy and spectrometry studies were also conducted. In these studies the differences in the $\nu(\text{O-O})$, $\nu(\text{N-C})$, $\nu(\text{N-H})$, $\nu(\text{C-O})$, $\delta(\text{CH}_3\text{-C})$ and $\delta(\text{C-O})$ bands for Raman and IR were established. Peroxide O-O vibrations were observed around $750\text{-}970\text{ cm}^{-1}$. Peroxide C-O were identified at $1000\text{-}1100\text{ cm}^{-1}$. Amine peroxides showed N-C vibration between 1200 and 1370 cm^{-1} . Amide peroxides (TMDD) showed a N-H stretching around 3340 cm^{-1} .

1. Introduction

Hexamethylene triperoxide diamine (HMTD) is one of the most common nitrogen based peroxides, also known as amine peroxides. This explosive compound has been known even before triacetone triperoxide (TATP). It was

synthesized by Legler in 1885 from ammonia and bishydroxymethyl peroxide¹. Later, many other investigators tried to synthesize HMTD by simpler methods and obtaining higher yields. Among these were Baeyer and Villiger, Von Girssewald, and Shaefer²⁻⁴. HMTD not only is more sensitive and unstable than TATP, but also this compound can be synthesized easier and it is more difficult to detect due to its lower vapor pressure. Recently, HMTD has been used in the terrorist acts of London⁵, and is considered a threat chemical for government buildings and transport services⁶. This event has promoted many researchers to develop innovative methods for its detection.

The first step in the characterization of HMTD was the determination of its structure using x-ray crystallography⁷. The vibrational spectra and NMR analysis showed that HMTD is a caged like cyclic peroxide⁸. Buttigieg presented an Ion Mobility Spectroscopy study for the detection of TATP and HMTD⁹. Karst and coworkers developed methods for their detection based on HPLC¹⁰. Recently, Zeiri proposed a method for the detection using metal cations¹¹⁻¹². In 1999, Edward and his colleagues synthesized other cage amine peroxides¹³. In 2000, Oxley and Smith determined the mass fragmentation by isotopically label HMTD and then in 2002, presented its thermal decomposition¹⁴⁻¹⁵. But the threat is not only HMTD, a recently mentioned peroxide made from urea is the next challenge: tetramethylene diperoxide dicarbamide (TMDD), synthesized by von Girssewald and Siegens in 1914¹⁶. This study presents the characterization and differentiation of HMTD, TMDD and other nitrogen based peroxides by FT-IR and Raman spectroscopy, using the Infrared and Raman studies of Sölze and

Klaeboe as reference for HMTD⁸. Also included is a mass spectrometry method development for trace analysis of HMTD. Other peroxides were also synthesized which produced common Raman peaks with TATP or DADP.

2. Methods

2.1. Reagents

The reagents used in this research were: acetone (98% w/w), urea (98% w/w), aniline (98% w/w), hexamethylene tetraamine (98% w/w)(Acros-Organics, Fairlawn, NJ), formaldehyde (CH₂O, 37% wt, Acros-Organics N.V., Fairlawn, NJ), hydrogen peroxide (H₂O₂, 50% in water, Fisher Scientific International, Fairlawn, NJ), and hydrochloric acid (HCl, 12 M, Merck, VWR International, Inc., West Chester, PA 19380), and methanosulfuric acid (HCH₃SO₃, Sigma-Aldrich Chemical Co., Milwaukee, WI).

2.2. Instrumentation

Fourier Transform Infrared (FTIR) spectrometer used was a Nicolet FT-IR spectrometer 8700 Nexus E.S.P with Attenuated Total Reflectance (ATR). Raman instrumentation used included Renishaw RM2000 Raman Microscope equipped with Renishaw high power solid state diode laser operating at 532 and 514.5 nm Coherent, Inc. INNOVA 308 Ar⁺ laser system. Dispersive Raman equipment operated in confocal mode. All spectrometers were equipped with polarization analyzers and de-scramblers.

2.3. Method of Analysis

The characterization of amine peroxides was made by vibrational techniques such as Fourier Transform-Infrared Spectroscopy (FTIR) and Raman Microscopy. To confirm the purity and to obtain positive identification of the compounds the samples were analyzed by melting point in an Electrothermal Melt-Temp, Barnstead International, Dubuque, IA. The infrared absorption studies were performed with a FT-IR Attenuated Total Reflectance using a germanium crystal, interfaced to a Thermo-Nicolet spectrometer, model Nexus E.S.P. The samples were dry and clear crystals and only approximately 2 mg were analyzed. For the Raman microanalysis, the samples were studied after basic purification to removed water. Commercially available HMTD diluted in acetonitrile was analyzed in a direct insertion probe of a JEOL GC-Mate II.

3. Results

3.1. Synthesis

The synthesis of the nitrogen based peroxides was specific for each compound. Most of them followed a similar preparation of TATP, but required the addition of formaldehyde. For security reasons, the syntheses will be only presented without the exact amounts. Figure 6-1 present a schematic synthesis of most of the amine peroxides.

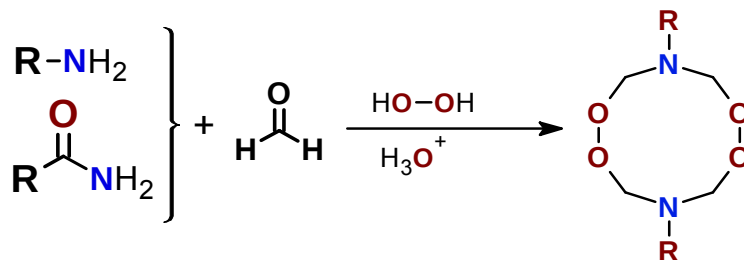


Figure 6-1. Schematic of preparation of nitrogen based organic peroxides

HMTD was made by dissolving hexamethylene tetramine in hydrogen peroxide at low temperature. Then a diluted solution of a strong acid or weak organic acid such as acetic or citric acid was added. Figure 6-2a shows the schematic synthesis of HMTD developed by Von Girssewald. The mixture was cooled in the refrigerator for 24 hours and the solution was then filtered. Since HMTD is not soluble in typical solvents purification crystallization cannot be performed easily. The crystals obtained are powder like, but in the microscope can be easily recognized as in Figure 6-2b.

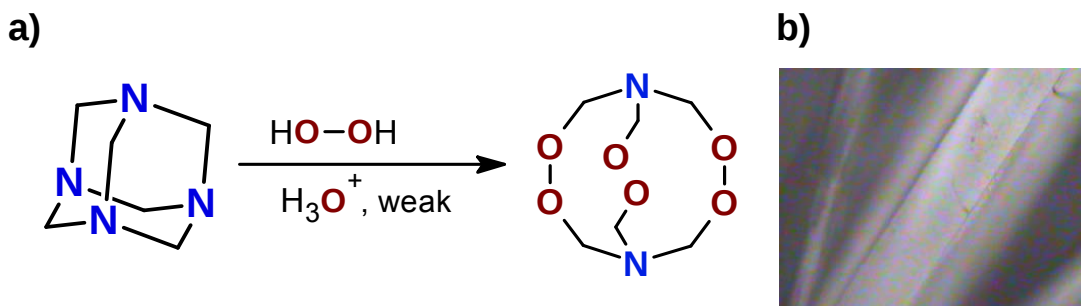


Figure 6-2. Von Girssewald Synthesis of HMTD; (a) Schematic of HTMD preparation; (b) white light micrographs of HMTD crystals.

TMDD and other amine and amide peroxides required a change in methodology. In a cold flask between 0°C and -5°C, formaldehyde and hydrogen

peroxide were mixed and then urea or the desired amine was added and dissolved in the mixture. After totally dissolving, a small portion of strong acid is added. The solution was then placed in a cold system for 3 or 5 days and a white precipitate was formed. TMDD was also difficult to dissolve. The purification with organic solvents only removed soluble impurities. Figure 6-3a shows the generally accepted mechanism of synthesis.

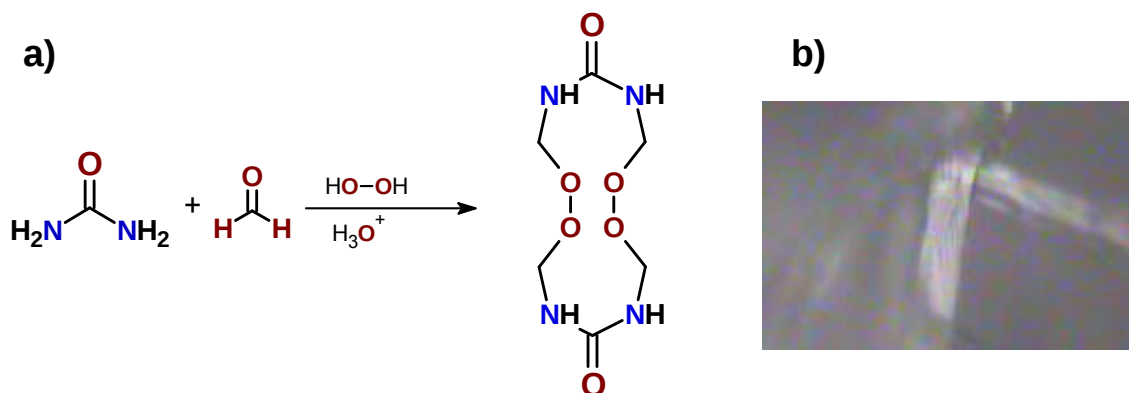


Figure 6-3. Synthesis of TMDD. a) Schematic of TMDD preparation and its possible structures; b) white light micrographs of TMDD crystals.

The synthesis of other cyclic amine and amide peroxides was tried using aniline, benzamide, m-nitroaniline and acetamide. However, most of the peroxides produce very low yields. Aniline and m-nitroaniline were synthesized but the exciting laser damaged the sample. Peroxides from benzamide did not produce observable crystals. Cyclic amide peroxide from acetamide was successfully synthesized with low yield and used as a representative compound for unknown peroxide characterization. These small crystals were analyzed by Raman spectroscopy.

3.2. Mass spectral analysis of HMTD

Figure 6-4 shows the mass spectral characterization of a commercial standard of HMTD developed by Direct Insertion Mass Spectroscopy (DI-MS). As shown, the molecular peak stands out very clearly at m/z 208 in contrast with TATP in where the molecular peak at m/z 222 is slightly seen in the fragmentation pattern. The base peak of HMTD is m/z 30 which a fragment of CH_2O^+ . This fragmentation could change depending on the temperature of the direct insertion probe. Other mass spectra experiments showed the based peaks at m/z : 42 ($\text{CH}_2\text{NCH}_2^+$) and 45 (CH_2NO^+). Other fragments of HMTD are m/z 58, 69, 73, 81, 88, 117, 176. This fragmentation can help to differentiate for the acetone peroxides that showed the following fragmentation pattern: base peak at m/z 43, peaks at m/z 58, 59, 75, 101 and 117.

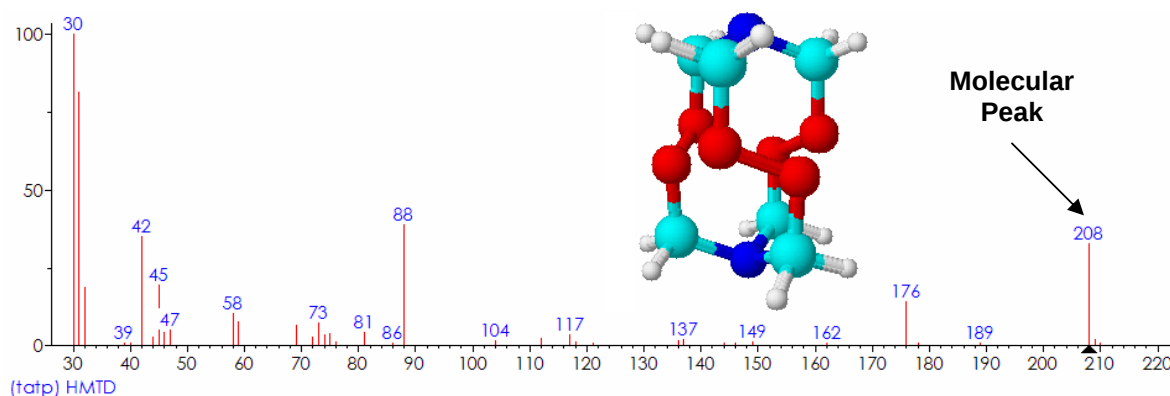


Figure 6-4. Direct Insertion Mass Spectrum of HMTD.

3.3. Vibrational spectroscopic analysis of HMTD

Infrared and Raman spectroscopies were useful tools in the characterization, especially when the experiments were run in the fingerprint region. Figure 6-5 presents the full vibrational spectra of HMTD by Raman and

Attenuated Total Reflectance FT-IR. Both techniques show a doublet band, at 2966 cm^{-1} and 2920 cm^{-1} that belongs to stretching of the CH_2 but the doublet can only be explained as a population problem the six-methylene groups. Amine vibrations of N-C are present at $1066(\text{Raman})$ and $1052(\text{IR})\text{ cm}^{-1}$, and between $1360\text{--}1310\text{ cm}^{-1}$ for the tertiary amine stretchings $\{\nu(\text{N-C})\}$. The characteristic intensity pattern of the peroxide bands (e.g., TATP) between 950 cm^{-1} and 750 cm^{-1} are inverted in both techniques: the 777 cm^{-1} symmetric vibration is stronger in Raman and the asymmetric stretches at 870 cm^{-1} and 945 cm^{-1} are stronger in IR. All these bands are consistent with the results of Sülzle and Klæboe ⁸. These results characterized and confirmed the synthesis of HMTD.

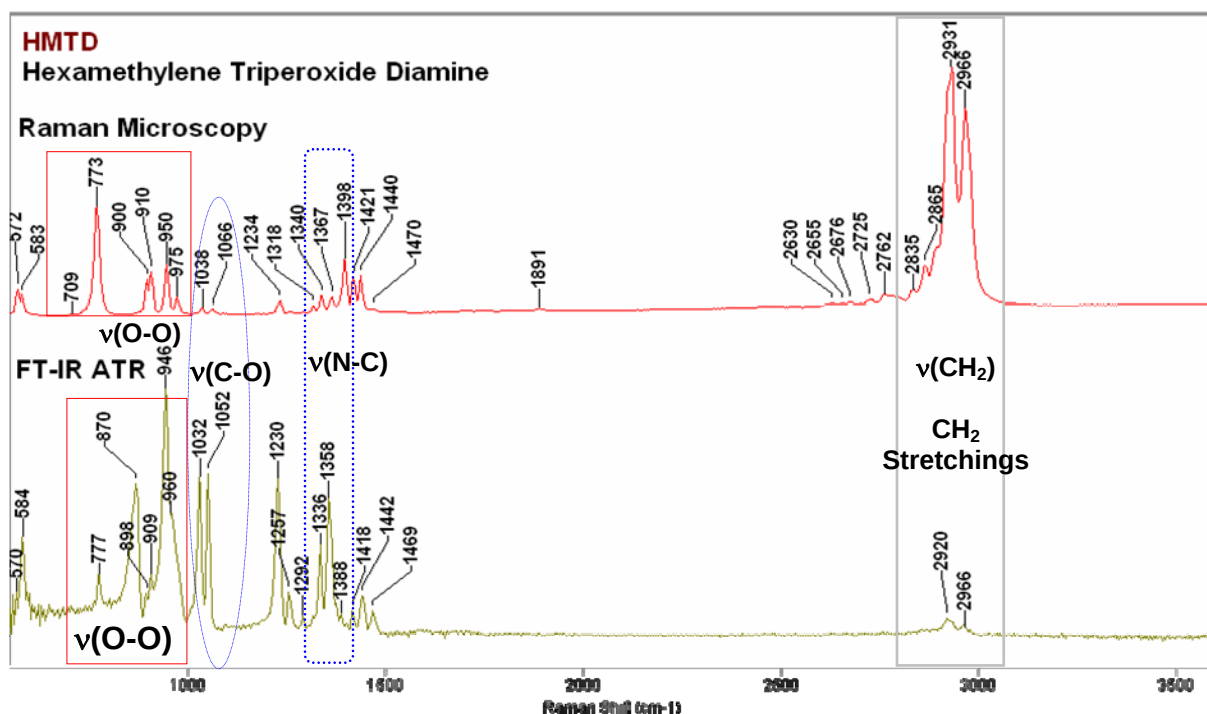


Figure 6-5. Vibrational spectra of HMTD by FT-IR-ATR and Raman at 514.5 nm.

3.4. Vibrational spectroscopic analysis of TMDD

TMDD did not have any previous spectroscopic data reported in literature that could be used to confirm its preparation. However, the simplicity of the spectra obtained allowed its characterization. Figure 6-6 shows the vibrational spectra of TMDD. The principal evidence of the synthesis of the carbamide compound, TMDD, was the strong absorption of the N-H stretching at 3336 cm^{-1} in FT-IR and 3346 cm^{-1} in Raman¹⁹⁻²⁰. Followed by CH_2 stretchings observed at 2946 and 3045 cm^{-1} in IR (2993 cm^{-1} and 2949 cm^{-1} in Raman). These frequencies were similar to those found in HMTD, which indicated that the molecule had methylene groups. However, stronger CH_2 vibrations at 2949 cm^{-1} suggested that TMDD produced more symmetric vibrations than HMTD. This unexpected results for a large ring cyclic peroxide predicted TMDD symmetric structure. Urea had strong carbonyl absorption in the range of $1700\text{-}1600\text{ cm}^{-1}$ and TMDD share this absorption. In the IR spectra, strong absorptions in the range of $1500\text{-}1660\text{ cm}^{-1}$ demonstrated the presence of a carbonyl group. In Raman, corresponding signal could be observed about $1650\text{-}1770\text{ cm}^{-1}$. Deformation CH_2 stretchings were observed around 1423 cm^{-1} (Raman: 1421 cm^{-1}). Amine N-C stretchings were identified at 1321 and 1300 cm^{-1} (Raman: 1319 and 1296 cm^{-1}). Characterization of the N-C present in amides could be observed at 1253 and 1127 cm^{-1} $\{\nu(\text{N-C})\}$. Peroxide C-O vibrations were identified at 1048 cm^{-1} (Raman: 1056 cm^{-1}). Finally, the most relevant evidence of the synthesis of the peroxide was the typical vibrations of the O-O bond $\{\nu(\text{O-O})\}$ between $980\text{-}700\text{ cm}^{-1}$. The white crystalline solid showed absorptions in the

O-O peroxide zone. In FT-IR, the asymmetrical O-O peroxide stretchings at 943 cm^{-1} and 910 cm^{-1} were very strong; in Raman, these peroxide stretches were weak at 974 cm^{-1} and 914 cm^{-1} , but the symmetrical peroxide stretches vibrations at 776 and 756 cm^{-1} were more intense than in IR. A doublet band at 2359 and 2340 cm^{-1} due the presence of CO_2 could be observed in the FT-IR spectrum. This band was absent in Raman.

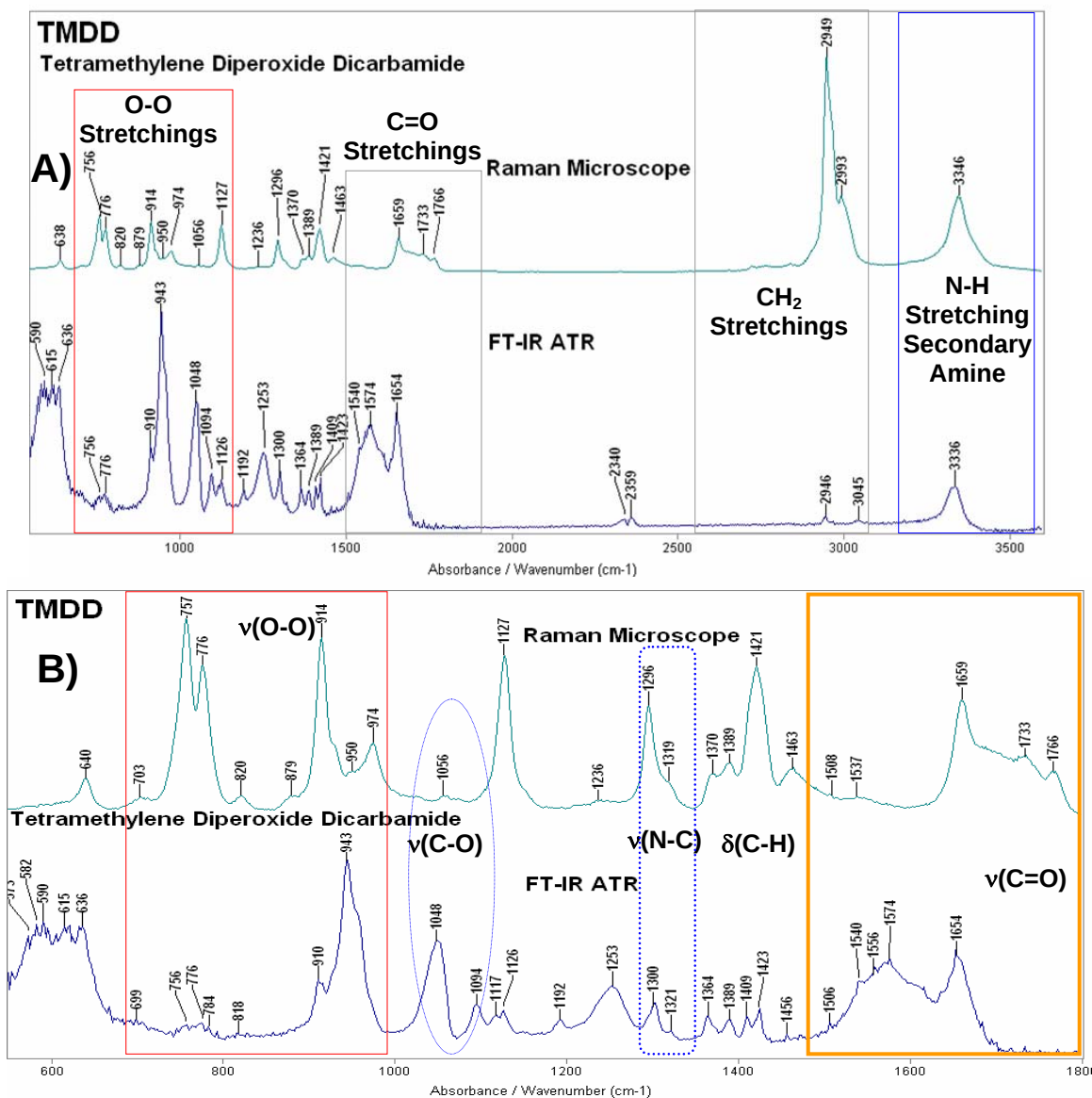


Figure 6-6. Vibrational spectra of TMDD by FT-IR-ATR and Raman at 514.5 nm: A) Full Spectrum; and B) Fingerprint Spectrum.

3.5. Vibrational Spectroscopic Analysis of other Cyclic Amide Peroxides

Other cyclic amine and amide peroxides synthesized also showed the $\nu(\text{O-O})$ region bands as well as peroxyacetones and HMTD. Aniline peroxides were too sensitive to laser and results would be not shown. Acetamide peroxide

was one example of a compound that needed to be analyzed by Raman microscopy, because only a small crystal could be obtained from the solution. Figure 6-7 showed the obtained Raman spectra of the amide peroxide made from acetamide. Peroxide spectra reveal that the most prominent absorptions in the range: 2960-2650 cm^{-1} are methylene groups of the compound and the methyl group of the acetamide. The absence of carbonyl group vibrations around 1600-1700 cm^{-1} suggested that acetamide also polymerized through its carbonyl, like acetone during TATP formation. Amine absorptions, $\nu(\text{N-C})$, can be observed at 1330, 1296, 1168, 1153 and 1103 cm^{-1} . Also, the marked bands assigned to $\nu(\text{O-O})$ were present in the small crystal around 800-975 cm^{-1} . Its strongest O-O peroxide vibrations were identified at 809, 842 and 974 cm^{-1} . There were bands between 1000-750 cm^{-1} which are consistent with other peroxides (HMTD, TATP and TMDD).

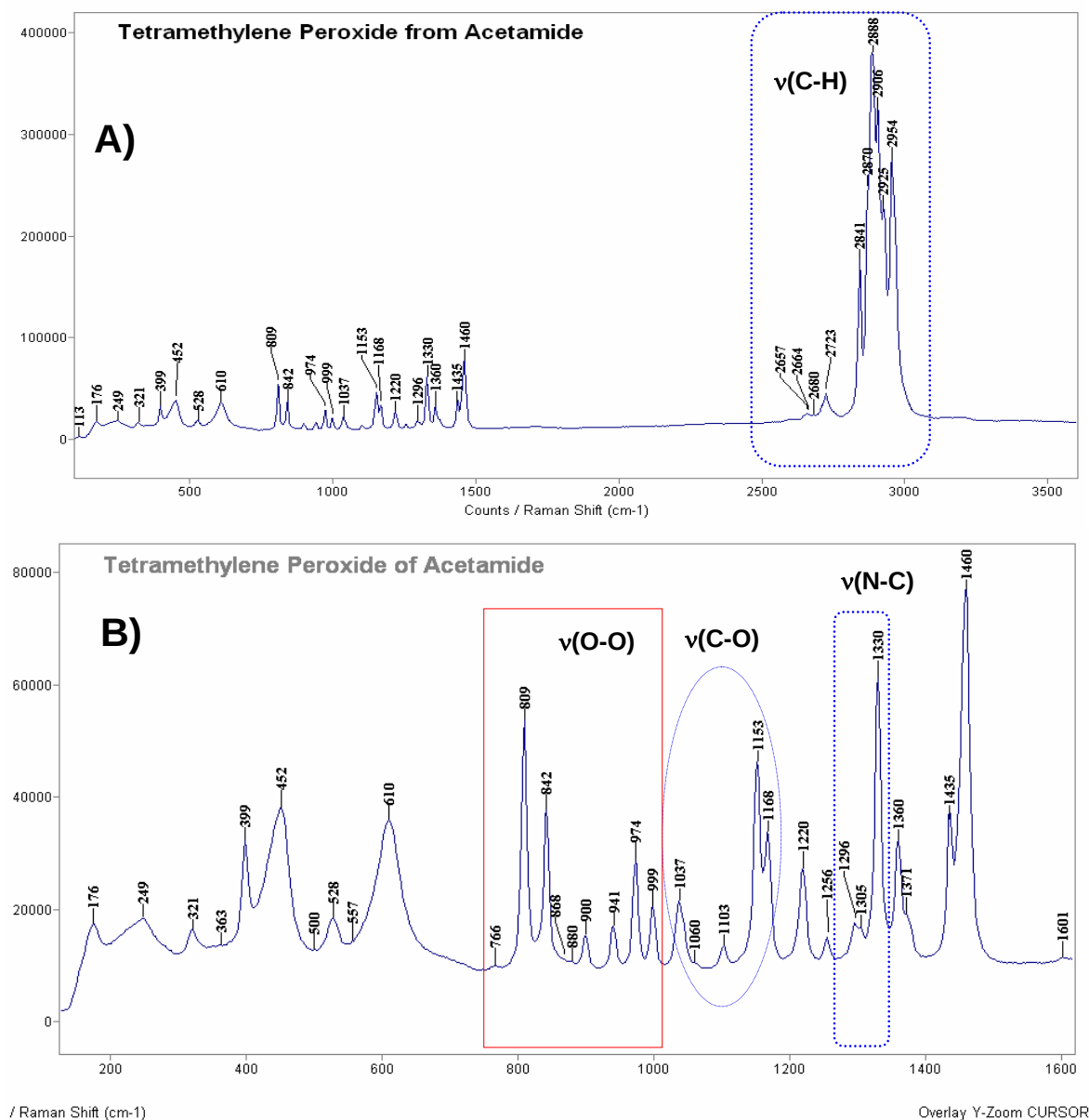


Figure 6-7. Raman spectra of cyclic amide peroxide from acetamide. A) Full Raman spectrum; and B) Fingerprint spectrum. Only small crystal was obtained and using microscope objective of 50 X allowed us to identify the presence of the peroxide.

4. Discussion

The results obtained confirmed that HMTD has been synthesized and characterized by vibrational methods. Infrared and Raman spectroscopy revealed that HMTD shares common vibrational bands with TATP, at 960, 975, 960, 950, 946, 910, 900, and 870 cm^{-1} . The bands at 773 and 777 cm^{-1} are characteristic of HMTD and these vibrations are consistent with previous results [13,19,20]. Raman was able to distinguish HMTD from other nitrogen based peroxides using very small sample amounts. Results also indicated that Raman is more suitable for insoluble solids than GC-MS and it can help for the identification of amine peroxides in forensic analysis.

Direct insertion mass spectrometry demonstrated also that is more suitable for the analysis of amine peroxides which are difficult to dissolve in most organic solvents. In addition, it does not require sample preparation and can give faster results than a GC-MS. High sample purity is required.

Tetramethylene diperoxide dicarbamide (TMDD) has been characterized by vibrational techniques and proven that it is peroxide made from common products, such as urea. Peroxide vibrations observed are 974, 950, 943, 914, 910, and 879 cm^{-1} . Signals at 776 and 754 cm^{-1} are present in both Raman and IR spectra. Among the peroxide vibrations that TMDD shares with HMTD are 974, 943, 910, and 776 cm^{-1} which indicates that these bands are characteristic of nitrogen based peroxides. Also, the differences between the intensities of the Raman and IR frequencies showed that TMDD shares some symmetry, even

with the complexity of the HMTD molecule. Figure 6-8 presents the possible structure of TMDD considering the spectroscopic results.

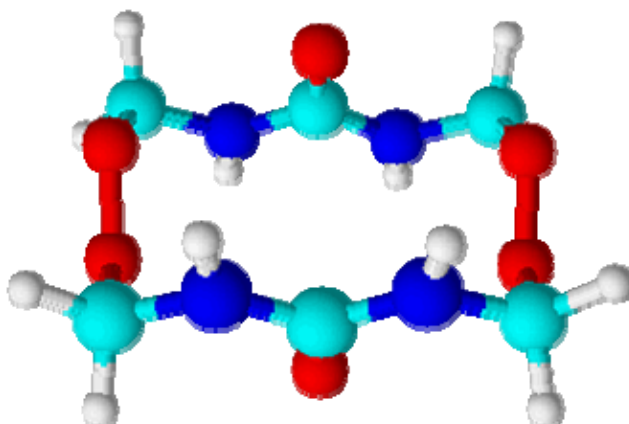


Figure 6-8. Tetramethylene Diperoxide Dicarbamide (TMDD) propoused structure.

Raman also proved to be an excellent technique along with ATR FT-IR for the characterization of less known peroxides. Raman microscopy can show morphology of the sample and Attenuated Total Reflectance FT-IR can be used as confirmation technique. The only requirement for the characterization of the bands is state that there are band that shows low intensity in the Raman spectrum but have high intensity in the IR spectrum, thus providing more information on the symmetry of the vibrational modes.

5. Conclusions

As part of this work to develop methods for detection of energetic organic peroxides, hexamethylene triperoxide diamine (HMTD) and tetramethylene diperoxide dicarbamide (TMDD) were synthesized in a simple and direct way with the purpose of studying their characterization using vibrational spectroscopy. The results presented indicate that FT-IR and Raman Microscopy can be used as useful tools for the characterization and identification nitrogen based peroxides. Due the low vapor pressure of amine and amide cyclic peroxides, it is required the development of trace methods for solid phase analysis such as Direct Insertion MS, Solid phase NMR, Raman and FT-IR Microscopy .

Chromatographic techniques are difficult to perform analysis for HMTD and TMDD due the low solubility in most organic solvents. FTIR and Raman spectroscopy proved to be robust techniques for analysis and trace detection for cyclic organic peroxides and complementary techniques to more established methods of analysis such as MS. Further studies in developing methodologies for the trace detection of these compounds by more sensitive equipments, such as DART-TOF that does not require sample preparation or the analysis are recommended.

6. References

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CHAPTER VII

Characterization of Organic Peroxides by Mass Spectroscopy and Raman Detection

Triacetone triperoxide and hexamethylene triperoxide diamine are among the most used and most studied non nitro based high explosives. Still, there are other peroxides which do not have reported methods for their detection. Direct Analysis in Real Time (DART) is an emerging ambient pressure ionization technique in mass spectrometry. This contribution presents the analysis, characterization and detection of Triacetone Triperoxide and Hexamethylene Triperoxide Diamine using DART Time of Flight Mass Spectrometry. Although typical experiments are done using helium, adding a small amount of ammonium hydroxide improved the detection down to 30 ppb. This study also presents the detection and identification of benzoyl peroxide, tricyclopentanone Triperoxide and Tetramethylene Diperoxide Dicarbamide by MS and Raman microscopy. TATP showed a single peak at m/z 240.144 $[M+NH_4]^+$ with the peaks at m/z 223 $[M+H]^+$ or 222 $[M]^+$ completely absent. Samples of the important cyclic peroxide with deuterium enrichment (TATP- d_{18}) were analyzed to compare results. These presented a similar peak at m/z 258.267 $[TATP-d_{18}+NH_4]^+$. HMTD showed a peak at m/z 209.078 $[M+H]^+$ and small adduct peak at m/z 226.103 $[M+NH_4]^+$ that allowed its detection in standard solution and laboratory preparations. TMDD presented several peaks with a base peak at m/z 101.033, molecular peak at m/z 237.081 $[M+H]^+$ and a strong peak adduct at m/z 254.108 $[M+NH_4]^+$. All samples

were analyzed by Raman Microscopy in order to characterize them and to confirm the MS results.

1. Introduction

Widespread use of organic peroxides in terrorist acts has required government security agencies to identify and promote new technologies for the detection of these compounds ^{43, 44}. Triacetone triperoxide (TATP) and hexamethylene triperoxide diamine (HMTD) are the more commonly used cyclic organic peroxides in terrorist acts, such as the 2005 London bombing ²⁴. Several new methods have been developed for detection at airports, government buildings entrances and mass transportation facilities ^{20, 23, 24, 43}.

In 1983, the first forensic analysis and characterization of TATP by electron ionization (EI) and chemical ionization (CI) mass spectrometry ²⁰ was reported. Characterization of HMTD by X-ray analysis to determine its structure was published in 1985 ¹⁰. Later in 1988, HMTD was fully characterized by Nuclear Magnetic Resonance (NMR), Raman and Infra Red (IR) spectroscopies ⁴⁵. One of the first HMTD mass spectra was presented in 2000 ⁴⁶. In the same year, Gas Chromatography-Mass Spectrometry (GCMS) based methodologies for TATP and diacetone diperoxide (DADP) detection at picogram levels were presented ³⁵. In 2001, a method for HMTD detection was described using High Performance Liquid Chromatography Mass Spectrometry (HPLC-MS) ⁴⁷. Later in the same year, the shoe-bomber case further motivated peroxide-based

explosives detection ⁴⁸. In 2002, detection methods for TATP were described using HPLC separation, post column derivatization, MS analysis ¹⁸, and direct HPLC/MS analysis ³¹. GC-Electron Capture Detector (ECD) was used to observe TATP and HMTD decomposition products and these studies included essential thermal properties for further analysis by other techniques ^{32, 42, 49}. In addition, a theoretical proposition of a method for detection using metal cations was presented ⁵⁰. In 2003, a HPLC method for detection of TATP in air was developed using vacuum system and headspace techniques ²⁷. This work was followed by a method to detect TATP using Ion Mobility Spectrometry (IMS) ³⁰. A year later, TATP trace detection methods for GC-MS were performed using headspace analysis ⁴¹ and Solid Phase Micro Extraction ⁵¹. Also in 2004, a method for TATP and HMTD analysis using HPLC-MS/MS was presented ¹⁵. In 2005, methods for acetone peroxide analysis using GC-MS, GC-FTIR and Raman microscopy were discussed ⁵².

Due to novel advances in mass spectrometry, 2006 witnessed a significant increment in studies of peroxide detection. A selected-ion flow-tube mass spectrometer was developed for TATP detection that provided 10 ppb detection levels ⁵³. The introduction of desorption electrospray ionization (DESI) was very useful for atmospheric pressure analysis of acetone peroxides reaching 15 ng detection limit ⁵⁴. Also, laser desorption-MS was used to analyze TATP, 2,4-dinitrotoluene (DNT) and 2,4,6-trinitotoluene (TNT) with 40 ppb detection levels ⁵⁵. Methodologies for TATP and HMTD were developed using IMS, direct insertion probe MS and Raman Scattering Microscopy in pure form and in crude

products^{56, 57}. Later in the same year, several methodologies for TATP detection were compared: GCMS with electron ionization (EI) and chemical ionization (CI)⁵⁸. Positive ion CI was induced using ammonium ion to generate a molecular adduct at m/z 240. This method enabled the detection of picograms levels of TATP. Finally, the computational method proposed earlier was proven by electrochemical detection of HMTD and TATP using a Prussian-blue electrode⁵⁹. In 2007, Direct Analysis in Real Time (DART) was used to detect TATP, HMTD and other peroxides, and the results were compared with EI^{44, 60, 61}. Recently, DESI was compared with desorption atmospheric pressure chemical ionization. The results showed that peroxides formed adduct ions with Na^+ , K^+ and NH_4^+ ⁶². These multiple representations of the analyte complicate the interpretation of the spectrum. In addition, a simple method for TATP analysis using electrospray ionization (ESI) direct injection was presented to demonstrate fragmentation of TATP under these conditions⁶³. Recent work focused on the analysis of TATP and its decomposition products by GC-MS using diluted sample insertion and solid phase micro extraction (SPME)⁶⁴.

This paper presents syntheses of cyclic organic peroxides, some of which are new and others were prepared for the study. Vibrational spectroscopy was used for characterization of known organic peroxides TATP, HMTD, benzoyl peroxide (BP), cyclopentanone triperoxide and a new cyclic amide peroxide: tetramethylene diperoxide dicarbamide (TMDD). Ambient pressure ionization TOF-MS was used as characterization tool and as a means of detecting these important chemical threats in open air. High resolution TOF measurements

allowed identifying all components even in complex mixtures. EI-MS and Open-Air-MS were compared and contrasted in organic peroxides characterization. Isotopic labeling experiments were used to help elucidate MS fragmentation mechanisms and assist in peak assignments for both MS and Raman spectroscopy spectra.

2. Procedures

2.1. Instrumentation

Vibrational characterization of cyclic organic peroxides was carried out using a Renishaw Raman Microspectrometer model RM2000 Renishaw, Inc. (Chicago, IL) equipped with CCD detector and Leica LM/LS microscope using an ultra long working distance 50x objective. HMTD, TATP, TATP-d₁₈, TMDD and cyclopentanone triperoxide spontaneous Raman analysis was accomplished at excitation lines: 488, 514, 532 and 785 nm using laser power at sample of < 10 mW. The excitation sources were INNOVA 308 Ar⁺ laser system wavelength selected for 488 nm blue line and 514.5 nm green line; VERDI-6 diode-pumped 532 nm laser with a variable output power of up to 6 W; and 899-01 Titanium/Sapphire ring laser operating at 785 nm pumped by the 532 nm laser (all laser systems from Coherent Laser Group, Santa Clara, CA.). Raman spectra were collected in the Raman Shift range of 100-4000 cm⁻¹, with three acquisitions and integration time of 10 s per scan. Dispersive Raman equipment was operated in confocal mode. Fourier Transform Infrared (FTIR) spectrometer used was a Thermo-Nicolet FT-IR spectrometer Nexus E.S.P with Attenuated

Total Reflectance (ATR) accessory and Bruker Optics model IFS 66v/S FT-IR microscope.

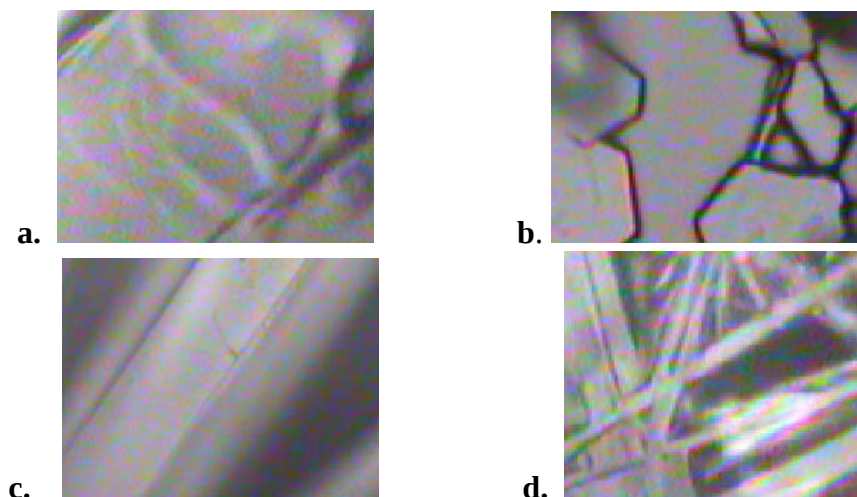


Figure 7-1. White light images of sublimated peroxides (50x magnification): (a) TATP; (b) cyclopentanone triperoxide; (c) HMTD; (d) TMDD.

An Agilent Technologies gas chromatograph model GC-MS 5890 GC system coupled to a 5790 mass selective detector was used in electron ionization (EI) mode-mass spectroscopy experiments. A JEOL GC-Matell direct probe system was also used to analyze by EI at 70 eV. A DART-TOF-MS (JEOL, USA, Inc., Peabody, MA) was used for the atmospheric pressure-CI-MS experiments.

2.2. Reagents

Chemical reagents used in this research included d_6 -acetone (99% isotope), acetone (98% w/w), cyclopentanone (98% w/w), hexamethylene tetraamine (98% w/w), benzoyl peroxide (98% w/w) and formaldehyde (CH_2O , 37% wt), all obtained from Acros-Organics, Fairlawn, NJ. Hydrogen peroxide

(H₂O₂, 50%) and urea (98% w/w) were obtained from Fisher Scientific International, Fairlawn, NJ. Hydrochloric acid (HCl, 12 M, VWR International, Inc., West Chester, PA) was used as catalytic agent. High purity acetonitrile *Omnisolv* (GC/HPLC/gradient analysis grade) was obtained from EMD Chemicals Inc., Gibbstown, NJ.

2.3. Preparation of Cyclic Organic Peroxides

HMTD and TATP, although commercially available as GC-MS standards (1 mg/mL), were synthesized to have a relatively large supply for the study. Recrystallized samples had lower impurities than commercial samples. Other cyclic organic peroxides were not commercially available and had to be synthesized and purified. White light images of TATP, cyclopentanone, HMTD and TMDD show well ordered crystals (Fig. 7-1 (a)- (d)).

2.3.1. TATP, d₁₈TATP and Cyclopentanone Triperoxide

TATP, d₁₈-TATP and cyclopentanone were synthesized following Wolffstein's original procedure ¹⁹. Briefly, the ketone and a catalytic amount of sulfuric acid were cooled to approximately 0°C in an ice bath in neat form or in dichloromethane solution. Ice cold hydrogen peroxide (50%) was added dropwise to prevent violent reactions. The reaction mixture was crystallized by ether evaporation and then purified by sublimation at a constant temperature of 80°C.

2.3.2. Hexamethylene Triperoxide Diamine, HMTD

HMTD was synthesized following the method used by Von Girsewald ⁶⁵. A sample of 0.80 grams of hexamethylene tetraamine was dissolved in 2.5 mL of 30% H₂O₂. The solution was stirred and cooled to near 0°C in an ice water bath. Then a small amount of dilute HCl_{aq} was added dropwise. This solution was stirred while cooling for three hours until a white crystalline precipitate formed. The crystals were filtered out and washed with water. Due the low yield of the preparation, no purification was performed.

2.3.3. Tetramethylene Diperoxide Dicarbamide, TMDD

TMDD was prepared using Von Girsewald and Siegens method ⁶⁶. A solution of formaldehyde and hydrogen peroxide was cooled below 5°C. Urea was added to the solution and a small amount of concentrated hydrochloric acid was added. After three days of standing at 0°C in a refrigerator, a white powder-like substance was obtained. This precipitate was filtered with a Büchner funnel and washed with distilled water. The crude product was allowed to dry and then recovered.

2.4. Ambient pressure ionization MS Analysis

Stock solutions of 1.0 mg/mL of TATP, d18-TATP, BP, HMTD and TMDD were prepared in acetonitrile. The sealed end of a capillary tube was dipped into the solutions and placed in the ambient pressure ionization zone (Fig. 7-2). Quantitative measurements were made using a 2 µL micropipette to aliquot an accurate amount of sample onto the capillary. Ammonium hydroxide can be used as a CI agent in some types of compounds ⁶⁰. The use of NH₄⁺ as an adduct

promoter is routinely used for CI-MS analysis of ketones, acids, alcohols and other oxygen-rich compounds such as peroxides and ethers ^{58, 67}. The effect of addition of a source of ammonium ions was investigated for organic peroxides studied.

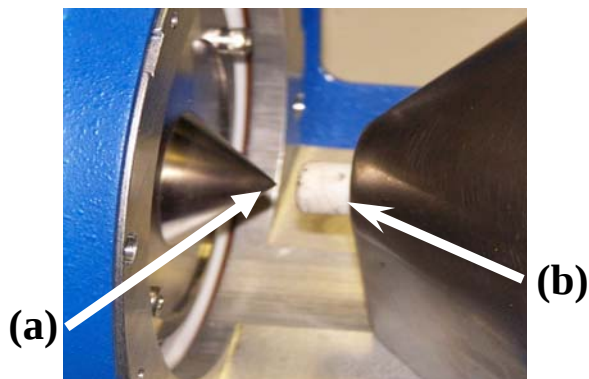


Figure 7-2. Ambient pressure ionization zone in the DART/AccuTOF system: (a) ambient pressure inlet to the time-of flight mass spectrometer; (b) ionization region of MS inlet system.

3. Results and Discussion

3.1. Raman Spectroscopy

Vibrational spectroscopy was the main characterization tool for the peroxides. Raman spectroscopy is an ideal technique for characterizing peroxides. The oxygen-oxygen bond vibration is unique to the peroxide moiety since it defines its chemical structure. These vibrations occur at 1000 cm^{-1} , 880 cm^{-1} and 870 cm^{-1} . These same bands were also observed for cyclopentanone triperoxide. The large vibrational shift of the methyl groups upon substitution of CH_3 for the CD_3 moiety was used to differentiate TATP from d_{18} -TATP. The

higher mass of the deuterium atoms causes the methyl stretching to shift from 3000-2700 cm^{-1} for TATP to 2300-2000 cm^{-1} for d_{18} -TATP (Fig. 7-3).

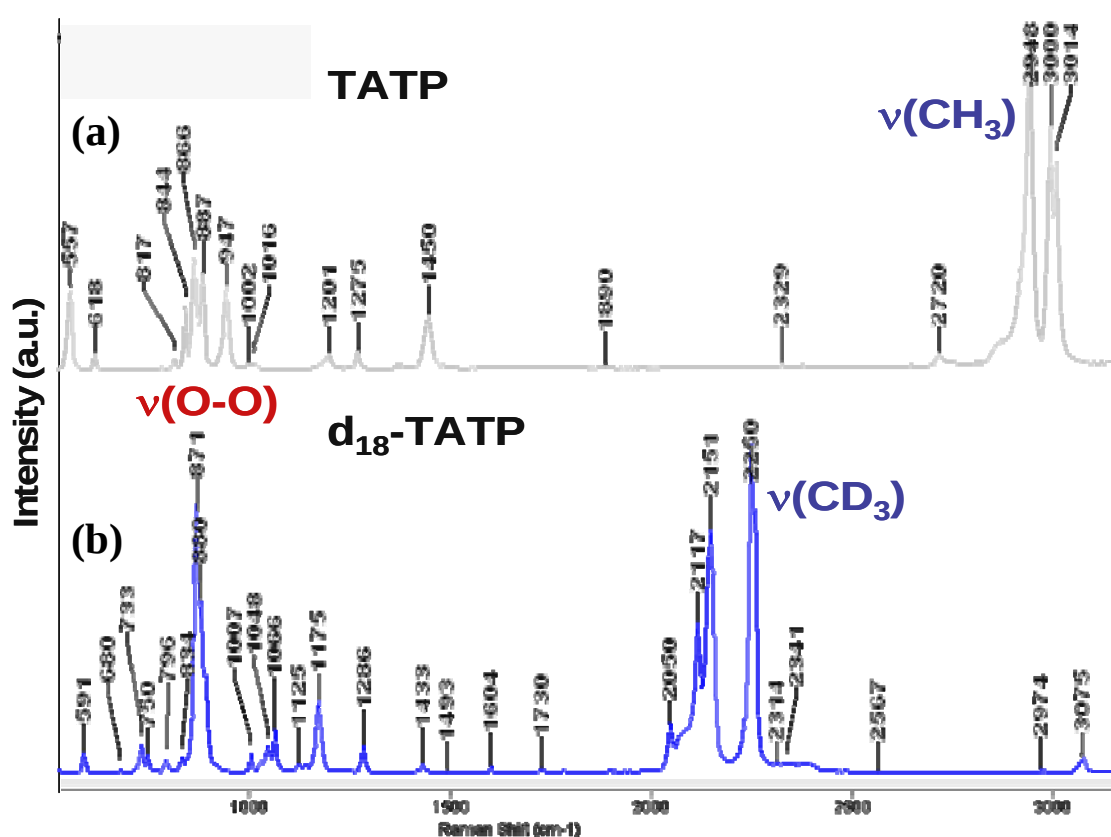


Figure 7-3. Raman spectra of: (a) TATP; and (b) d_{18} -TATP.

HMTD and TMDD exhibited similar methylene vibrational signal patterns ca. 2990-2830 cm^{-1} . Characteristic peroxide bands were observed in the range of 980-900 cm^{-1} and near 770 cm^{-1} . HMTD Raman spectrum compared favorably with previous results⁴⁵. No reference data for TMDD was found. The principal evidence for the synthesis of a carbamide compound is the strong absorption of the N-H stretching at 3336 cm^{-1} in FTIR absorption and 3346 cm^{-1} in Raman

scattering^{68, 69}. Urea has a strong carbonyl absorption in the range of 1700-1600 cm^{-1} ; TMDD also showed the presence of this important vibrational signature.

In the IR spectra, strong absorptions in the range of 1500-1660 cm^{-1} demonstrate the presence of a carbonyl group. The corresponding Raman signal was observed about 1650-1770 cm^{-1} . Characterization of the N-C present in amides can be observed at 1253, 1296 and 1127 cm^{-1} $\{\nu(\text{N-C})\}$. These results not only verify that TMDD was prepared but predicts a possible structure for it, that only mass spectrometry could confirm (Figure 6-10 and 7-11).

3.2. Gas-Chromatography Mass Spectrometry GCMS

GC-MS using electron impact ionization is a common analytical technique. A weak molecular ion is produced for the fragile TATP molecule. (Fig. 7-4), and abundant fragment ions at m/z 117 $[\text{C}_5\text{H}_9\text{O}_3]^+$, 101 $[\text{C}_5\text{H}_9\text{O}_2]^+$, 75 $[\text{C}_3\text{H}_6\text{O}_2]^+$, 59 $[\text{C}_3\text{H}_7\text{O}]^+$, 58 $[\text{C}_3\text{H}_6\text{O}]^+$ and a base peak at m/z 43 $[\text{C}_2\text{H}_3\text{O}]^+$ were observed.

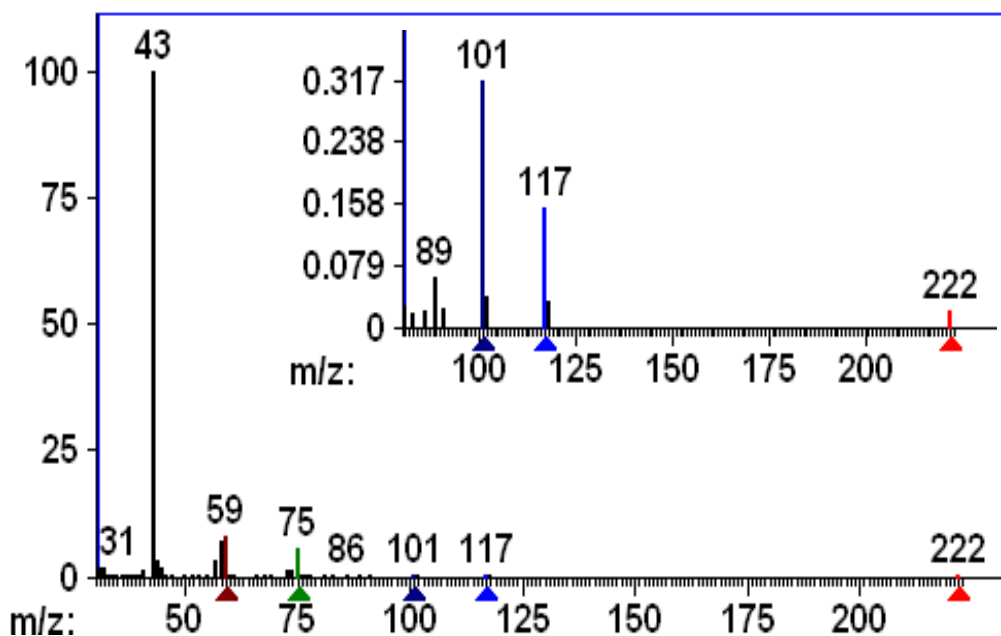


Figure 7-4. Mass spectrum of TATP by GC-EI-MS. Inset: zoom of high mass end region.

The identity of the fragment ions is supported by predicted mass shifts for the d_{18} -TATP analog. A molecular ion m/z 240, followed by m/z 126 $[C_5D_9O_3]^+$, 110 $[C_5D_9O_2]^+$, 82 $[C_3D_7O_2]^+$, 66 $[C_3D_7O]^+$, 64 $[C_3D_6O]^+$ and the base peak at m/z 46 $[C_2D_3O]^+$ (Fig. 7-5). The presence of these fragments together with the Raman results was used to characterize and verify the synthesis of TATP and of d_{18} TATP. GC/MS also presented a single peak in the chromatograms which confirms TATP purity by sublimation.

HMTD, on the other hand, had difficulties to determine its purity by GC methods due low vapor pressure. However, direct insertion analysis and EI spectrum was very simple to characterize. Comparing results with those of Oxley^{46, 49} HMTD presented an unusually strong molecular peak at m/z 208, in contrast with TATP where m/z 222 molecular peak is slightly seen in the EI spectrum. This molecular peak is followed by the loss of an oxygen molecule at m/z 176,

and the half breakup of this formed molecule at m/z 88. Other typical fragments were observed at m/z : 149, 117, 112, 104, 73, 59, 58, 45 $[\text{CH}_2\text{NO}]^+$, 42 $[\text{CH}_2\text{NCH}_2]^+$, 32, 31, and 30 $[\text{CH}_4\text{N}]^+$. At the GCMate-II magnetic sector MS the base peak of HMTD was m/z : 30. These results were very important because they can be used to compare results with the ambient pressure ionization-MS pattern.

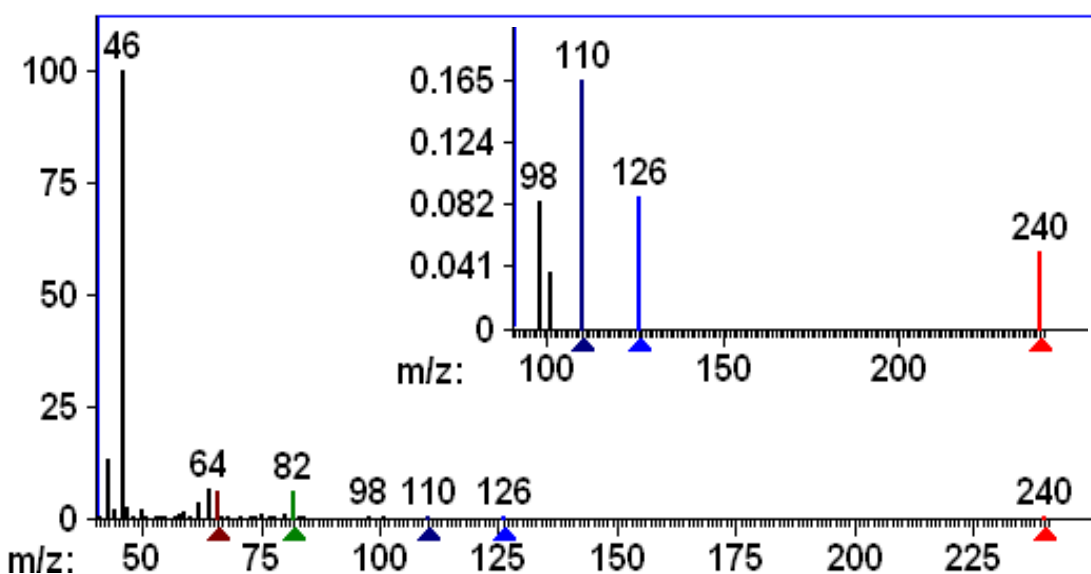


Figure 7-5. Mass Spectra of d_{18} -TATP by GC-MS EI.

3.3. Cyclic Ketone Peroxides and Benzoyl Peroxide

Aliphatic peroxides, including cyclic structures studied, did not produce molecular peaks by ambient pressure ionization. Instead, the adduct peak with air ammonium was observed. To increase peroxides MS signal, ammonium hydroxide vapor was added in front of the ionization probe. This simple improvement to ambient pressure detection enhanced the production of peroxide molecular adduct ions, even at relatively high temperatures (200°C).

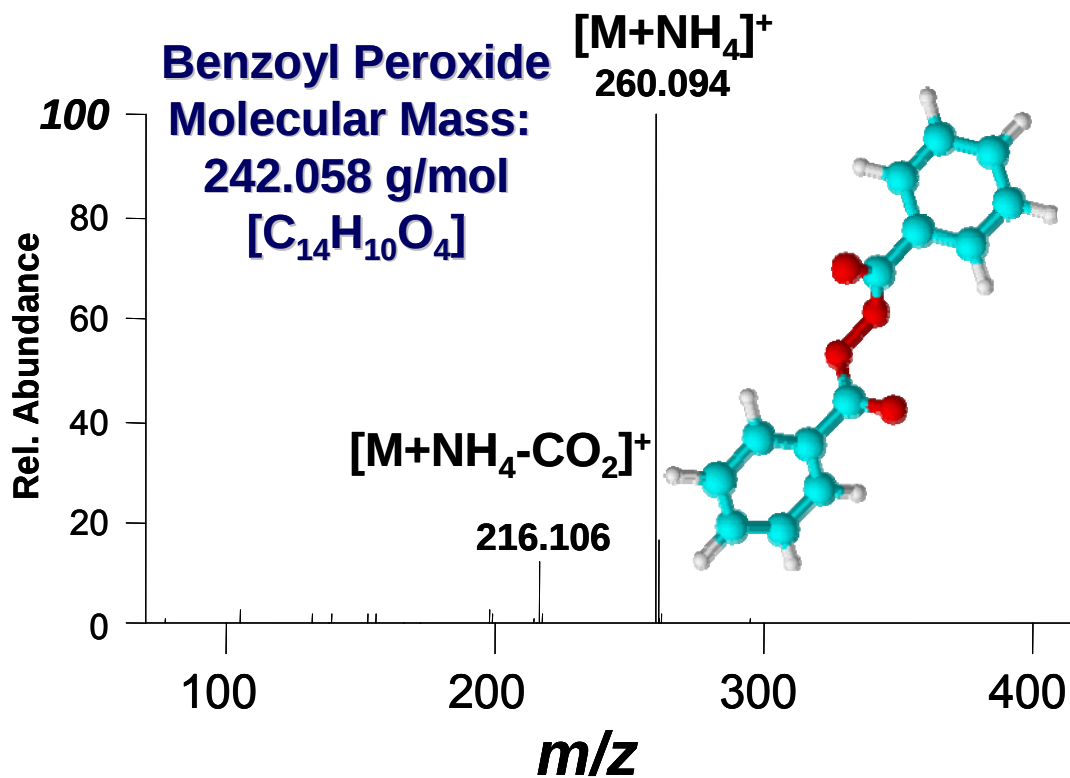


Figure 7-6. Benzoyl peroxide mass spectrum by API-TOFMS at 150°C.

Benzoyl peroxide (BP) was chosen to being analyzed by ambient pressure ionization-MS because it is commercially available and it is extensively used in medical treatments. BP has a molecular mass of 242.06 g/mol. API-MS produced a strong peak at m/z 260.09 [BP+NH₄]⁺ (Fig. 7-6). The next peak of significant intensity was located at m/z 216.106 could be observed under certain conditions. This signal can be assigned to [M+NH₄-CO₂]⁺. By changing the temperature of the ionization chamber additional fragmentation was observed.

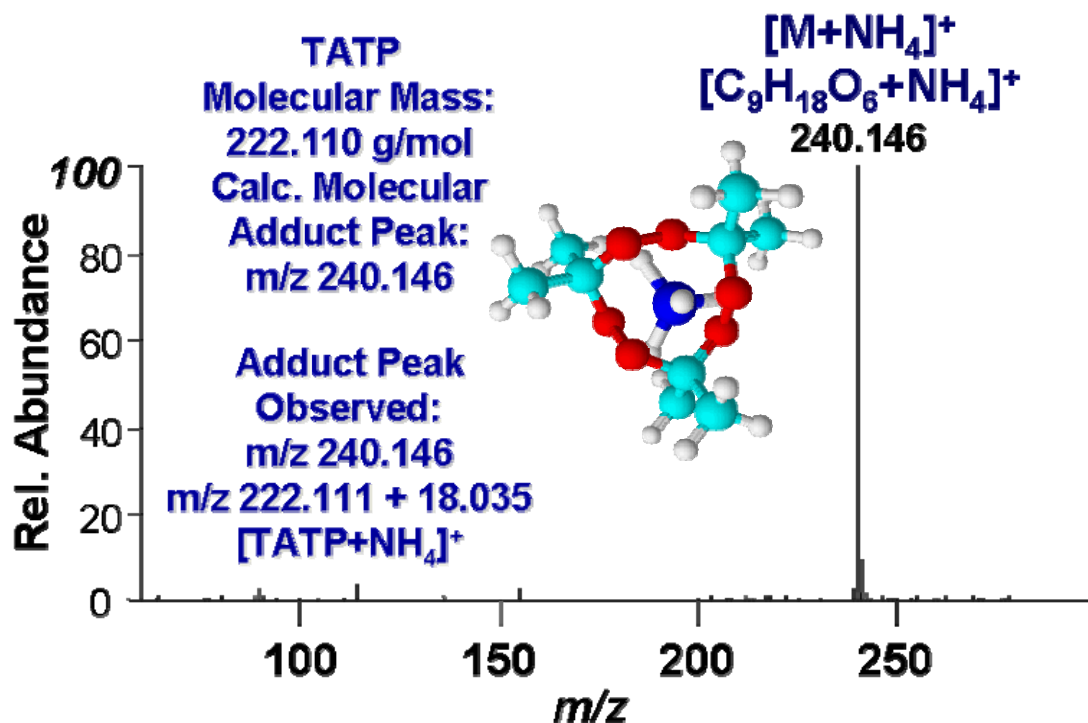


Figure 7-7. Mass spectrum of pure TATP by API ionization at 200°C.

TATP was analyzed at different temperatures and in contrast with GC/EI-MS that requires low detector temperatures, API-MS analysis with NH₄OH vapor produced the molecular adduct at 200°C, above TATP flash point at 150°C. Figure 35 shows the mass spectrum of TATP which presents a molecular adduct at m/z 240.146 [TATP+NH₄]⁺. No molecular peaks were observed at m/z 222.110 [TATP]⁺ or at m/z 223.118 [TAPT+H]⁺. These results indicate that ammonium hydroxide stabilized the ionization of TATP and increased its detection. This property was also observed when d₁₈-TATP was analyzed by API-MS. A strong peak was observed at m/z 258.258 [d₁₈-TATP+NH₄]⁺ with complete absence of signals at m/z 240.223 [d₁₈-TATP]⁺ and at m/z 241.231 [d₁₈-TATP+H]⁺ (Fig. 7-7).

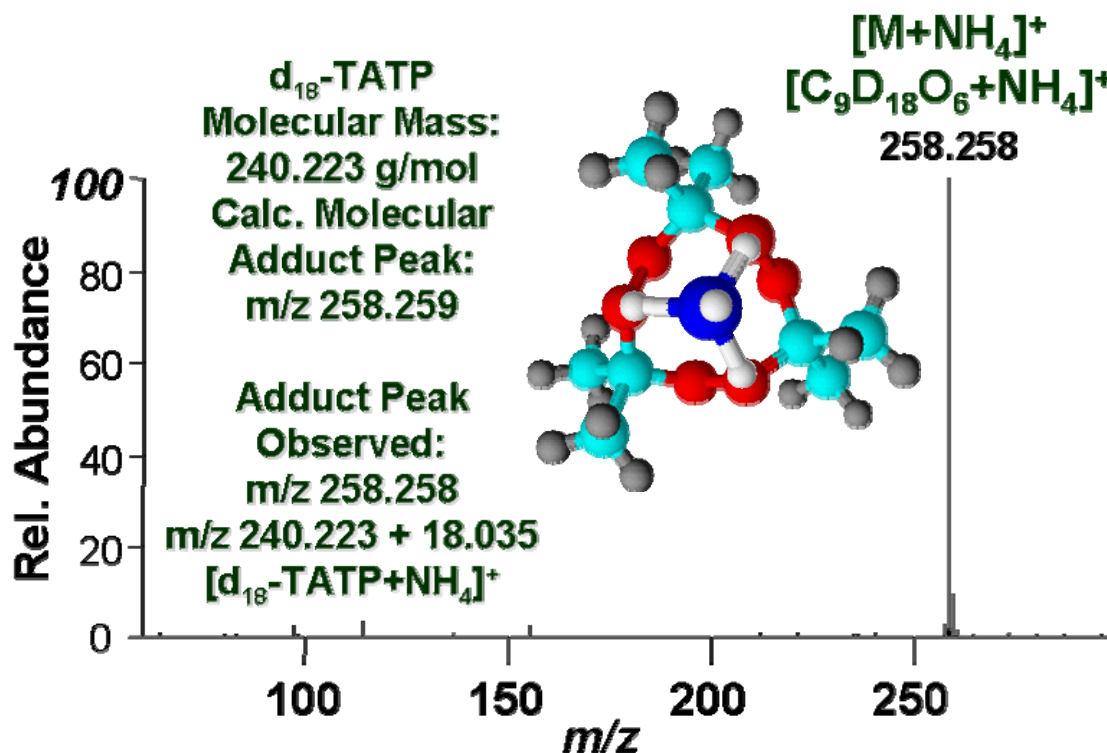


Figure 7-8. Mass spectrum of d₁₈-TATP at 200°C using ambient pressure ionization MS.

Cyclopentanone triperoxide showed also a similar behavior as TATP, at m/z 318.190 [M+NH₄]⁺ (Fig. 7-8). An additional peak at m/z 101.059 belongs to an ion that is ascribed to an oxidized form of cyclopentanone, [C₅H₉O₂]⁺. This peak can be attributed to a contaminant or a decomposition product of the peroxide studied.

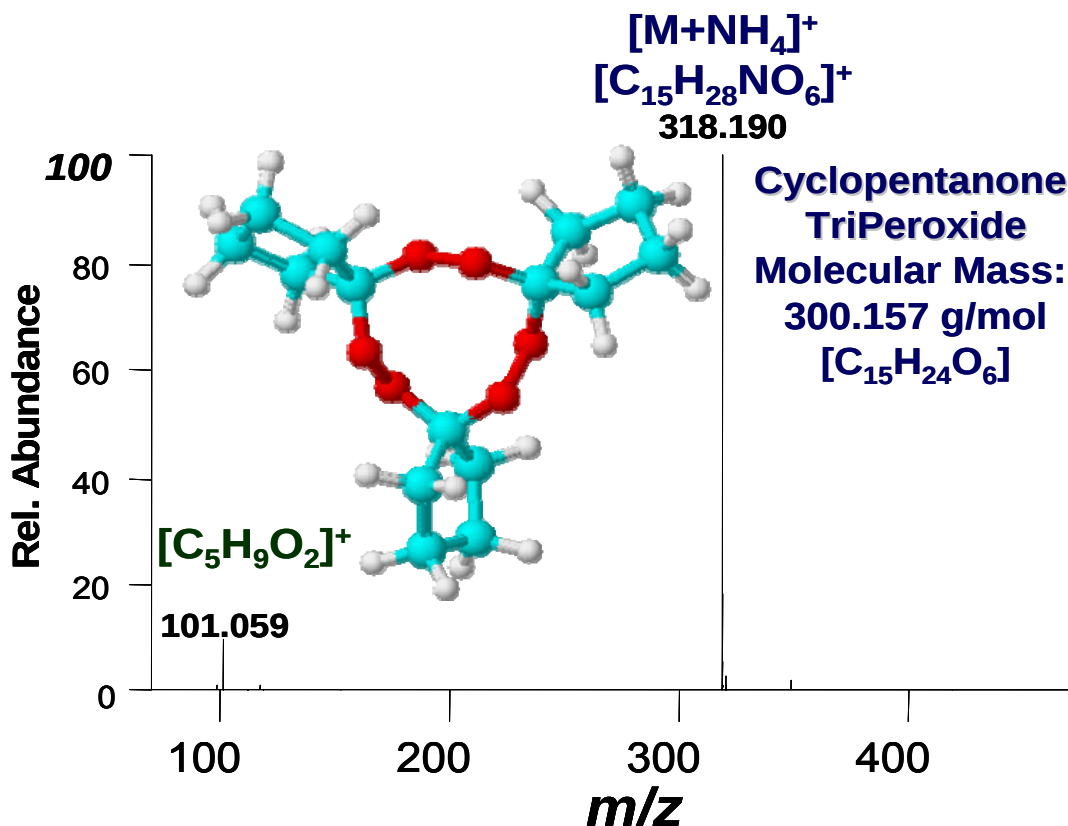


Figure 7-9. API-TOFMS spectrum of cyclopentanone triperoxide.

3.4. Amine and Amide Peroxides: HMTD and TMDD

HMTD has low solubility in most common solvents used and very low vapor pressure, which limits analysis by gas chromatography. It is slightly soluble in chloroform, dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF). TMDD is insoluble in most organic solvents. This hampers most chromatographic analysis, including GC and HPLC. API-TOF-MS provided an excellent method for detection with considerably low detection limits. HMTD does not require ammonium hydroxide to promote the observation of the molecular ion, but adding NH₄OH solution increases the intensity of [M+H]⁺ helping to detect this peroxide compound by chemical ionization.

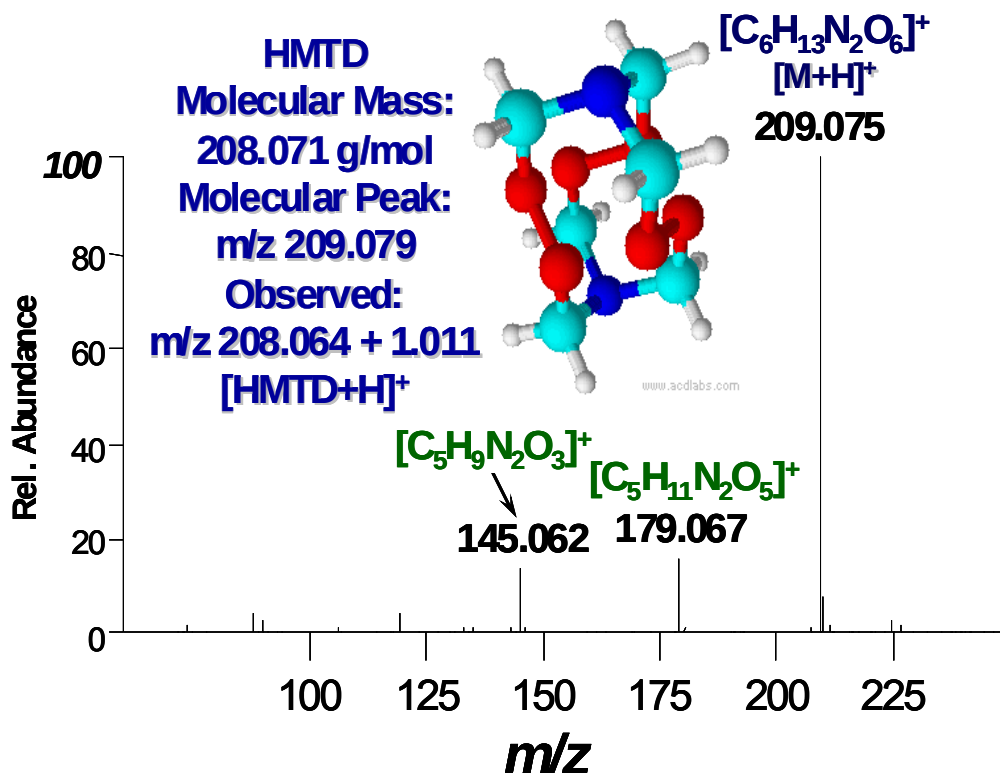


Figure 7-10. API-TOF-MS spectrum of HMTD at 150°C.

Figure 7-10 presents HMTD mass spectrum by API-TOF-MS with molecular mass at m/z 209.078 [HMTD+H]⁺. Other significant mass fragments observed in lower abundance were located at m/z 226.104 [M+NH₄]⁺, the adduct ion; m/z 179.067 [C₅H₁₁O₅N₂]⁺, loss of formaldehyde; m/z 145.062 [C₅H₉O₃N₂]⁺, loss of hydrogen peroxide; and m/z 88.040 [C₂H₆O₂N]⁺. These peaks are constant at different ionization chamber temperatures, but intensities were different as the temperature increased. The optimal temperature for HMTD analysis by API-TOF-MS was found to be 150°C. In the presence of ammonium hydroxide it was possible to observe the strong molecular ion at even at 200°C.

TMDD was detected close to its melting point at approximately 180°C. After the first mass spectrum was obtained and confirmed using different

ionization port conditions including using NH_4OH to generate NH_4^+ dopant, it was possible to lower the detection temperature to 150°C . In the absence of ammonium hydroxide, TMDD showed the molecular peak at m/z 237.085 $[\text{TMDD}+\text{H}]^+$, as HMTD, but it was also possible to observe considerable fragmentation along with adduct ion $[\text{M}+\text{NH}_4]^+$ at m/z 252.111. When NH_4^+ vapor is added, TMDD behaves similar to TATP, showing a strong molecular adduct ion⁴³. Figure 7-11 shows TMDD mass spectrum with API-TOF-MS at low inlet temperature (150°C). Even at this low temperature considerable fragmentation was observed with peaks at m/z 189.062, 175.083, 161.068, 146.058, 130.062, 118.061, and 102.069. To our knowledge, these results represent the only reported method of analysis for TMDD characterization and detection. Other mass spectrometry analysis methods were tried including GC/EI-MS and HPLC/EI-MS and direct insertion probe EI-MS, but results were limited by the low solubility of TMDD in the solvents tested and its extremely low vapor pressure.

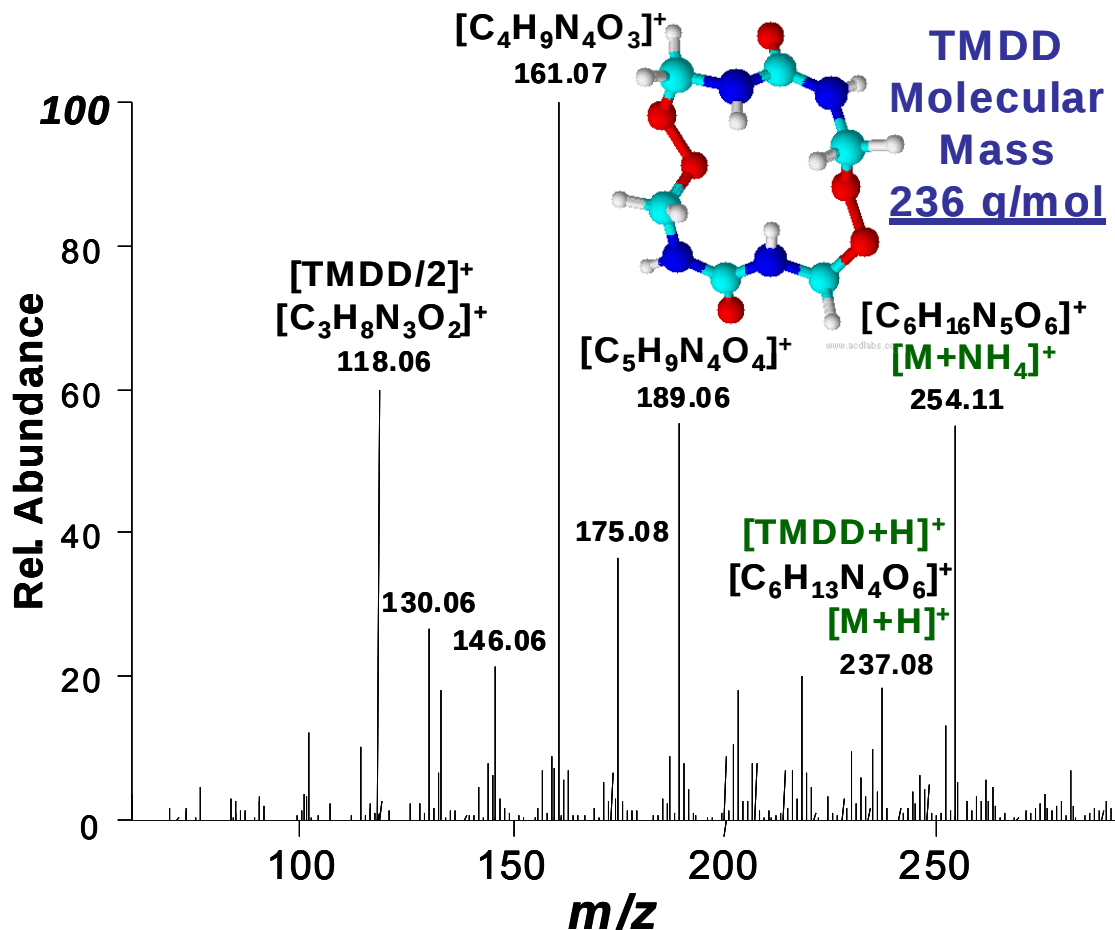


Figure 7-11. Mass spectrum of TMDD at 150°C.

3.5. TATP and HMTD mixture analysis

The ionization ability to work in chemical ionization mode combined with high resolution mass spectrometry from the reflectron TOF allowed identification of mixtures of peroxides. When a TATP sample was placed in the API stream it was common to observe a peak at m/z 223.097, that was wrongly assigned to [TATP+H]⁺. This peak is a typical environmental contamination due to diethyl phthalate that can be confirmed by its mass fragments of m/z 152.020, 100.077, 77.027, and 59.053. This problem was corrected by adding a source of

ammonium from NH_4OH solution and a TATP peak with an ammonium adduct was observed.

A mixture of HMTD and TATP gave the expected molecular ions at m/z 240.146 $[\text{TATP}+\text{NH}_4]^+$ and 209.079 $[\text{HMTD}+\text{H}]^+$ (Fig. 7-12). These results show that HMTD and TATP are ionized by different mechanisms. This result is useful because the analyte is detected without regard to ionizing preparation conditions. This is not the case with other ionization techniques, such as DESI. There, both compounds share a similar behavior regarding the type of adducts generated, and it depends on the preparation conditions rather than on the analyte.

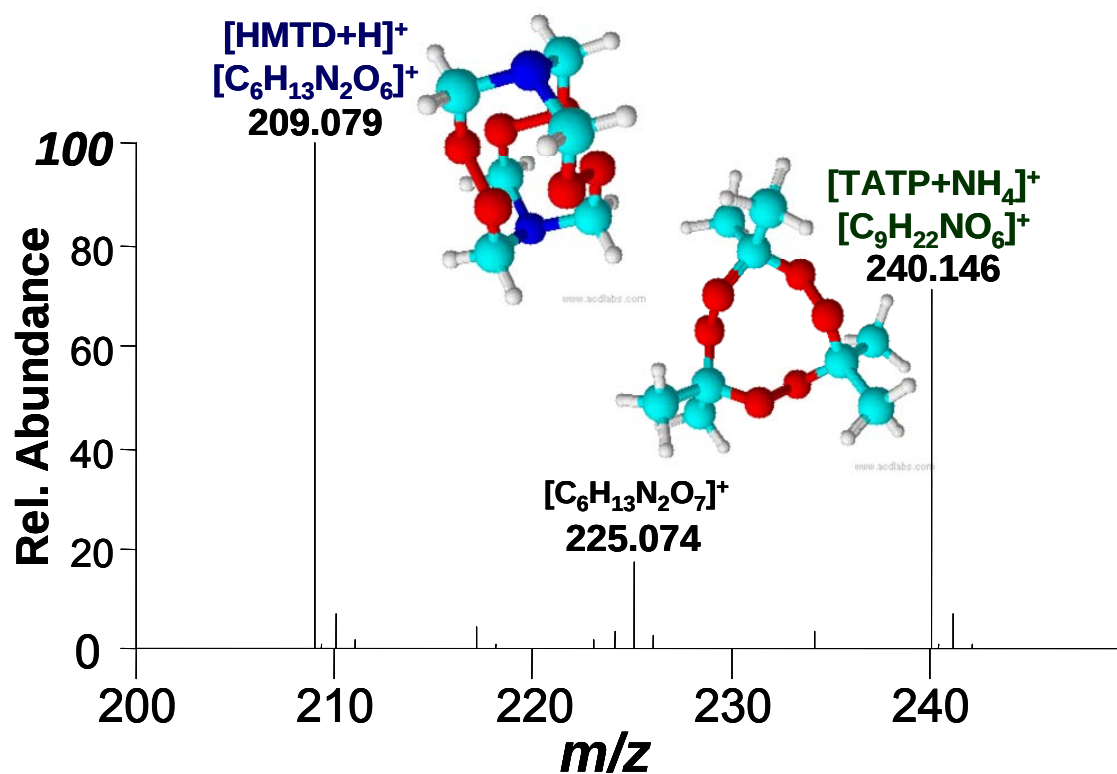


Figure 7-12. Mass spectrum of HMTD and TATP mixture.

Although quantitative assessment of detection limits for TATP and HMTD was not done, an estimate of the detection capability for both compounds was obtained by diluting a 350 ppm stock solution mixture of the explosives by a factor of 10 and transferring two microliters to the sampling capillary tube. This corresponded to 70 pg of TATP and HMTD and resulted in a signal to noise ratio (S/N) of > 10:1. Experiments for lower detection limits are in progress but somewhat hindered by the fast decomposition of HMTD and the increase in the relative abundance of the fragments ions at m/z 179 (Loss of Formaldehyde) and 145 (Loss of Formaldehyde + Hydrogen Peroxide).

4. Conclusions

A method for detecting energetic organic peroxides using ambient pressure chemical ionization mass spectrometry (API-MS) was presented. The high mass accuracy of the TOF instrumentation allowed for rapid determination of the peroxide analytes (within seconds) even in the presence of contaminants. In contrast, other chromatographic based methods coupled to mass spectrometric detection require at least minutes for a single analysis.

TATP and HMTD ionize by different CI mechanisms to produce different types of molecular ion adducts, even when both chemicals are ionized simultaneously *in situ*. In the case of TMDD, the formation of both types of molecular ion adducts was observed, although the adduct form with NH_4^+ was more intense. In contrast to other organic peroxides analyzed by OS-MS, TMDD produced profuse fragmentation. Some TMDD fragments were identified. The

possibility of achieving parts-per-billion to parts-per-trillion detection levels without sample preparation in open air sampling makes OA-MS an attractive technique for Defense and Security applications.

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CHAPTER VIII

Mass Spectrometry analysis of tetramethylene diperoxide dicarbamide by Open-Air Chemical Ionization-Time of Flight

The first mass spectrometry characterization of tetramethylene diperoxide dicarbamide (TMDD) using Open-Air Chemical Ionization High-Resolution Time-Of-Flight MS (OACI-HR-TOF-MS) is reported. Thermal gravimetric analysis (TGA) assisted the TMDD DART analysis by providing the best ion source temperature at 150°C to obtain a mass spectrum. Under the presence of ammonia vapor, open-air chemical ionization mass spectrum of TMDD showed a strong ammonium adduct peak at m/z 254.111 $[M+NH_4]^+$ as well as its protonated molecular mass at m/z 237.084 $[M+H]^+$. TMDD MS base peak was observed at m/z 161.068 $[C_4H_9N_4O_3]^+$. In contrast with other peroxides under OA chemical ionization, TMDD undergoes substantial fragmentation. Some of the other common fragment peaks in TMDD mass spectra were: m/z 189.063 $[C_5H_9N_4O_4]^+$, 175.083 $[C_5H_{11}N_4O_3]^+$, 146.057 $[C_4H_8N_3O_3]^+$, 130.062 $[C_4H_8N_3O_2]^+$ and 118.062 $[C_3H_8N_3O_2]^+$. Other interesting peaks observed were the loss of water peak at m/z 218.089 $[(M+NH_4)-2H_2O]^+$ and loss of hydrogen peroxide at m/z 203.078 $[M-H_2O_2]^+$. OACI mechanisms for most of TMDD fragments are proposed.

1. Introduction

1,2,8,9-tetraoxa-4,6,11,13-tetraazacyclotetradecane-5,12-dione, or tetramethylene diperoxide dicarbamide (TMDD) is a compound that can be prepared from urea, formaldehyde, and hydrogen peroxide (Figure 8-1). It was prepared in 1914 by von Girsewald and Siegens ¹. However, there are few spectroscopic and physical data to identify this peroxide ². TMDD also has limited solubility in most organic solvents, and von Girsewald informed that TMDD was soluble only in sulfuric acid, which clearly limits the methods that can be used for characterization by LC-MS and GC-MS.

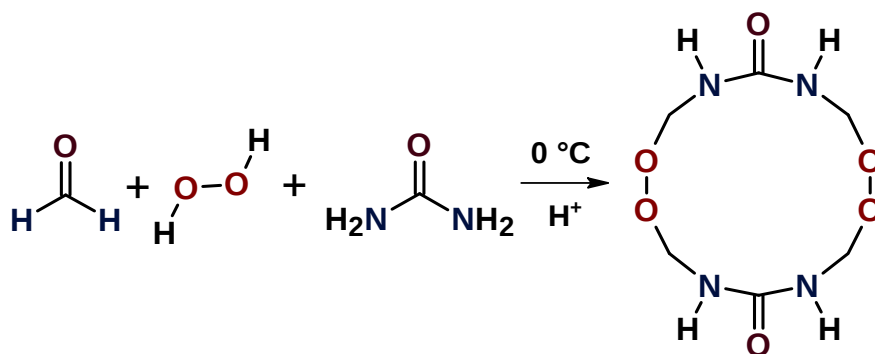


Figure 8-1. Synthesis reaction schematic of TMDD by Von Girsewald.

Open-Air Chemical Ionization (OACI) is one of the most novel methods of atmospheric pressure sample ionization mass spectrometry ^{1, 3}. With substantial simplicity, metastable helium or nitrogen atoms are used to generate ions stabilized by water clusters that produce the reactions that ionize molecules before entering the mass spectrometer orifice ^{4, 5}. The recent advances in Time

of Flight (TOF) mass spectrometry have resulted in very high resolution and sensitivity allowing the technique to identify any organic compound and separate the information from possible interferences. The combination of OACI and high resolution TOF permits to detect organic compounds with immediate results and little sample preparation ⁶⁻⁸. This contribution presents the first mass spectrometry study of TMDD performed by a recent OACI coupled to HR-TOF mass spectrometry (OACI-HR-TOF-MS).

2. Experimental Details

2.1. Reagents.

Chemical reagents used in this research were: acetone, urea (98% w/w), formaldehyde (CH₂O, 37% wt, Acros-Organics N.V., Fair Lawn, NJ), hydrogen peroxide (H₂O₂, 50% in water, Fisher Scientific, Fairlawn, NJ), and hydrochloric acid (HCl, 12 M, Merck, VWR International, Inc., West Chester, PA 19380), and sulfuric acid (H₂SO₄, Aldrich-Sigma).

2.2. Synthesis.

TMDD was prepared via a simple synthetic route (Figure 8-1). A mixture of 40-50% hydrogen peroxide and 35% formaldehyde was made at room temperature. Then ground urea was dissolved in the mixture using a magnetic stirrer and then cooled between 5°C and 0°C with an ice bath. After all urea was

dissolved and cold, a small portion of concentrated strong acid was added. The solution was placed in a refrigerator for 3 to 5 days and a white precipitate formed. Filter the product was washed with water and then with acetone to removed organic impurities. Crystals obtained were powder like, but under the microscope crystalline appearance could be easily recognized as Figure 8-2. TMDD did not dissolve in any of many organic solvents tested; it could be maintained in suspension in a mixture of methanol-water. For characterization, solid state techniques, such as Raman microscopy, ATR-FTIR and Direct Insertion Probe-MS have to be employed.

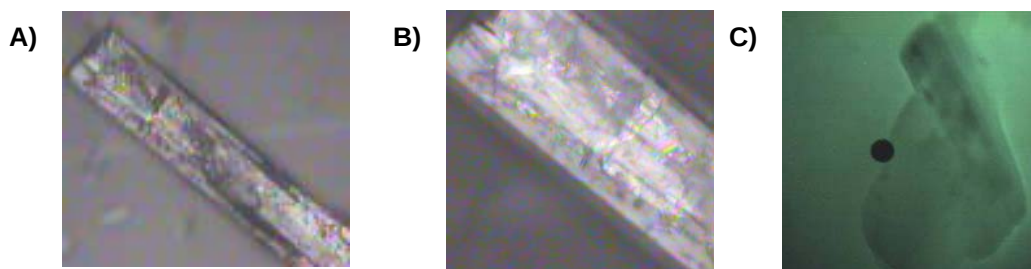


Figure 8-2. TMDD crystals white light micrographs: (a) 10X and (b) 20X; (c) TEM image 25,000X.

2.3. Equipment

Characterization of TMDD was done by vibrational techniques: Fourier Transform-Infrared Spectroscopy (FTIR) and Raman Microscopy. To confirm the purity and to obtain positive identification of the compounds, the samples were analyzed by their melting point in a Melt-Temp apparatus. Thermo gravimetric

analysis (TGA) was performed using a TA-2950 thermo-balance in an inert environment (high purity helium). The temperature was increased at 5°C/min from 30-250°C. Mass spectrometry analysis was performed by JEOL-USA Direct Analysis in Real Time (DART™)-AccuTOF. Chemical ionization region used a helium flow rate set at 2 L/min, the needle voltage was 3500 V, electrode 1 was set 150 V and electrode 2 at 250 V. TMDD has a limited threshold of detection due its thermal properties. At 200°C, no molecular peak is observed, but at 150°C the molecular peak is very clear. As commonly in peroxides mass analysis, ammonium dopant was added to increase MS signals. A cotton swab was immersed in ammonium hydroxide solution and then placed in front of the OACI stream to promote chemical ionization (Figure 8-3).

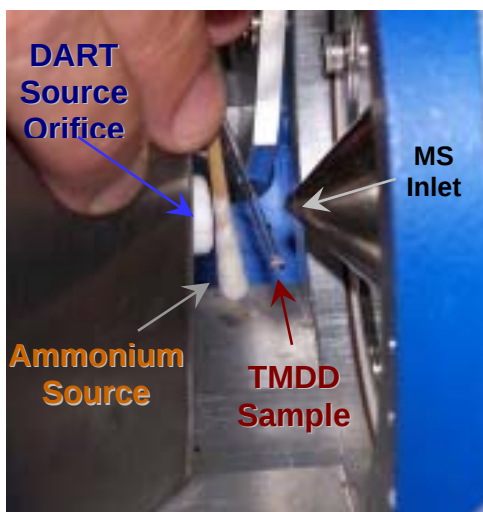


Figure 8-3. DART ion source and sample treatment with ammonium.

3. Results and Discussion

3.1. Differential Thermal Gravimetric Analysis

The reported melting point for TMDD is 175°C¹. Current results show that TMDD had a solid-liquid change of state at 181.5°C, but at this temperature it started to decompose. Melting point measurements were typically accompanied by a small scale detonation leaving the capillary tube used for determinations intact and producing significant moisture and a brownish residue. Differential Thermal Gravimetric Analysis (DTGA) measurements evidenced a physical transition beginning at 150°C and showing a maximum peak at 189.9°C (Figure 8-4). These results were very useful in determining the optimal temperature that could be used to analyze TMDD by mass spectrometry before it decomposed.

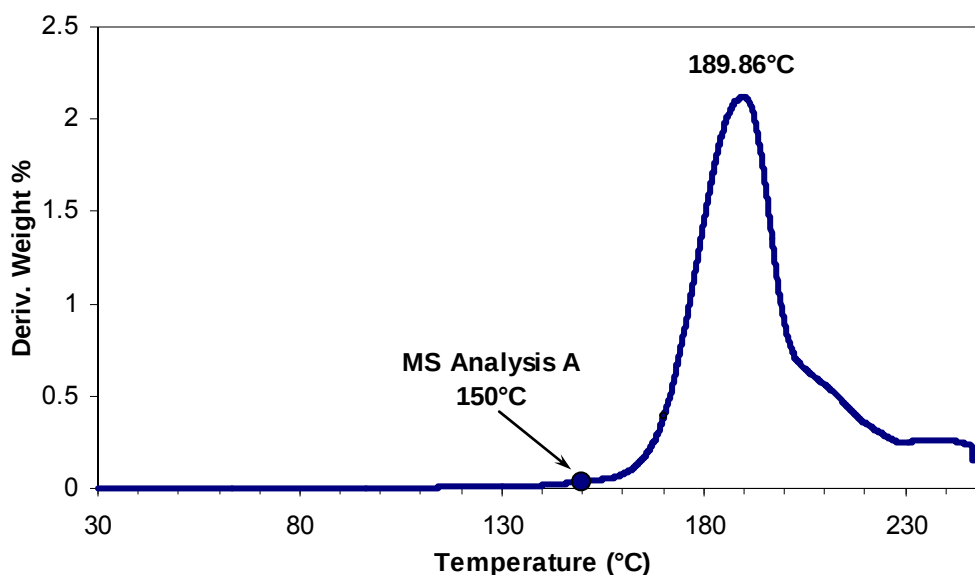


Figure 8-4. Differential thermal gravimetric analysis (DTGA) of TMDD under helium purge at temperature range from 23 °C to 250 °C.

3.2. Open-Air Chemical Ionization Mass Spectrometry

TMDD presented an unexpected high stability with respect to impact and heat and a surprisingly low vapor pressure. The later property became a problem for the analysis of the peroxide by vaporization methods such as GC-MS. It's extremely low solubility, in most organic solvents limited the analysis using Electrospray Ionization High Pressure Liquid Chromatography (ESI-HPLC)-MS. Von Girsewald reported that TMDD was soluble in sulfuric acid ¹. However, most chromatographic and MS equipment would be affected by the presence of concentrated strong acids. Thus open air ionization mass spectroscopy was the only technique that allowed mass analysis. To prevent thermal decomposition, the mass analysis was performed at 150°C.

OACI-MS of TMDD presented a profusion of peaks in contrast with other peroxides (Figure 8-5), such as TATP and HMTD that show very little fragmentation ⁹. Using high resolution MS (HR-TOF) was essential to identify TMDD and its fragments. OA-chemical ionization commonly produces even-electron ions (EE^+), and its soft ionization allowed observing the molecular peak plus one. The most important peak at m/z 237.0850 was assigned to the molecular peak plus one $[TMDD+H]^+$, which proves that the compound was properly synthesized and had the expected molecular mass. However, in the presence of ammonium vapor, TMDD produced a higher intensity signal at m/z 254.1112 that was assigned to the molecular ion adduct $[TMDD+NH_4]^+$. Figure

8-6 illustrates possible pathway for the adduct peak formation. This behavior is consistent with mass spectra of other peroxides, such as TATP⁹. Figure 8-7 shows the mechanism that could produce the molecular peak from $[M+NH_4]^+$. The persistent intense fragments should presumably be produced from $[M+H]^+$ or from $[M+NH_4]^+$.

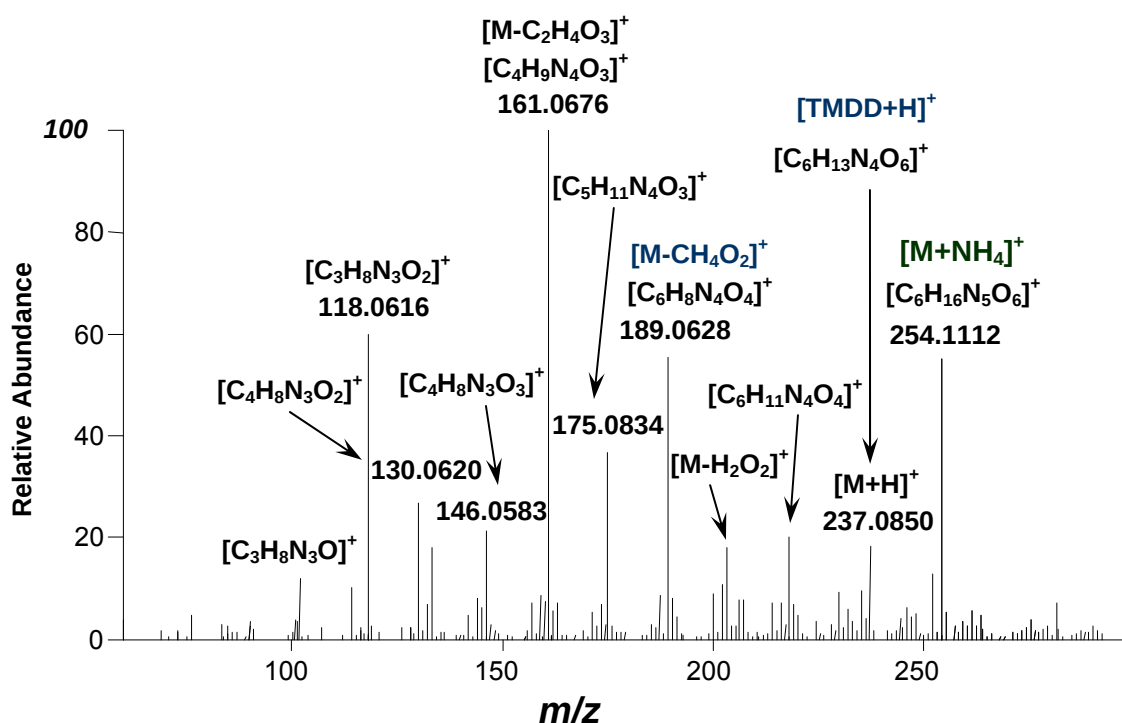


Figure 8-5. Open-Air Chemical Ionization (OACI) mass spectrum of TMDD by DART ion source at 150 °C.

The first important fragment observed was at m/z 218.0928 $[C_6H_{12}N_5O_4]^+$, assigned to $[M+NH_4-2H_2O]^+$ with the loss of 36.018 Da, corresponding to losing two water molecules. To obtain this loss, multiple bond cleavage should occur from a ionize TMDD that breaks its peroxide bond to form to hydroxyl groups

(Figure 8-8). Another low intensity peak was observed at m/z 203.0807 $[C_6H_{11}N_4O_4]^+$, corresponding to a loss of 34.004 Da that belongs to one molecule of hydrogen peroxide from $[TMDD+H]^+$ (Figure 8-8). Following, a similar process of multiple bond cleavage along with H-rearrangement to keep the peroxide bond, this initial evidence indicated us that TMDD ionization would produce hydrogen peroxide, in contrast with ammonium-doped TMDD that would eliminate water dimers without losing the ammonium addition. This phenomenon can be only explained the ion reaction from different structures and molecules. Figure 8-8 presents the differences in mechanism for the formation of both fragment peaks.

The next peak is m/z 189.0628 $[C_5H_{11}N_4O_4]^+$ is assigned a loss of methyl peroxide from the molecular peak MH^+ at m/z 237.0850 $[C_6H_{13}N_4O_6]^+$. As seen in Figure 8-8, m/z 203.0807 and 189.0628 proceed from the initial H-rearrangement, but the final rearrangement to close back the fragmented TMDD ring ended in different ionized structures. Peak abundances indicate that the formation of m/z 189.0624 is more favored than the loss of hydrogen peroxide (fragment with m/z 203.0807). The m/z 175.0834 $[C_5H_{12}N_4O_4]^+$ is also related to $[TMDD+H]^+$, but this process follows a more complex reaction leading the loss of carbonic acid (H_2CO_2). It would also be possible to associate this fragment to loss of carbon monoxide from m/z 203.0807. However, both cases follow from complex rearrangements and multiple bond cleavages.

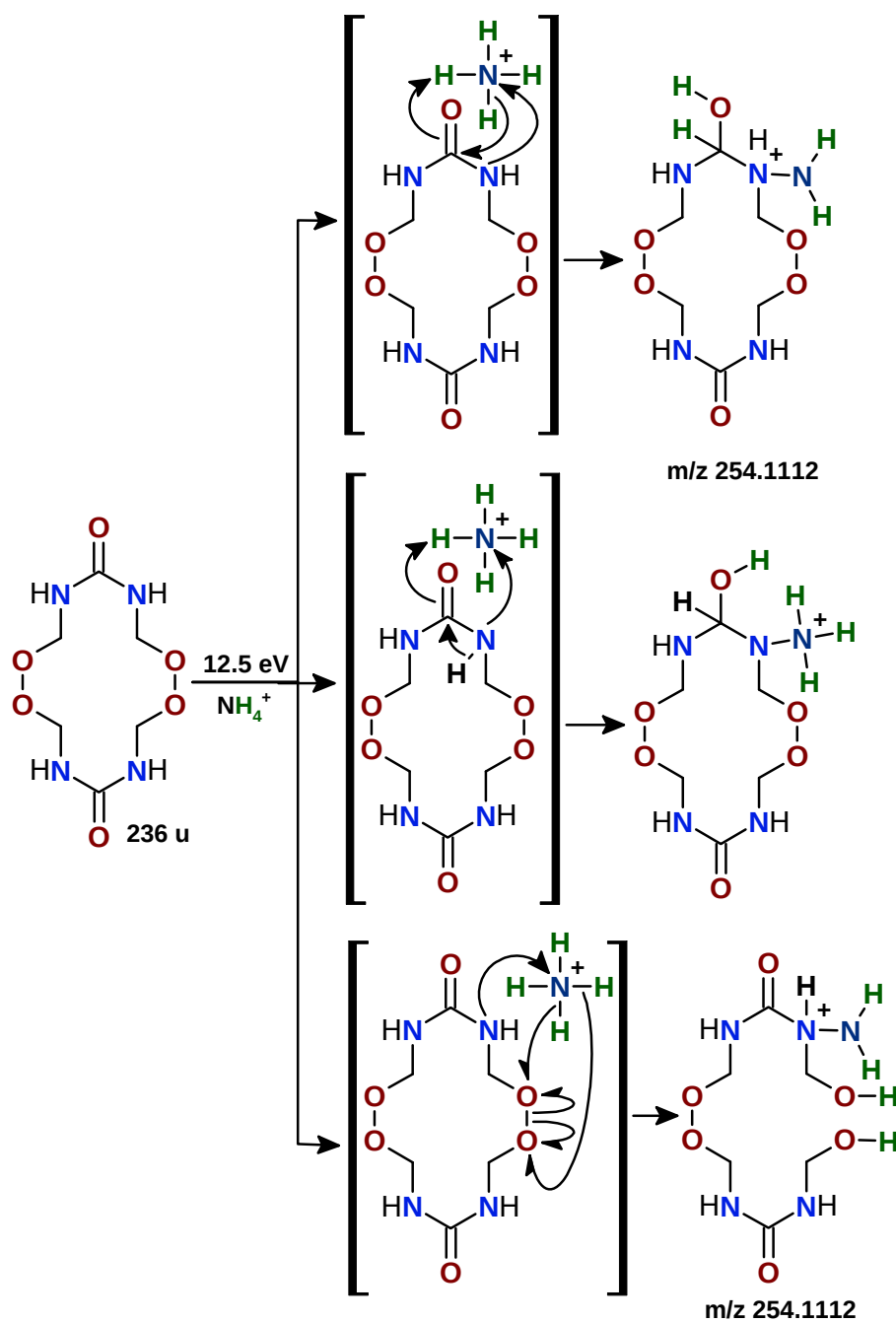


Figure 8-6. Proposed mechanisms for TMDD ammonium adduct peak at m/z 256.1112 $[M+NH_4]^+$.

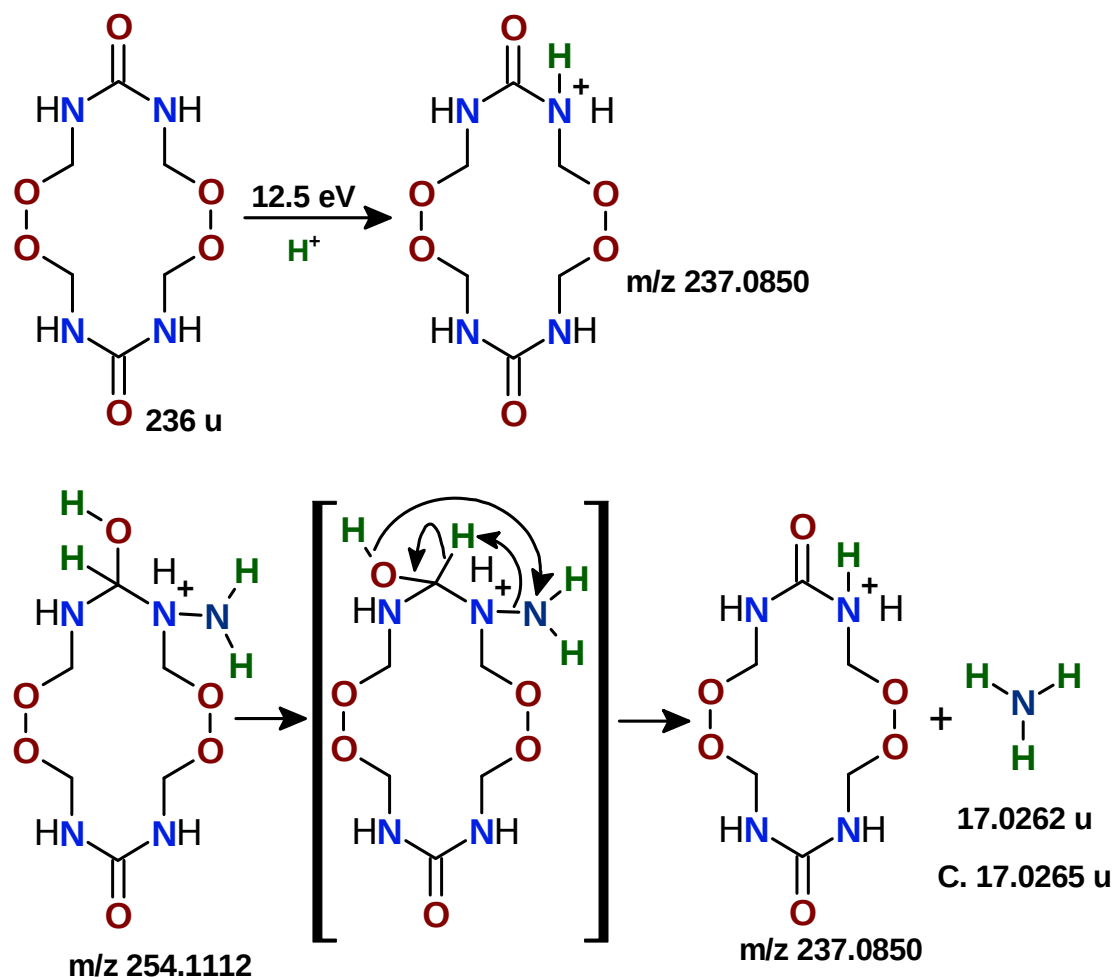


Figure 8-7. Proposed mechanisms for TMDD molecular ion plus one at m/z 237.0850 $[M+H]^+$.

One of the most important fragments is the base peak at m/z 161.0676 $[C_4H_9N_4O_3]^+$ which is more likely to be formed from fragmentation of the ammonium adduct peak $[TMDD+NH_4]^+$ (Figure 8-9). However, as proposed in Figure 8-9 it is possible that the same peak could be formed from the fragment with m/z 189.0624 by losing carbon monoxide. The mechanism suggests that m/z 161.0676 structure from the $[M+NH_4]^+$ losing one of the original TMDD

nitrogen atoms. All proposed mechanisms related to TMDD-ammonium adduct favored the formation of an open-chain amine peroxide.

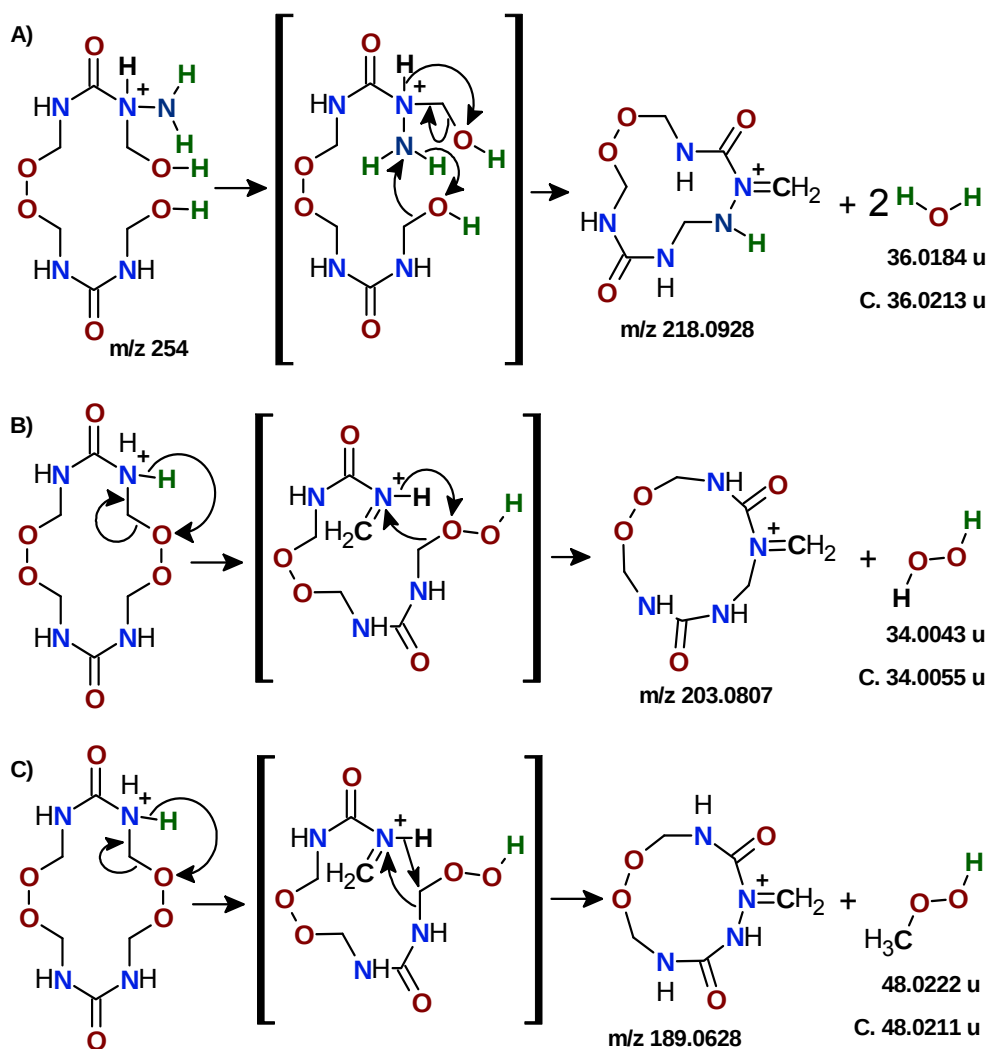


Figure 8-8. Proposed mechanisms for TMDD fragments formation between m/z 189-219. (A) Loss of a water dimer from TMDD adduct $M+NH_4^+$ at m/z 218.0928; (B) Loss of hydrogen peroxide from TMDD molecular peak MH^+ at m/z 203.0807; and (C) loss of methyl peroxide from MH^+ at m/z 189.0628.

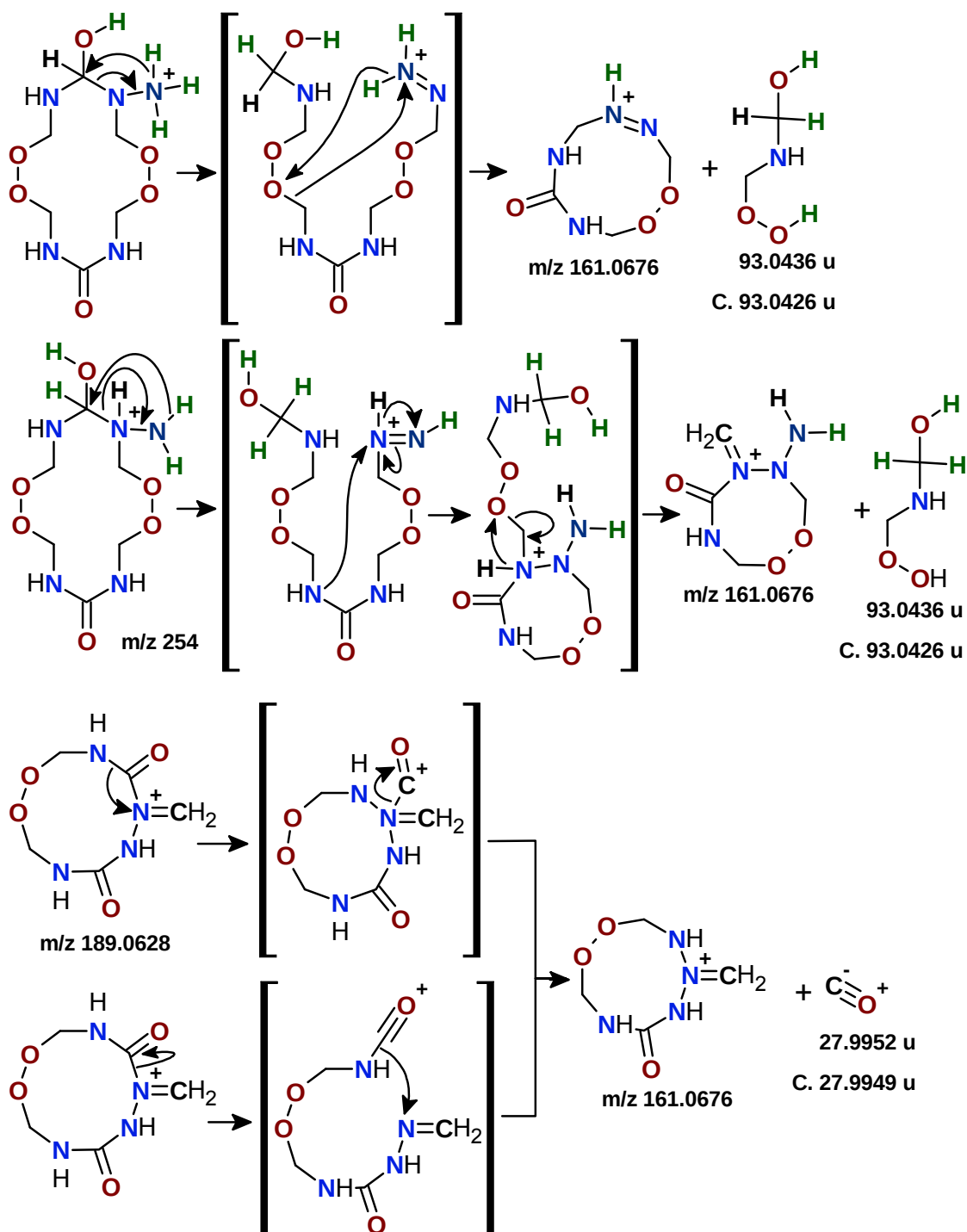


Figure 8-9. Proposed mechanisms reaction for the formation of TMDD mass spectrum base peak at m/z 161.0676 $[C_4H_9N_4O_3]^+$.

The following fragments: m/z 146.0583 $[\text{C}_4\text{H}_8\text{N}_3\text{O}_3]^+$, m/z 133.0729 $[\text{C}_3\text{H}_9\text{N}_4\text{O}_2]^+$ and m/z 130.0620 $[\text{C}_4\text{H}_8\text{N}_3\text{O}_2]^+$; were more complex to produce and their relative abundance was significantly lower as Figure 8-5 illustrates. The m/z 146.0583 fragment could be related to the loss of simple amide peroxide from m/z 237.0835. It could also be formed from m/z 203.0807, 175.0834, and even from the base peak, m/z 161.0676 by losing N-H. Fragment m/z 133.0729 initially could be related to the base peak by losing carbon monoxide from m/z 161.0676, but also can be related to m/z 189.0624 when it losses two molecules of CO. However, the m/z 133.0729 fragment could be proposed to come from $[\text{M}+\text{H}]^+$ by several rearrangements. The m/z 130.0620 fragment could be formed from the loss of HNO from fragment ion with m/z 161.0767. Finally, m/z 118.0617 was observed from the rearrangement of the structure that produce m/z 218.0889, but following a different path (Figure 8-10). As for m/z 161.0676, there are many possible explanations for the formation of this fragment. Also, this peak could be formed from previous fragments such as m/z 189.0628 and m/z 161.0676. Figure 8-10 presents some of the possible pathways that result in the formation of m/z 118.0617.

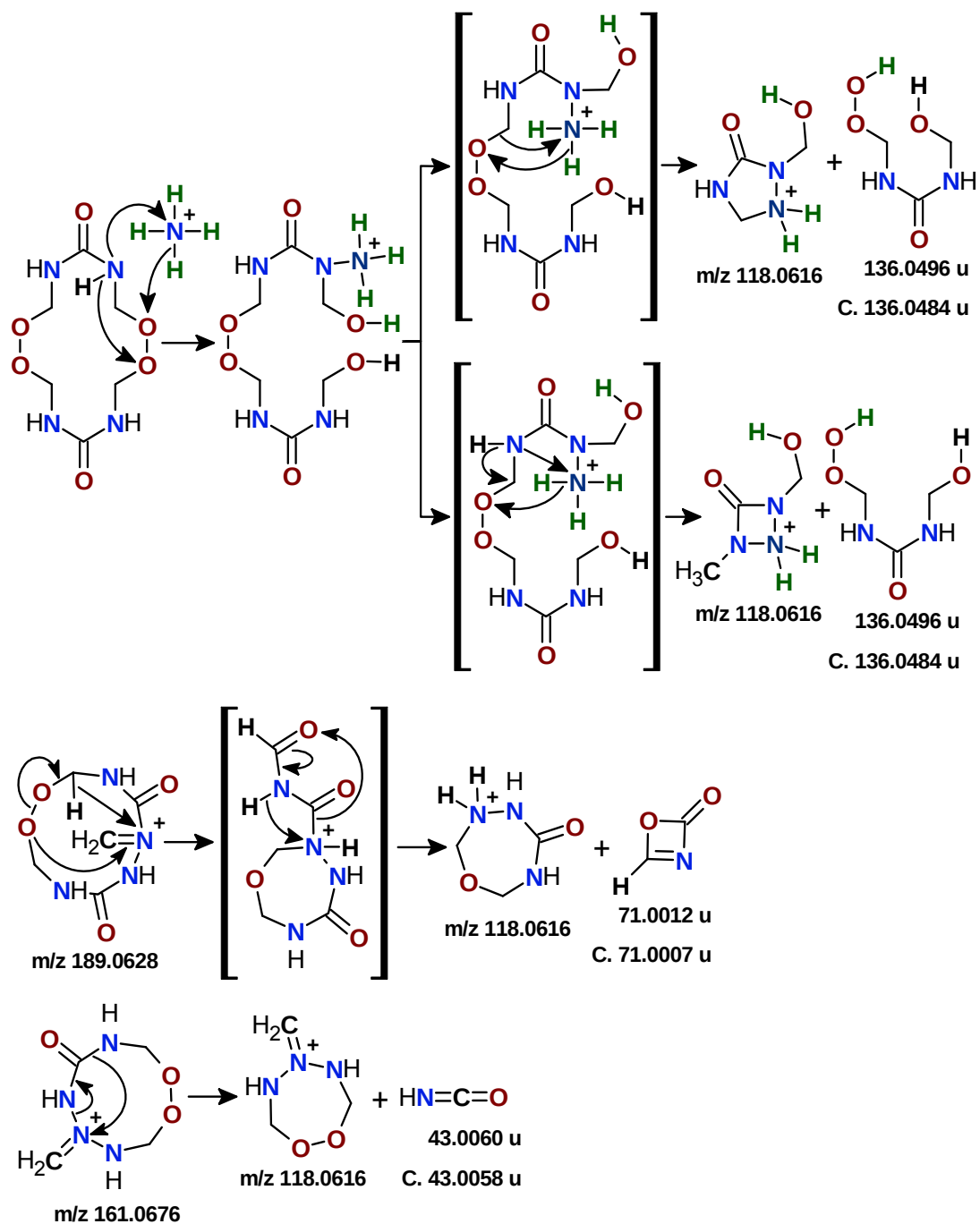


Figure 8-10. Proposed mechanisms for TMDD fragment peak at m/z 118.0616 $[C_3H_5N_3O_2]^+$.

When the analysis was performed in a higher temperature, most of the peaks remained, but intensities changes. Other peaks appeared and the fragmentation was a little more complex due inclusion of decomposition compounds that were easier to find when the ammonium had lower concentrations. Ammonium adduct still strong under harder conditions. Table 1 summarizes all OACI data obtained by DART-HRTOF.

Table 8-1: Mass Fragments of TMDD by OACI-TOF-TOF

Ion Observed	Composition	Abundance	Measured	Calculated	RBD	Diff.
TMDD+NH ₄	C ₆ H ₁₆ N ₅ O ₆	54.96%	254.1112	254.1106	1.5	1.142
TMDD+H	C ₆ H ₁₃ N ₄ O ₆	18.18%	237.0850	237.0835	2.5	1.491
TMDD+NH ₄ -2H ₂ O	C ₆ H ₁₂ N ₅ O ₄	20.04%	218.0928	218.0889	3.5	3.871
TMDD-H ₂ O ₂	C ₆ H ₁₁ N ₄ O ₄	17.98%	203.0807	203.0780	3.5	2.67
TMDD-CH ₄ O ₂	C ₅ H ₉ N ₄ O ₄	55.37%	189.0628	189.0624	3.5	0.42
TMDD-CH ₂ O ₃	C ₅ H ₁₁ N ₄ O ₃	36.78%	175.0834	175.0831	2.5	0.285
TMDD-C ₂ H ₄ O ₃	C ₄ H ₉ N ₄ O ₃	100.00%	161.0676	161.0675	2.5	0.135
TMDD-C ₂ H ₅ NO ₃	C ₄ H ₈ N ₃ O ₃	21.28%	146.0583	146.0566	2.5	1.734
TMDD-C ₃ H ₄ O ₄	C ₃ H ₉ N ₄ O ₂	17.98%	133.0729	133.0726	1.5	0.349
TMDD-C ₂ H ₅ NO ₄	C ₄ H ₈ N ₃ O ₂	26.86%	130.0620	130.0617	2.5	0.348
TMDD-C ₃ H ₅ NO ₄	C ₃ H ₈ N ₃ O ₂	59.92%	118.0616	118.0617	1.5	-0.052
TMDD-C ₃ H ₅ NO ₅	C ₃ H ₈ N ₃ O	11.98%	102.0689	102.0667	1.5	2.163

4. Conclusions

The mass spectrum of TMDD was presented by the use of an OACI-HR-TOF-MS technique. With the help of thermal analysis it was possible to determine the optimal temperature to allow OACI-MS observed a few peaks and the molecular peak in the form of [M+H]⁺ and [M+NH₄]⁺. Ammonium adduct of

TMDD helped to increase the signal of the peroxide and helped to produce other fragments that were used in the characterization of TMDD by mass spectrometry. High resolution time-of-flight allowed identifying the exact fragments of TMDD and assisted in the prediction of the mechanisms that govern this type of chemical ionization. This research also presented a simple method for the analysis and detection of TMDD by mass spectrometry.

5. References

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CHAPTER IX

Mass Spectrometry Analysis of Hexamethylene Triperoxide

Diamine by its Decomposition Products

ABSTRACT

Hexamethylene triperoxide diamine (HMTD) is a well known amine peroxide that starts to decompose at ambient temperature. At 40°C HMTD began to break up into volatile pungent compounds, including trimethyl amine. The production of these compounds could be useful for the vapor detection of HMTD by common techniques such as GC-MS and IMS. GC-MS analysis was performed and several volatile amines could be detected including initial reagents, such as hexamine. IMS produced an alarm indicating the presence of other compounds. Open-Air Chemical Ionization (OACI)-Time of Flight (TOF)-Mass Spectroscopy was the most useful technique for the analysis of HMTD. Even at high temperatures (250°C), it was possible to detect the molecular ion at m/z 209.078. Other fragments observed in the mass spectrum were the loss of formaldehyde at m/z 179.069 and the loss of hydrogen peroxide at m/z 145.060. A mixture of 30 ppb of HMTD and triacetone triperoxide (TATP) was successfully analyzed by OACI-TOF-MS, thus demonstrating its feasibility for trace analysis of organic peroxides and related compounds.

1. INTRODUCTION

Analysis of the decomposition products is a current method of detection for high explosives (HE)^{1, 2}. Current detection technologies use methodologies based on gas chromatography (GC) and mass spectrometry (MS). Compounds such as TNT and RDX have been analyzed through this method using GC-MS³⁻⁶. Most organic peroxides properties allow detecting them by GC analysis and ion mobility spectrometry (IMS) such as triacetone triperoxide (TATP) and benzoyl peroxide (BPO)⁷⁻¹¹. However, other peroxides, such as amine peroxides, are difficult to analyze through chromatographic methods due to low vapor pressure and limited solubility¹²⁻¹⁴. Hexamethylene triperoxide diamine (HMTD) is one of the most important amine peroxides¹⁵⁻¹⁷, based on common use in terrorist acts¹⁸, but it have limited detectability with GC methods¹⁰. High pressure liquid chromatography (HPLC) is capable to analyze HMTD^{14,19,20}, but it has limited speed. IMS is capable of detecting also, but it is commonly mistaken with interferences⁸. HMTD decomposes under ambient temperature²¹, which makes difficult to identify the compound through its molecular mass. Its decomposition has been analyzed by GC methods^{10, 11, 21, 22}, revealing the formation of smelly substances such as trimethyl amine. However, no fast method had observed HMTD degradation products.

Open-Air Chemical Ionization-Time-of-Flight (OACI-TOF) is a technique with capabilities for analysis of any kind of sample by mass spectrometry²³. With

substantial simplicity, ionized helium or nitrogen is used to generate water clusters that produce the reactions that ionize molecules before the MS orifice^{24,25}. The recent advances in (TOF)-MS allows to identify any organic compound by its high resolution and sensitivity. This combination of equipments permits to detect organic compounds with immediate results and little sample preparation^{26, 27}. This paper presents the analysis and detection of HMTD by its decomposition products by OACI-HR-TOF. This study also compares results obtained by this technology to more established GC-MS equipped with electron ionization. In addition, samples were observed at different temperatures to determine the optimal conditions for HMTD detection.

2. METHODS

2.1. Reagents

The reagents used in this research were: acetone, hexamethylene tetraamine, hydrogen peroxide and hydrochloric acid. Organic solvents for MS analysis were: acetonitrile and chloroform. Figure 9-1a shows the synthesis of HMTD developed by Von Girsewald¹⁷. HMTD was made by dissolving hexamethylene tetraamine in hydrogen peroxide at low temperature. Then a dilute solution of hydrochloric acid (HCl) was added. The mixture was stirred for three hours below 5°C. Finally, the solution was filtered and washed with water thoroughly. Since HMTD is not soluble in most solvents purification by

crystallization could not be performed. The crystals obtained were powder like and could be easily recognized under a white light microscope as in Figure 9-1b. HMTD is prone to decompose under room temperature. To keep samples from decomposing is they were kept damped in water and stored in a freezer. Even acetonitrile solutions were stored at -10°C.

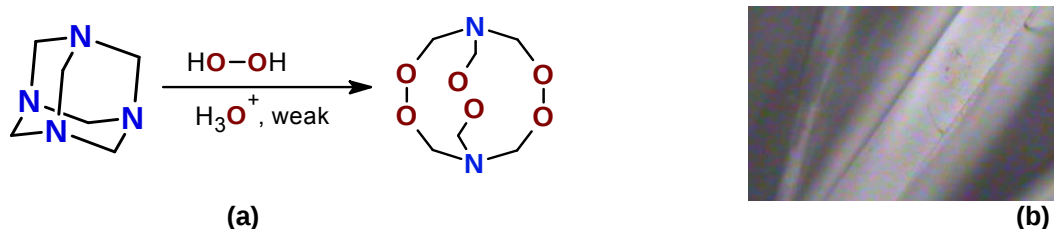


Figure 9-1. (a) Von Girssewald synthesis of HMTD; (b) white light micrographs of HMTD crystals.

2.2. Instrumentation

An Agilent GC model 5890 coupled to a 5790 mass selective detector was used for decomposition analyses. The GC was equipped with a Supelco SPB-5 (5% diphenyl/95% dimethylsiloxane, 15m * 0.25mm i.d.*0.25 μm) column. The mass spectra of the organic peroxides were obtained by injecting 0.2 μL of a slightly dilute solution of HMTD in chloroform. GC parameters were adapted to induce thermal decomposition. The API-MS system was a JEOL DART-AccuTOF mass spectrometer. Images of the ionization region of this system can be observed in Figure 9-2²⁵.

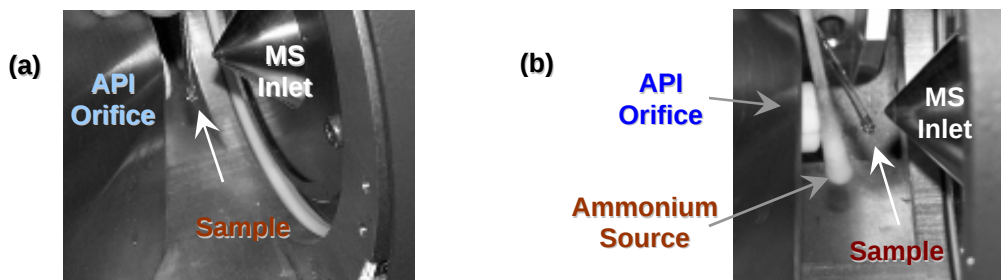


Figure 9-2. API ionization zone: (a) typical analysis; (b) ionization assisted with ammonium source.

2.3. Method of analysis

Characterization of HMTD was made by Fourier Transform-Infrared Spectroscopy and Raman Microscopy. HMTD solutions in acetonitrile were analyzed in a direct insertion (DI) probe of a JEOL GC-Mate II since samples were insoluble in most solvents. The mass spectra of the amine peroxide samples were obtained in a HP GC-MS by injecting 0.1 μL of a dilute solution of the peroxide. The GC parameters were adapted to prevent thermal decomposition. Helium flow rate was set at 2 L/min, the needle voltage was 3500 V, electrode 1 used 150 V and electrode 2 was set at 250 V, all with respect to ground. HMTD samples were studied at 100, 150 and 200°C.

3. RESULTS

3.1 Mass spectral analysis of HMTD: EI and OACI

HMTD has a very low vapor pressure at ambient temperature, which prevents its analysis by GC methods. It is imperceptibly soluble in chloroform, acetonitrile, dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF), which also limits the chromatographic analysis. To obtain a mass spectrum using Electron Ionization (EI)-MS it was necessary to use direct insertion (DI) probe. Figure 9-3 shows the mass spectral characterization of HMTD obtained by DI/EI-MS. As shown, the molecular peak at m/z 208 is shown as base peak. This result indicates that HMTD is very stable even under strong ionization of 70 eV electron impact. Another important peak was the loss of oxygen molecule at m/z 176, an odd electron structure²². The next peaks are: m/z 88 that was formed from splitting the fragment of m/z 176 in half; m/z 73 formed from loss of a methyl group of m/z 88; m/z 59 could be identified as the trimethylamine; m/z 45 $[\text{CH}_2\text{NO}]^+$ and 42 $[\text{CH}_2\text{NCH}_2]^+$ are typical fragments of amine groups.

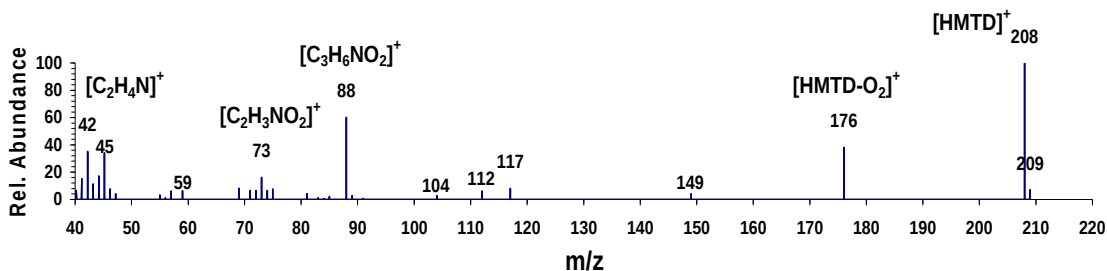


Figure 9-3. Electron Ionization mass spectrum of HMTD obtained in a magnetic sector MS.

Another useful technique for direct insertion analysis is the OACI-TOF-MS DART™, which does not require sample preparation. DART™ works soft chemical ionization technique that provides even electron fragments and neutral losses. High Resolution TOF-MS provided useful tool to identify compounds by high accuracy mass detection and significantly low detection limits. In the presence of other peroxides such as TATP and BPO, it is possible add an ammonium adduct in the OACI stream to improve the detection of all species but without strong adduct formation effect on HMTD. This effect assisted in the differentiation of aliphatic organic peroxides from amine peroxides. Figure 9-4 shows the ammonium adduct effect in presence of TATP. Using this method, it was possible to observe 70 pg of both peroxides simultaneously. Limit of detection studies for HMTD were hampered by degradation even at low temperatures.

However, the open-air mass spectra of HMTD presents three to four peaks more than TATP single peak spectrum under DART. Complete fragmentation is produced on electron impact ionization of TATP, leaving no molecular peak. Using OACI-MS TATP showed a molecular ion adduct peak at m/z 240¹². In the other hand, HMTD produced consistently fragments at m/z 179, 145, 90, and 88. Figure 9-5 presents the OACI mass spectrum of a freshly prepared sample of HMTD at 150°C. Initially, HMTD molecular mass was the strong base peak of mass spectrum at m/z 209.0781 $[M+H]^+$, which proves again

that HMTD cage structure is quite stable. It was possible to observe an ammonium adduct peak at m/z 226.1029 $[M+NH_4]^+$, but this peak depends on the temperature of the OACI stream. At higher temperatures this peak is completely absent for HMTD. Along with molecular mass base peak, the mass spectrum shows loss of formaldehyde at m/z 179.0607 $[C_5H_{11}O_5N_2]^+$, followed by the loss of hydrogen peroxide at m/z 145.0601 $[C_5H_9O_3N_2]^+$. The high accuracy of the reflectron TOF, allowed the clear identification of these molecular losses. OACI is a gentle ionization and few fragment ions were observed for HMTD. The low mass end peaks observed were m/z 90.0557 $[C_2H_8O_2N]^+$, 88.0396 $[C_2H_6O_2N]^+$ and 60.0472 $[C_2H_6ON]^+$. These peaks were below the 10% of abundance level and were not used in HTMD identification of pure samples.

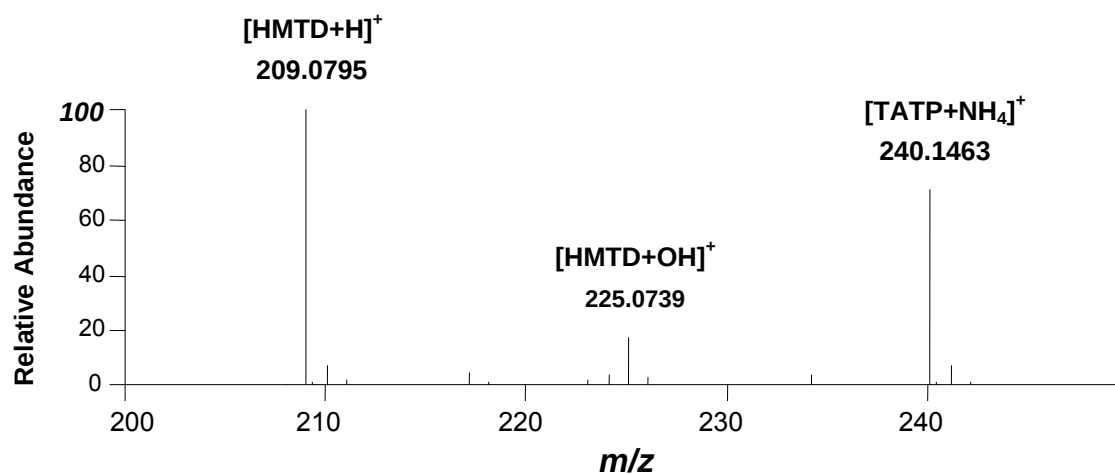


Figure 9-4. DART-mass spectrum of HMTD and TATP mixture in presence of ammonium vapor.

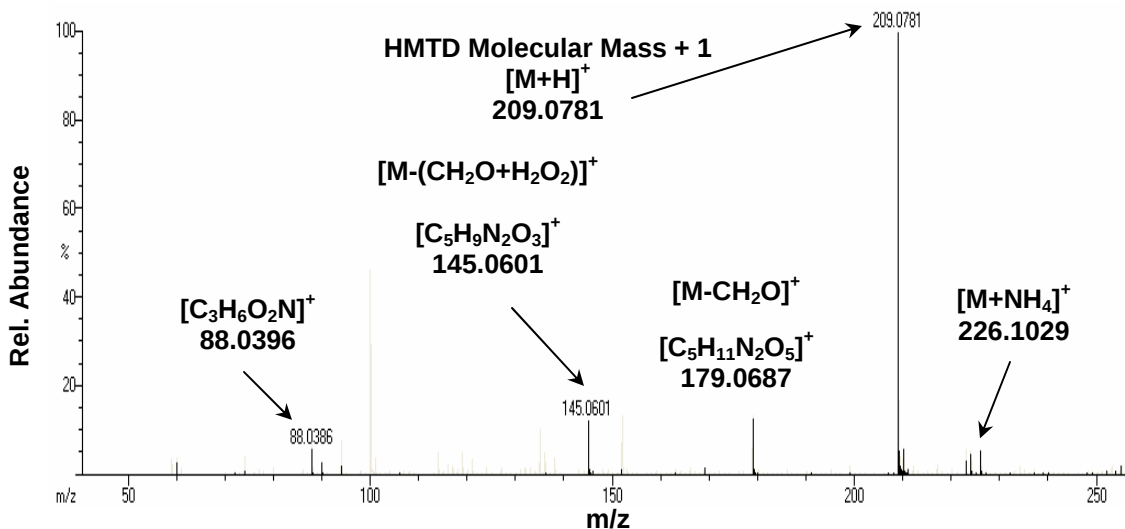


Figure 9-5. Open-Air Chemical Ionization Mass Spectrometry of HMTD by DART™-HR-TOF at 150 °C.

3.2 GC-MS analysis of HMTD

To achieve a successful GC analysis of HMTD it was necessary to increase the temperature to observe thermal degradation products. Figure 9-6 shows the results of a reconstructed chromatograph from a GC-MS run of a diluted sample of HMTD with an injector temperature of 150°C. No peak corresponding to HMTD was observed. During these analyses, only three peaks could be clearly identified. Even with limited detection, the first peaks observed in the HMTD samples were clearly identified by their molecular masses and their fragmentation patterns. At 3.01 min, an amine compound with m/z 75 $[C_3H_{10}NO]^+$ molecular mass is observed, the peaks observed in the chromatogram were

slightly resolved. Fragments at m/z 57 and 45 confirm that the structure was N, N dimethyl amino methane (Figure 9-7-A). At 4.19 min, another amine like structure with a molecular mass at m/z 87 $[C_3H_5NO_2]^+$ appeared. Fragments at m/z 75, 74, 58, and 46 confirmed that the structure was a tertiary amine. Due HMTD structure, it was possible to identify the structure as show in figure 9-7-B. At 5.61 min (Figure 9-7-C), there was a small peak that had an interesting mass spectrum. With a molecular mass at m/z 140, followed by fragments at m/z 85 and 42, this structure was identified as hexamethylene tetraamine (HMT) or hexamine, one on the reactants. However, DART analysis of the fresh same sample does not show the presence of hexamine. This fact suggested that HMTD could decompose to reactants. Figure 9-7-D presents an aliphatic amine with fragments at m/z 78, 73, 59, and 45. The fragments suggested the presence of the amine, but the molecular mass was not possible to identify due high background.

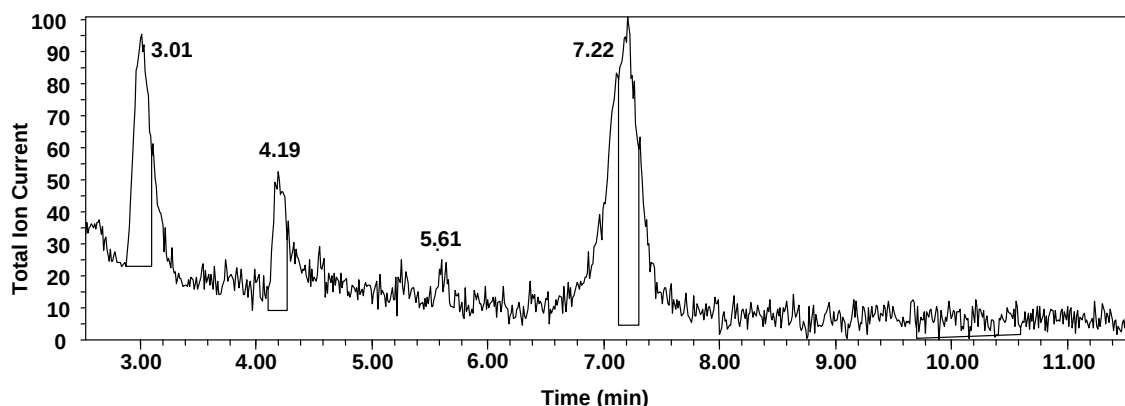


Figure 9-6. Reconstructed chromatogram from GC-MS of HMTD.

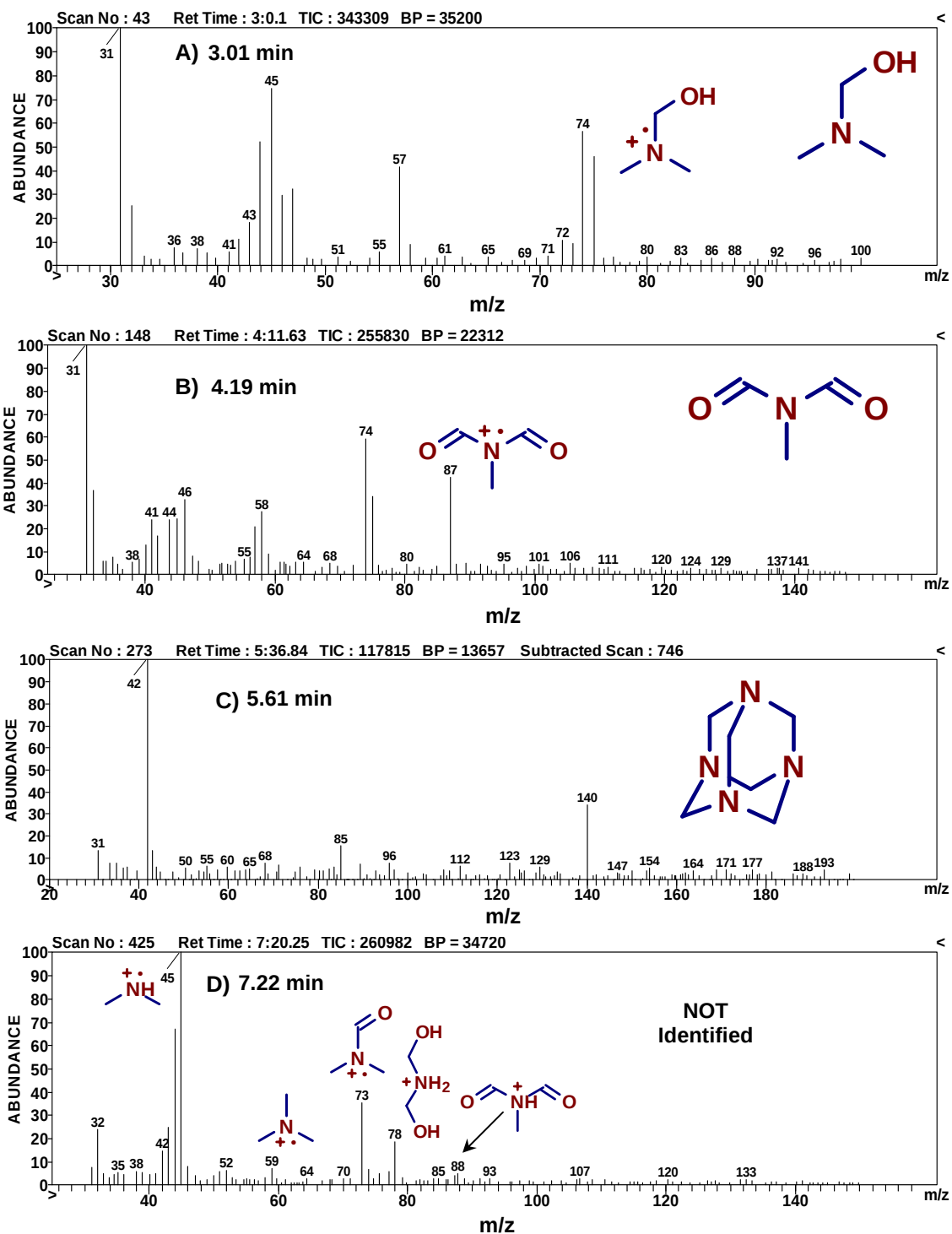


Figure 9-7. Mass spectra of the decomposition products of HMTD.

3.3 OACI analysis of HMTD

The open-air ion source was found to be useful for analysis of gas, liquid and solid samples. OACI-HR-TOF provided excellent molecular mass precision of compounds and fragmented structures. With a simple after-analysis calibration with polyethylene glycol (PEG 600), is capable of analyzing samples with no sample preparation. Figure 9-8 presents an analysis of HMTD at different ion source temperatures. The illustration shows how results could be observed during study. PEG 600 was added before and after each analysis.

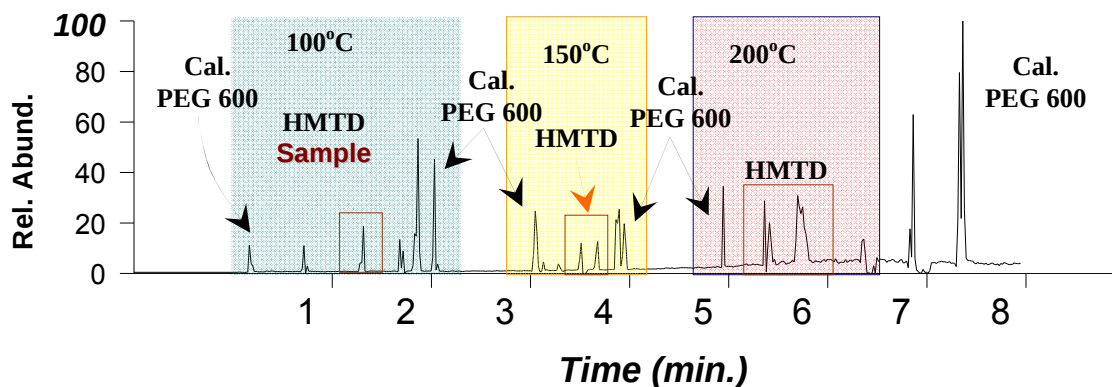


Figure 9-8. Analysis of HMTD at different ion source temperatures.

To obtain useful HMTD mass spectra it was necessary to increase the temperature of the ion source close to 150°C. At low temperatures, it was not possible to analyze HMTD using its molecular mass and fragments. Figure 9-9 shows the mass spectrum at 100°C. This spectrum could be used as background for HMTD analysis.

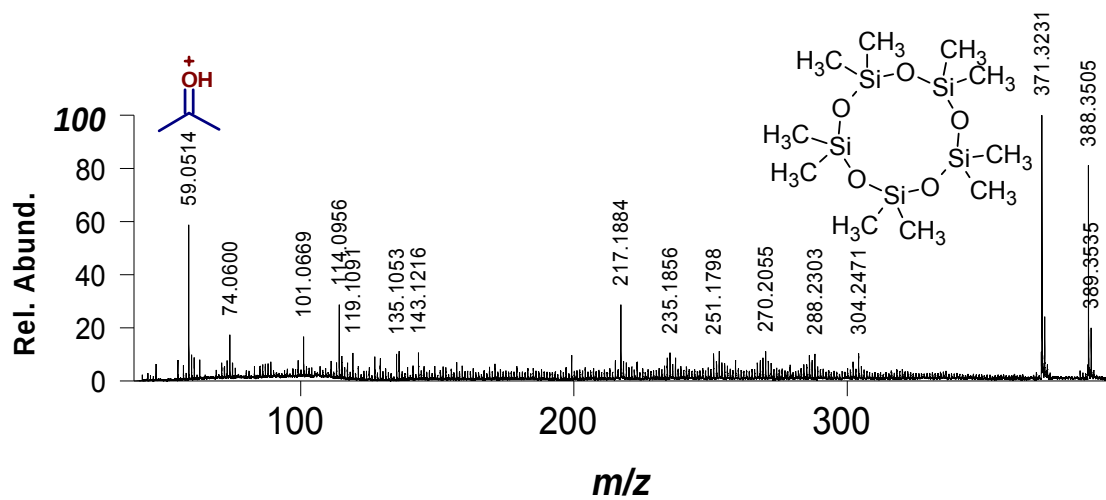


Figure 9-9. OACI MS analysis of HMTD at 100 °C. Only background signals were observed.

At optimal temperature conditions, HMTD mass spectrum presented significant fragmentation and molecular ion signals for analysis. Figure 9-10 shows the HMTD mass spectrum of an old sample store in a refrigerator. If this HMTD spectrum is compared with preview spectrum, no background peaks with strong intensities such as m/z 371.3231, 217.1884 and 59.0514 were observed. However, aged samples of HMTD were run the spectra exhibited the same peaks as in Figure 9-5 using a freshly prepared sample with marked differences in their intensity pattern. At 150 °C, HMTD presented the adduct peak of $[M+NH_4]^+$. HTMD molecular mass was observed at m/z 209.0833 with strong peak intensity however, the base peak was m/z 88.0397 $[C_2H_6O_2N]^+$. The loss of formaldehyde at m/z 179.0674 and the additional loss of hydrogen peroxide at m/z 145.0665 also increased their peak intensities. Other peaks that increased their peak abundance were m/z 90.0675 $[C_2H_8O_2N]^+$ and 60.0457 $[C_2H_6ON]^+$.

Increase in the abundance of fragment peaks suggests that HTMD experienced a structural change that was more sensible to OACI soft ionization. Also, this evidence gave clue of the origin of the low abundance peaks observed in Figure 9-5. Peaks at m/z 88.04 and 90.07 were formed from the structures of m/z 179.07 and 145.07. It was not possible to determine from which one because both could generate these peaks. A new peak at m/z 74.0597 $[\text{C}_3\text{H}_8\text{ON}]^+$, can be associated with the loss of one oxygen of m/z 90.07. Another very important peak was found at m/z 42.0348 $[\text{C}_2\text{H}_4\text{N}]^+$. This peak is a clear MS signature of amine compounds was not present in the background MS spectrum.

During the same analysis, temperature was increased to 200 °C, above HMTD decomposition temperature (150 °C) ²¹. HMTD mass spectrum did not change at the high analysis temperature. Due to its thermal sensitivity, fragmentation was expected increase together with reduction of intensities in some peaks. However, results indicated something different. At higher temperatures, the adduct peak $[\text{M}+\text{NH}_4]^+$ was not favored and disappeared in the background. This results suggests that HMTD adduct was sensitive to temperature, a behavior substantially different to TATP in which other studies suggest that TATP adduct becomes more stable¹². The only important peak that reduced slightly its intensity was HMTD molecular mass peak. In addition, other peaks were absent such as m/z 42.03 $[\text{C}_2\text{H}_4\text{N}]^+$.

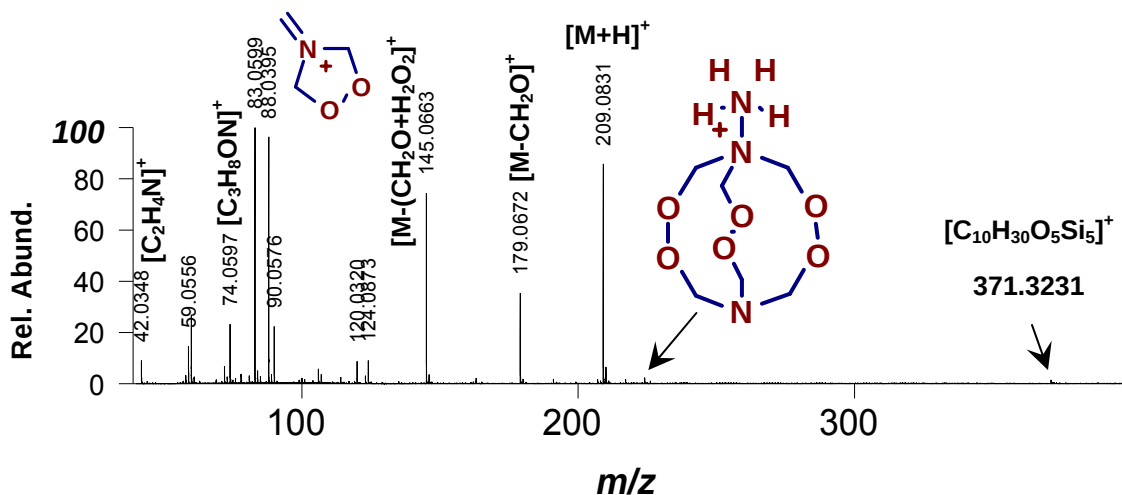


Figure 9-10. OACI mass spectrum of HTMD at 150 °C.

After storing for prolonged periods, it was common to find that HMTD samples acquired an unpleasant odor of rotten fish. If sample was not kept in a refrigerator this odor became stronger and it could be used as proof that the sample had decomposed. Figure 9-11 presents the same sample of Figure 9-10, but left outside the refrigerator and analyzed a month later. The important peaks of HMTD that were still present in this decomposed mixture were: m/z 209.0782, 179.0651, 145.0617, 90.056, and 88.0421.

Table 9-1. Relevant HMTD mass fragments observed for decomposed samples at 200 °C.

Ion Observed	Composition	Measured	Calculated	Dev. (mMass)
HMTD+H	$C_6H_{13}N_2O_6$	209.0782	209.0774	0.8
HMTD- CH_2O	$C_5H_{11}N_2O_5$	179.0651	179.0668	-1.7
HMTD-($CH_2O+H_2O_2$)	$C_5H_9N_2O_3$	145.0617	145.0613	0.3
HMTD- $C_3H_7NO_4$	$C_3H_6NO_2$	88.0421	88.0399	2.2

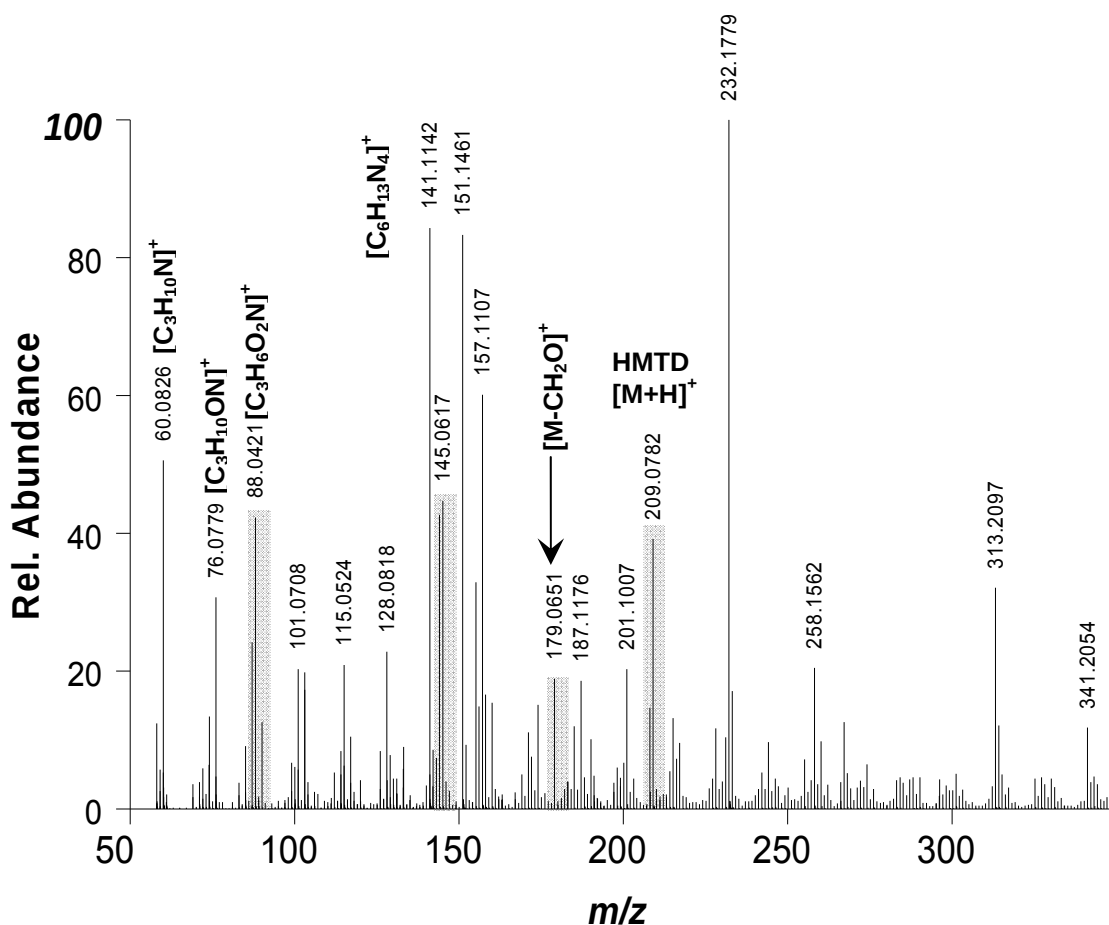


Figure 9-11. OACI mass spectrum of decomposed HMTD sample at 200 °C.

Mass accuracy was not affected (Table 9-1). However, most of the peaks were hidden between the strong decomposition products. Other peaks that appear to be uncommon but very useful for HTMD detection were the presence of hexamine (HMT) at m/z 141.1142 and a hydroxide adduct at m/z 157.1107. In contrast with other HMTD mass spectra, these peaks were completely absent. These results suggest that HMTD could change back to its reactants. Fragments such as m/z 60.0458 that belongs to $[C_2H_5NO]^+$ were not observed. Instead, a

strong peak of trimethylamine was observed at m/z 60.0826 $[\text{C}_3\text{H}_{10}\text{N}]^+$ along with its hydroxide adduct at m/z 76.0779. These peaks could be used for HMTD detection because trimethyl is very volatile. Table 9-2 shows some of these uncommon peaks.

Table 9-2. Decomposition Products of passed HMTD sample detected.

Ion Observed	Composition	Measured	Calculated	Dev.
HMT+OH	$\text{C}_6\text{H}_{13}\text{N}_4\text{O}$	157.1107	157.1089	1.8
HMT (Hexamine)	$\text{C}_6\text{H}_{13}\text{N}_4$	141.1142	141.1140	0.2
Trimethyl Amine	$\text{C}_3\text{H}_{10}\text{N}$	60.0826	60.0813	1.3

4. CONCLUSIONS

Mass Spectrometry was used for HMTD mass analysis, identification and trace detection in the presence of other peroxides. Results confirmed that HMTD characterization was difficult to achieve due its thermal sensitivity. As the important amine peroxide degrades into amine compounds, such as trimethyl amine and hexamine, solid prove direct insertion and GC-MS methods became more difficult. Electron ionization MS was able to analyze freshly prepared HMTD samples by its strong molecular ion peak and its common fragments: m/z 176, 88, and 45. GC-MS did not detect HMTD even after reducing temperature to 150°C , due in low volatility. Open-Air Chemical Ionization-MS was capable of observing HMTD through its molecular peak plus one $[\text{M}+\text{H}]^+$. This technique

provided a useful means of identifying HMTD molecular mass even in complex mixtures with other compounds or in presence of other peroxides such as TATP. However, the most important results were the characterization of important signature peaks of HTMD located at: m/z 179, 145, 90 and 88. These molecular losses under soft chemical ionization methods helped to detect the presence of HTMD.

This research also proved that using high resolution mass spectrometry like reflectron time-of-flight could discriminate between decomposition products and HMTD fragments. OACI ionization temperature did not affect precision results. TOF-MS proved to be robust technique for identification and trace detection of HMTD. Finally, OACI-TOF-MS promises to be an important tool in forensic investigations and for airports, marine ports and government buildings checkpoints.

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CHAPTER X

Conclusions

A method for detecting energetic organic peroxides using Open-Air Chemical Ionization Mass Spectrometry (OACI-MS) was presented. The high mass accuracy of the TOF instrumentation allowed for rapid determination of the peroxide analytes (within seconds) even in the presence of contaminants. In contrast, other chromatographic based methods coupled to mass spectrometric detection require at least minutes for a single analysis.

TATP and HMTD ionize by different CI mechanisms to produce different types of molecular ion adducts, even when both chemicals are ionized simultaneously *in situ*. In the case of TMDD, the formation of both types of molecular ion adducts was observed, although the adduct form with ammonium was more intense. In contrast to other organic peroxides analyzed by OA-MS, TMDD produced profuse fragmentation. Some TMDD fragments were identified. The possibility of achieving parts-per-billion to parts-per-trillion detection levels without sample preparation in open air sampling makes OA-MS an attractive technique for Defense and Security applications.

The developed methodology can be used to detect traces of TATP after an explosion, thus represents an excellent alternative to be used in forensic and criminal scenarios.

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