

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/7363154>

Application of Selected-Ion Flow Tube Mass Spectrometry to the Real-Time Detection of Triacetone Triperoxide

ARTICLE *in* ANALYTICAL CHEMISTRY · FEBRUARY 2006

Impact Factor: 5.64 · DOI: 10.1021/ac051501b · Source: PubMed

CITATIONS

29

READS

33

3 AUTHORS, INCLUDING:



Murray Mcewan

University of Canterbury

186 PUBLICATIONS 3,470 CITATIONS

SEE PROFILE

Application of Selected-Ion Flow Tube Mass Spectrometry to the Real-Time Detection of Triacetone Triperoxide

Paul F. Wilson, Barry J. Prince, and Murray J. McEwan*

Department of Chemistry, University of Canterbury, PB 4800, Christchurch, New Zealand, and Syft Technologies Ltd., P.O. Box 28149, Christchurch, New Zealand

A fast, efficient, real-time method for the quantitative analysis of the peroxide explosive, TATP, is described. The method utilizes rapid ion–molecule reactions of chemical reagent ions with the vapor above solid TATP. The reactions of three reagent ions (H_3O^+ , O_2^+ , NO^+) were examined. Although all three ions exhibited a near-collision-rate reaction with TATP, only NO^+ showed product ions that provide unequivocal evidence for a TATP-based explosive. The limit of detection of TATP in the gas phase is 10 ppb ($4 \times 10^{-10} \text{ mol L}^{-1}$).

3,3,6,6,9,9-Hexamethyl-1,4,7-cyclononatriperoxane (Figure 1), more commonly known as triacetone triperoxide (TATP), is an unstable peroxide that has been used as an improvised explosive material by terrorists including the July 2005 London transport bombings^{1,2} and criminals including the so-called “shoe bomber”.³ Although TATP is too sensitive and unstable for use as a commercial explosive, the precursors, acetone and hydrogen peroxide, are readily available to the general public, and the preparation by one-step acid catalysis is simply carried out without extensive chemical skill or apparatus. Recipes for the preparation of TATP are widely available on the Internet. We note that peroxide explosives are dangerous materials and great care should be taken in their preparation.

Unlike many of the conventional high explosives, TATP contains no nitro groups, is unstable, and so despite having a relatively high vapor pressure is not detected easily by existing analytical techniques.^{1,4} The high vapor pressure means also that TATP residues readily sublime, so speed is an important requirement in the analysis of suspect residues. Calculations and X-ray structure determinations have indicated that, unlike conventional explosives, TATP explosions are entropy driven yielding four molecules from a single TATP molecule.⁵

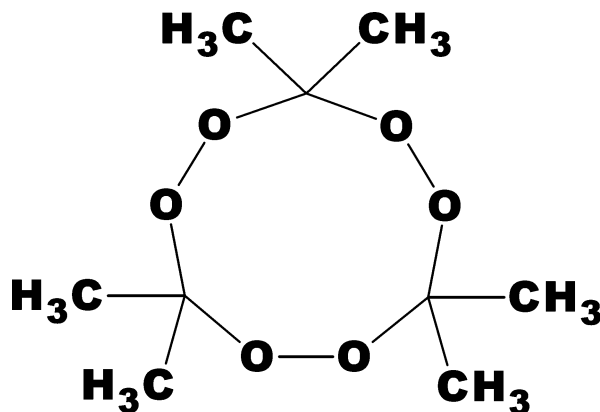


Figure 1. Triacetone triperoxide.

One of the main difficulties in the rapid detection of peroxy-based unstable explosives such as TATP is that it is thermally labile and does not lend itself readily to monitoring by conventional analytical techniques. Among the analytical methods that have been applied to TATP with varying degrees of success are the following: HPLC-fluorescence,^{4,6} HPLC–MS/MS,⁷ GC/MS of headspace using solid-phase adsorbants or SPME,⁸ ion mobility spectrometry,⁹ and cavity ringdown spectroscopy.¹⁰ These methods (with the exception of the last) rely upon analysis of a liquid sample (in which a suspect residue is dissolved in a suitable solvent) or upon preconcentration on an adsorbate. Preliminary work has also been carried out to address the possibility of developing suitable solid-state sensors for TATP.¹ We report here the use of selected-ion flow tube mass spectrometry (SIFT-MS) to analyze TATP in a headspace sample in real time with a minimum of sample preparation.

EXPERIMENTAL SECTION

Preparation of TATP. The dangers of TATP and the precautionary measures advisable in its preparation have been well stated

* To whom correspondence should be addressed. E-mail: murray.mcewan@canterbury.ac.nz.

- (1) Dubnikova, F.; Kosloff, R.; Zeiri, Y.; Karpas, Z. *J. Phys. Chem. A* **2002**, *106*, 4951–4956.
- (2) James Bennet, cited from article in *New York Times*, Monday April 22, 2002; *CBC News Report*, Friday July 15, 2005.
- (3) Simon Reeve, cited from article in *San Francisco Chronicle*, Sunday, January 6, 2002.
- (4) Schulte-Ladbeck, R.; Kolla, P.; Karst, U. *Anal. Chem.* **2003**, *75*, 731–735.
- (5) Dubnikova, F.; Kosloff, R.; Almog, J.; Zeiri, Y.; Boese, R.; Itzhaky, H.; Alt, A.; Keinan, E. *J. Am. Chem. Soc.* **2005**, *127*, 1146–1159.

- (6) Schulte-Ladbeck, R.; Kast, U. *Anal. Chim. Acta* **2003**, *482*, 183–188.
- (7) Xu, X.; van de Craats, A. M.; Kok, E. M.; de Bruyn, P. C. A. M. *J. Forensic Sci.* **2004**, *49* (6), 1230–1236.
- (8) Muller, D.; Levy, A.; Shelef, R.; Abramovich-Bar, S.; Sonenfeld, D.; Tamiri, T. *J. Forensic Sci.* **2004**, *49* (5), 935–938.
- (9) Buttigieg, G. A.; Knight, A. K.; Denson, S.; Pommier, C.; Denton, M. B. *Forensic Sci. Int.* **2003**, *135*, 53–59.
- (10) Todd, M. W.; Provencal, R. A.; Owano, T. G.; Paldus, B. A.; Kachanov, A.; Vodopyanov, K. L.; Hunter, M.; Coy, S. L.; Steinfeld, J. I.; Arnold, J. T. *Appl. Phys. B* **2002**, *75*, 367–376.

in previous work.⁴ While the materials required for the production of TATP are readily available, it is unlikely that pure precursor compounds would be encountered in the field. The preparation of organic peroxides from acetone is known to produce a number of different peroxide and related compounds including diacetone diperoxide⁷ and 2,2'-dihydroperoxy-2,2'-diisopropyl peroxide.¹¹ For this reason, it was decided to prepare a sample of TATP in a manner that might approximate (with appropriate safety measures) a covert manufacture. The preparation was based initially on that used by Milas and Golubovic,¹¹ but the later synthesis of Dubnikova et al.⁵ provided a more satisfactory route. In the latter synthesis, acetone (6 g) was mixed with hydrogen peroxide (10 mL, 30%) at 0 °C and 5 drops of concentrated sulfuric acid was added with continuous stirring. The mixture was kept at room temperature for 24 h and filtered. Samples of this precipitate were treated in two different ways.

Sample 1 was extracted with warm hexane and left to crystallize. The process of recrystallization was repeated with the product appearing as large clear prismlike crystals.

Sample 2 was simply filtered and the white solid washed with cold water and allowed to dry in air. The result was a white pastelike solid. Sample 2 more closely represents TATP produced in a covert synthesis.

After undertaking the experiments outlined here, the unused samples were destroyed using a hot ethanolic solution of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$.¹²

SIFT-MS Instrument. SIFT-MS is a technique that combines the soft ionization of chemical ionization methods with the well-defined ion–molecule reaction conditions of a flow tube technique. SIFT-MS¹³ is closely related to proton-transfer mass spectrometry¹⁴ but allows the use of more than one precursor ion. The technique lends itself to real-time analyses of gas or headspace mixtures and can be used to provide quantitative information of the sample mixture without the use of internal calibrants. The technique has been well described in the literature,^{13,15,16} and a detailed account of the method will not be provided here. Only a sufficient description of the technique will be given as it applies to the analysis of TATP. A schematic outline of the equipment is shown in Figure 2.

Mass-selected reagent ions from the ion selection region are transmitted into the flow tube (ion reaction region) where they are carried along the flow tube in a stream of inert carrier gas (typically helium). The headspace from a vial containing TATP is drawn into the lower pressure flow tube via a heated capillary tube (380 K). The bore of the capillary tube is such that the flow of sample from the headspace into the flow tube is conductance-limited at 1.9 Torr L s⁻¹ (137 standard cubic centimeters per minute). A rapid chemical reaction then occurs between the reagent ion and analytes in the sample in which mass-identifiable products from the chemical ionization of the reagent ion are recorded in the ion detection region by a second quadrupole mass spectrometer in real time. Providing the rate constants for the

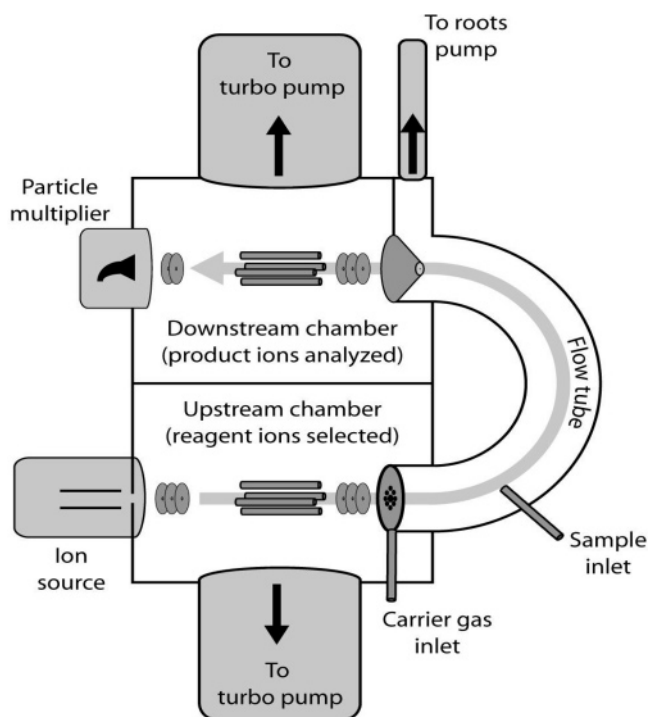


Figure 2. Schematic diagram of the Syft Technologies Ltd. Voice100 SIFT-MS instrument.¹⁷

reaction of the precursor ion with the analyte molecules are known along with the various flow tube parameters, then the ratio of the product ions to reagent ions in the detection region provides a quantitative measure of the analyte concentration within the headspace.^{13,15} The rapid transfer of the headspace mixture through the heated capillary into the flow tube (<1 s) allows the analysis of reactive and stable analyte molecules with equal efficiency. All the mass spectra shown in this study were recorded on the large laboratory SIFT¹⁶ instrument at Canterbury University. For the purpose of displaying the mass spectra without significant mass discrimination between low and high mass in Figures 3–6, the mass resolution was reduced. The designated mass assignments were determined at higher mass resolution. The pressure of helium carrier gas in the flow tube was 0.46 Torr. Because of the unstable nature of the TATP reactant neutral, we calculated the rate coefficient for H_3O^+ as described in the next section and estimated rate coefficients for O_2^+ and NO^+ relative to H_3O^+ . The uncertainty in these estimates is $\pm 30\%$ for H_3O^+ and $\pm 50\%$ for O_2^+ and NO^+ .

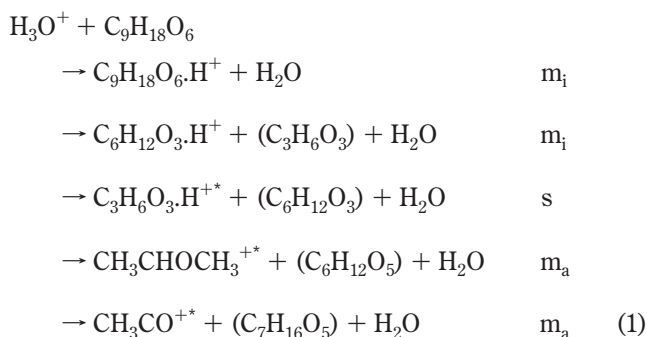
For the analysis of TATP described here, three reagent ions, H_3O^+ , O_2^+ , and NO^+ were used. Because the rate constants and reaction products for the reaction of these ions with TATP were not known, it was necessary to obtain them before a method for the quantitative measurement of the TATP concentration could be developed.

Sampling Procedure. The two samples of TATP were each placed in a 125-mL vial, sealed with a Teflon septum pierced by a syringe needle to allow atmospheric air to flow into the vial as gas passed via another syringe needle into the sample inlet of the SIFT-MS instrument. The use of the air inlet allowed a constant sample flow through the calibrated capillary inlet. The headspace samples were extracted at room temperature.

- (11) Milas, N. A.; Golubovic, A. J. *Am. Chem. Soc.* **1959**, *81*, 6461–6462.
- (12) Bellamy, J. A. J. *Forensic Sci.* **1999**, *44* (3), 603–608.
- (13) Spanel, P.; Smith, D. *Med. Biol. Eng. Comput.* **1996**, *34*, 409–419.
- (14) Lindinger, W.; Hansel, A.; Jordan, A. *Int. J. Mass Spectrom. Ion Processes* **1998**, *173*, 191.
- (15) Smith, D.; Spanel, P. *Mass Spectrom. Rev.* **2005**, *24*, 661–700.
- (16) Milligan, D. B.; Wilson, P. F.; Freeman, C. G.; McEwan, M. J.; Mautner, M. N.; Clough, T. J.; Sherlock, R. R. *J. Environ. Qual.* **2002**, *31*, 515–524.

RESULTS AND DISCUSSION

H₃O⁺ as Reagent Ion. Both samples 1 and 2 yielded broadly similar mass spectra when H₃O⁺ was used as the reagent ion with product ion peaks that were common to both. The relative intensities, however, were different mainly due to the presence of acetone solvent residues in sample 2. This difference in product ion abundance between the samples demonstrated that they varied in composition as would be expected from the different postsynthesis treatment of the samples. The reaction chemistry of H₃O⁺ with TATP obtained from analysis of the headspace from sample 2 is summarized in reaction 1. Only the more significant ion products observed are reported (*m_i* = minor; *s* = significant; *m_a* = major). Asterisks indicate product ions for which subsequent secondary chemistry ion products arise due to ion association reactions with water or acetone.



The rate coefficient for the reaction was estimated to occur at the collision rate coefficient but could not be accurately measured due to the unstable nature of the reactant. Instead, the polarizability for TATP was estimated as $20 \times 10^{-24} \text{ cm}^3$ and the Langevin rate coefficient was calculated to be $k = 2.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. This choice of a collision rate reaction is expected as proton transfer (or in this case, dissociative proton transfer) reactions are known to occur with high efficiency.¹⁸

The mass spectra arising from the chemical ionization of “raw” TATP from H₃O⁺ (sample 2, see Figure 2) can be largely explained using the major ion products outlined in reaction 1. The primary ion, H₃O⁺, at *m/z* = 19 is prominent, and as usual for samples of ambient or moist air, the water clusters of H₃O⁺·(H₂O)_{*n*} are found at *m/z* = 37, 55, and 73. A small proton-transfer parent peak at *m/z* = 223 was observed, but the major ion products of the reaction were the result of dissociative ion–neutral processes. The major ion product was protonated acetone, CH₃CHOCH₃⁺ at *m/z* = 59 and its association products arising from secondary reactions with water *m/z* = (59+18) = 77 and TATP or acetone at *m/z* = (59 + 58) = 117. There is also a minor signal corresponding to the fragment ion CH₃CO⁺ at *m/z* = 43. This peak cannot occur from the reaction of H₃O⁺ and acetone and appears to be a product of H₃O⁺ and TATP. The minor peak at *m/z* = 133 is probably C₆H₁₂O₃·H⁺. The *m/z* = 91 peak may have a very minor contribution from H₃O⁺·(H₂O)₄, but the magnitude of the peak relative to the other H₃O⁺ water clusters indicates that the major component of the *m/z* = 91 product is a dissociative proton-transfer fragment ion of TATP, C₃H₆O₃H⁺. This ion is not

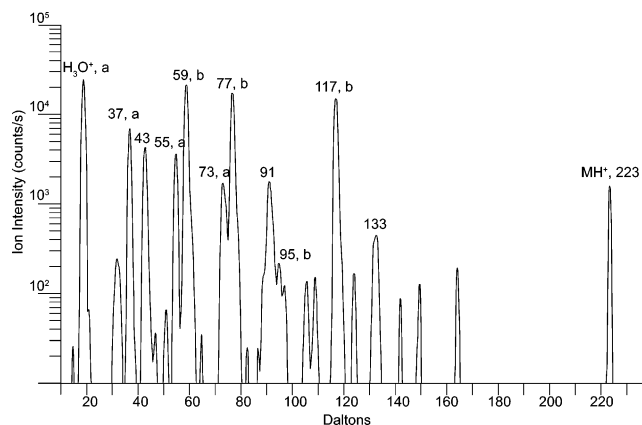
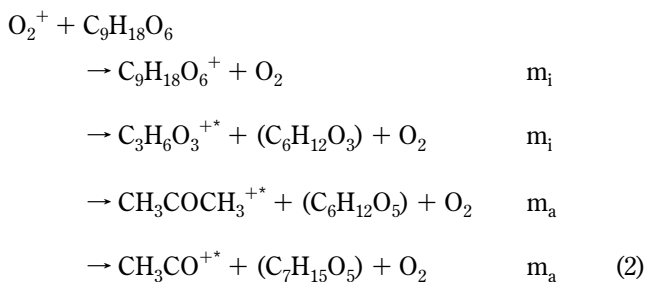


Figure 3. H₃O⁺ ionization spectrum of TATP sample 2. The numbers adjacent to each peak refer to the mass in daltons. Peaks due solely to water and water clusters are labeled “a”, and those due to TATP/acetone are labeled “b”.

generated directly from H₃O⁺ and acetone and appears to be a dissociative product of H₃O⁺ and TATP. The water cluster of this ion at *m/z* = 91 + 18 = 109 is also present. The ion products containing acetone arise both from fragmentation of the TATP molecule and from excess acetone remaining in the sample of TATP from the synthesis. Acetone is also a known dissociation product of TATP.^{5,19} However, as the product channels shown in reaction 1 are present as major ions in both samples including the sample twice recrystallized from hexane, we attribute a large part of their production to dissociative proton-transfer fragmentation of the TATP molecule by H₃O⁺.

O₂⁺ as the Reagent Ion. Where O₂⁺ was used as the precursor ion, both samples showed the characteristic fragments of TATP identified in the reactions of H₃O⁺ but without proton transfer. The important primary peaks in the O₂⁺ spectrum are seen from sample 2 in Figure 3. A summary of the reactions exhibited from O₂⁺ chemical ionization of TATP is shown in reaction 2. Only the more significant ion products are reported (*m_i* = minor; *s* = significant; *m_a* = major)



The rate coefficient for reaction was not measured, but based on the extent of product formation, the reaction rate appears close to the collision rate of $k = 1.9 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$.

In Figure 4, which displays the chemical ionization mass spectrum from O₂⁺ of sample 2, the reagent ion is clearly evident at *m/z* = 32, as is a small H₃O⁺ peak at *m/z* = 19 and the associated water clusters arising from H₃O⁺ at *m/z* = 37, 55, and

(17) Supplied by Syft Technologies Ltd, www.syft.com.

(18) Bohme, D. K. In *Interaction between Ions and Molecules*; Ausloos, P., Ed.; NATO ASI Series 6; Plenum Press: New York, 1975; pp 489–504.

(19) Oxley, J. C.; Smith, J. L.; Chen, H. *Propellants, Explos, Pyrotech.* **2002**, *27*, 209–216.

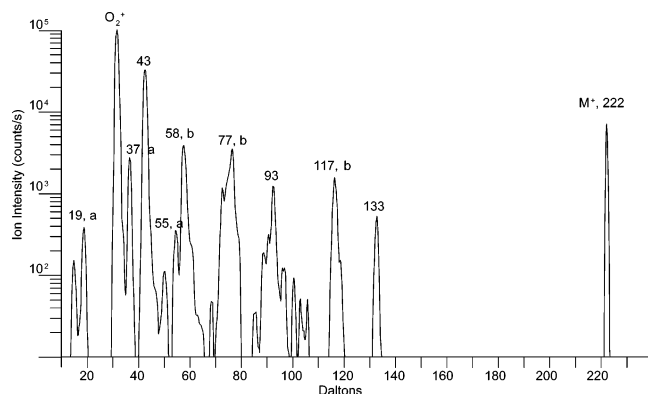


Figure 4. O_2^+ chemical ionization spectrum of TATP in sample 2. Peaks due solely to water clusters are labeled "a", and those due to TATP/acetone are labeled "b".

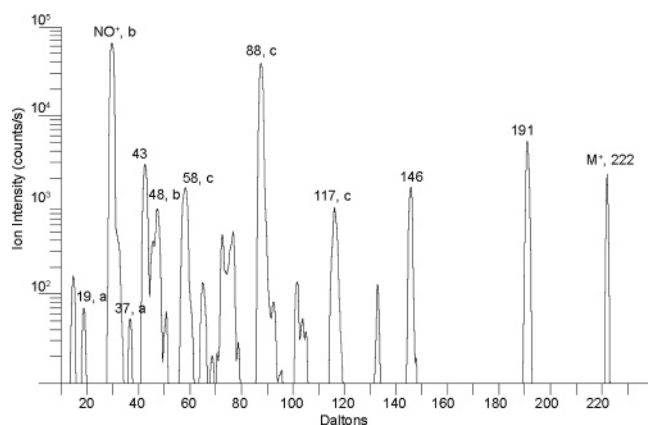


Figure 5. NO^+ chemical ionization spectrum of TATP from sample 2. Peaks due solely to water clusters are labeled "a", those due to NO^+ and water clusters are labeled "b", and those due to NO^+ and TATP/acetone are labeled "c".

73. A charge-transfer product occurs at $m/z = 222$, but the two dominant products from O_2^+ are the fragment ions CH_3CO^+ at $m/z = 43$ and $\text{CH}_3\text{COCH}_3^+$ at $m/z = 58$. These are the same products that occur in reactions of O_2^+ with acetone. As was evident in the chemical ionization mass spectra of H_3O^+ and TATP, both samples 1 and 2 yielded acetone-like products from O_2^+ . However, the peak at $m/z = 43$ is considerably larger than would be observed from acetone alone and has a significant contribution directly from TATP. The smaller mass peaks at $m/z = 77$ ($\text{CH}_3\text{COHCH}_3 \cdot \text{H}_2\text{O}$), 133 ($\text{C}_6\text{H}_{12}\text{O}_3 \cdot \text{H}^+$), and 93 arise from secondary reactions.

NO^+ as the Reagent Ion. Again the major products observed in the chemical ionization spectrum of TATP from NO^+ are the CH_3CO^+ product at $m/z = 43$ and the association product at $m/z = 88$ ($\text{CH}_3\text{COCH}_3 \cdot \text{NO}^+$) (Figure 5). In addition, significant mass peaks were also observed corresponding to charge transfer ($m/z = 222$) and a substantial product ion at $m/z = 191$. The identity of this latter ion is uncertain but it is present in all samples of TATP tested and is indicative of the presence of TATP. It could be argued that a plausible channel for the $m/z = 191$ peak is a reaction of NO^+ with TATP that involves a hydride ion transfer, which is characteristic of reactions of NO^+ with some compounds, followed by loss of HCHO . It is a major peak in samples 1 and 2

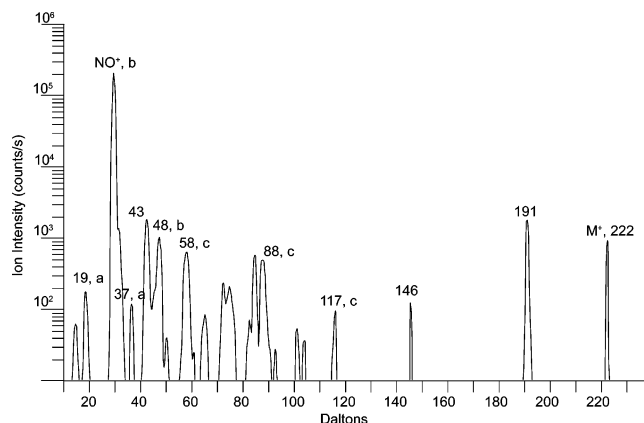
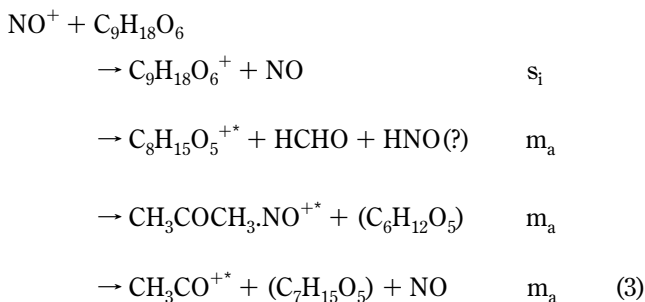


Figure 6. NO^+ chemical ionization spectrum of TATP from sample 1. Peaks due solely to water clusters are labeled "a", those due to NO^+ and water clusters are labeled "b", and those due to NO^+ and TATP/acetone are labeled "c".

as well as from recently prepared TATP and also from samples more than 3 months old.



The TATP molecule in its ion chemistry appears to behave much the same as acetone does with each of the reagent ions. With H_3O^+ the dominant ion product is protonated acetone ($m/z = 59$), with O_2^+ it is the acetone charge-transfer product ($m/z = 58$) and its dissociation product, CH_3CO^+ ($m/z = 43$), and with NO^+ it is the association product $\text{CH}_3\text{COCH}_3 \cdot \text{NO}^+$ at $m/z = 88$. However, when the mass spectrum from sample 1 is examined, the same products are observed except that the relative amounts differ (Figure 6). A comparison of the two samples shows that free acetone is present to a much greater extent in sample 2 (approximating a covert manufacture) than in sample 1 which underwent two stages of recrystallization.

Sensitivity of SIFT-MS to TATP Detection. The reagent ion most successful in the detection of TATP is NO^+ by virtue of the combination of product peaks at $m/z = 191$ and 88 and the presence of the parent ion at $m/z = 222$. Having a knowledge of the NO^+ rate constant along with the fractional product ion distribution, the sensitivity of the TATP measurement can be determined. Based on the extent of NO^+ reaction with TATP relative to that of H_3O^+ , our estimate of the rate coefficient is $k = 1.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. The $m/z = 191$ product peak makes up 27% of the total product ions due to NO^+ reaction with TATP. Thus, with the typical operating conditions of the Voice100 instrument (800 000 counts/s of precursor ions; detection efficiency of 0.2 at $m/z = 191$ relative to $m/z = 30$), the $m/z = 191$ product ion can be routinely detected at a TATP concentration of 10 parts per

billion for the vapor which is equivalent to 4×10^{-10} ($\pm 50\%$) mol L⁻¹.

CONCLUSIONS

The measurement of TATP by direct sampling of the head-space shows potential for detection and identification of the explosive by SIFT-MS. The primary advantage of this technique is speed and simplicity of operation allowing real-time identification without sample preparation. All of the three reagent ions examined (H_3O^+ , O_2^+ , NO^+) showed acetone as the primary reaction product for TATP. However, only NO^+ (and to a lesser extent O_2^+) exhibited unequivocal identification of TATP yielding a significant charge-transfer product and a reaction product at $m/z = 191$. The method offers high sensitivity for detection even when the explosive is made under conditions approaching a covert synthesis. It is also apparent from examination of the chemical ionization

spectra that TATP contained in a *sealed* container showed little degradation over a 3-month period. The ratio of the $m/z = 191/222$ products remained constant over the 3 months but the ratios of $m/z = 222$ /acetone-derived products increased substantially in the same 3-month period.

ACKNOWLEDGMENT

P.F.W. thanks the Marsden Fund for the award of a Postdoctoral Fellowship. B.J.P. thanks New Zealand Science and Technology for the award of a Postdoctoral Fellowship.

Received for review August 21, 2005. Accepted November 3, 2005.

AC051501B