TECHNICAL NOTE

CRIMINALISTICS

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The Identification of Chlorinated Acetones in Analyses of Aged Triacetone Triperoxide (TATP)

ABSTRACT: The organic peroxide explosive triacetone triperoxide (TATP) is regularly encountered by law enforcement agents in various stages of its production, storage, or usage. In a previous study, it has been demonstrated that isolated, rigorously purified, TATP may degrade to form a series of chlorinated acetones when directly treated with excess concentrated hydrochloric acid. The current study extends this work to examine whether this phenomenon may be measured during the more feasible scenario of aging of rudimentarily purified TATP contaminated with trace reaction mixture. It was demonstrated that solid-phase microextraction gas chromatography/mass spectrometry analyses of aged TATP that was synthesized utilizing hydrochloric acid catalyst may identify the presence of the degradation products chloroacetone and 1,1-dichloroacetone. Upon aging of TATP synthesized utilizing either sulfuric or nitric acid catalyst, no acid specific degradation products could be identified. These findings may be exploited by forensic chemists in the analyses of TATP samples.

KEYWORDS: forensic science, analytical chemistry, triacetone triperoxide, diacetone diperoxide, gas chromatography/mass spectrometry, improvised explosive

The synthesis of the organic peroxide explosive triacetone triperoxide (TATP; Fig. 1) was first reported in 1895 by Wolffenstein (1). TATP readily decomposes to form the cyclic dimer diacetone diperoxide (DADP; Fig. 1) and hence has never been seriously considered for use by the military (2–4). Furthermore, both TATP and DADP are very sensitive to initiation from impact, heat, and electrostatic and frictional stimuli (5). Despite the instability of TATP, it has become an explosive of choice for backyard chemists and terrorists alike because of its ease of manufacture and the availability of the precursor compounds (6,7). TATP has featured in several well-publicized illegal activities and has been encountered by law enforcement agents in various stages of its manufacture, storage, or usage (8,9).

Acid catalyzed degradation of TATP has been well documented. It has been shown that either sulfuric, hydrochloric, or nitric acid catalyst may be included within TATP crystals and that the susceptibility of the peroxide to degrade is reliant on the acid utilized in the synthesis and the extent of subsequent purification procedures (6,10). It has also been shown that isolated, purified TATP treated with concentrated sulfuric acid (solution or vapor) may degrade to form DADP and acetone (11). Treatment of the explosive with concentrated hydrochloric acid resulted in the formation of chlorinated acetones by a described mechanism (11). Furthermore, an examination of the headspace above hydrochloric acid catalyzed TATP reaction mixtures identified the formation of chloroacetone within the normal time frame of the synthesis (24 h) (12). Upon further aging of the reaction mixture, additional chlorinated acetones were also identified. These species were not present when the catalyst was either sulfuric or nitric acid (12). The presence of side products during TATP syntheses has been reported previously (13).

The current study, an extension of previous works (11,12), aimed to determine whether TATP synthesized utilizing hydrochloric acid catalyst and isolated from the reaction mixture by simple filtration may, upon prolonged storage, display the presence of chlorinated acetones. Sulfuric and nitric acid catalyzed syntheses were also examined to demonstrate the acid specificity of chlorinated acetone degradation products.

Experimental Studies

The syntheses of peroxide explosives detailed in this report were carried out in specialized facilities by chemists experienced in the production and handling of explosives. TATP is a very sensitive and powerful explosive and as such should only ever be handled by those properly equipped and qualified.

Reagents

TATP and DADP standards were synthesized following established procedures and the purity confirmed by differential scanning calorimetry and gas chromatography/mass spectrometry (GC/MS) (14,15). Thirty-seven percent w/v spectroscopic grade hydrochloric acid, >95% chloroacetone, AR acetone (Merck, Kilsyth, Vic., Australia), 98% w/v analytical reagent (AR) grade sulfuric acid, 70% w/v nitric acid (APS Group, Seven Hills, NSW, Australia), 30% w/v AR grade hydrogen peroxide, and

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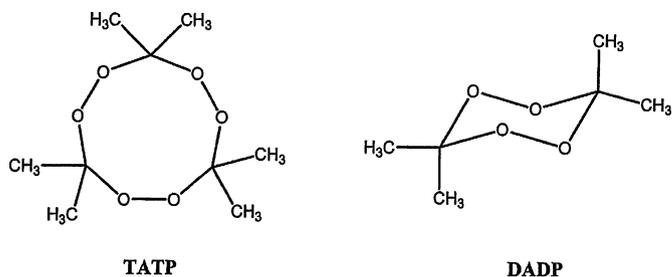
FIG. 1—*Molecular structures of triacetone triperoxide (TATP) and dimer diacetone diperoxide (DADP).*

1,1-dichloroacetone (Sigma-Aldrich, Castle Hill, NSW, Australia) were used as supplied.

Synthesis

The syntheses of TATP were adapted from reported procedures (10). Hydrochloric acid (1.9 M, 15 mL) was added to a stirred, chilled (5°C) mixture of acetone (5 mL, 68.2 mmol) and 30% w/v hydrogen peroxide (1.5 mL, 13.2 mmol). Stirring was continued for 5 min, then the stirring bar was removed and the mixture stored (24 h, 5–9°C). The precipitated reaction product was then isolated by gentle vacuum filtration. Immediately upon isolation, four samples of crystalline solid (10 mg) were removed from the bulk sample and sealed in separate solid-phase microextraction (SPME) vials. All vials were protected from light and stored at room temperature (19–21°C) for subsequent analyses by SPME GC/MS.

For the experiments detailed herein utilizing different mineral acids, the synthetic procedure and sampling method (above) were repeated using either sulfuric acid (1.9 M, 15 mL) or nitric acid (1.9 M, 15 mL).

Instrumentation

SPME headspace sampling was performed using polydimethylsiloxane/Carboxen/divinylbenzene (Supelco, Bellefonte, PA) fibers (coating thickness 50/30 μm). This type of fiber has been used previously to examine peroxide explosives and chloroacetones, and it is acknowledged that each species must possess a different affinity for the SPME fiber (11). However, automation of the sample delivery minimized SPME fiber absorption and desorption variability for each species between experiments allowing qualitative interpretation of chromatograms to be made. The crimp top SPME vials (70 × 22 mm) were fitted with silicone/Teflon septa and extracted for a period of 30 sec using a CombiPal autosampler (CTC Analytics, Schlieren, Switzerland).

MS experiments were carried out using a Varian 4000 ion trap GC/MS instrument (Varian, Palo Alto, CA), maintaining a 500:1 sample split ratio and an injector temperature of 120°C. SPME desorption time was 5 min onto a Restek RTX®-5SilMS, 30 m × 0.25 mm × 0.25 μm capillary GC column (Chromalytic Technology Pty, Boronia, Vic., Australia). The carrier gas was helium (1 mL/min). For each GC run, the initial oven temperature was maintained at 50°C for 2 min, increased at 10°C/min to 90 °C and held for 3 min, and then increased at 20°C/min to 200°C and held for 2 min. Total run time was 16.5 min.

The mass spectrometer utilized an internal electron ionization source in positive ion mode with 70 eV electron energy and 10 μA current. The ion trap conditions were target total ion count 20,000, maximum ion time 2500 μsec, multiplier offset 300 V, and scan time 0.54 sec/scan. The transfer line to the mass spectrometer was heated to 170°C. The ion trap temperature was 150°C. The scan range was *m/z* 40–400 with a 0.35-min filament delay. Detection limits were chloroacetone and 1,1-dichloroacetone (5 ng). The NIST mass spectral library (version 2d, April 26, 2005) was used for tentative compound identification, with the identity of each compound subsequently confirmed by comparison with spectra and retention times to authentic standards (16).

Results

Three differently catalyzed TATP syntheses were conducted, one each for mineral acids hydrochloric, sulfuric, and nitric acid. Typically, illegal syntheses of TATP utilize one of these three acids. Upon completion of the reaction period (24 h), the precipitated reaction products were collected by gentle vacuum filtration and immediately sampled (4 × 10 mg) and stored for later analyses by SPME GC/MS. Relative, rather than absolute, quantitation was employed to elucidate degradation characteristics so as to facilitate more meaningful comparisons to TATP produced utilizing different synthetic procedures. All experiments were repeated to confirm consistency of results. For full experimental details, see Experimental Studies.

SPME GC/MS chromatograms of the headspace above TATP that was synthesized utilizing hydrochloric acid catalyst are included in Fig. 2. The chromatogram recorded at day 0 (1 h after being sealed in a vial) displayed relative peak areas because of acetone (77%) and TATP (100%). There were no peaks attributed to chlorinated acetones. The chromatogram measured at day 2 was similar to that of day 0. However, the chromatogram recorded at day 13 displayed minor peaks because of chloroacetone (9%, compared to TATP at 100%) and 1,1-dichloroacetone (<1%). The relative peak areas of the chlorinated acetones further increased at day 27 (chloroacetone 26% and 1,1-dichloroacetone 18%).

Data detailing the SPME GC/MS headspace analyses of the reaction products from the TATP synthesis that utilized sulfuric
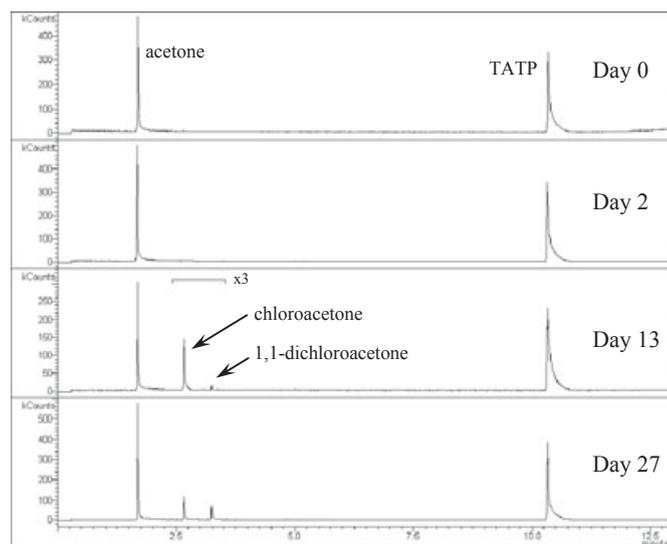
FIG. 2—*GC/MS chromatograms of the headspace above TATP that was synthesized utilizing hydrochloric acid catalyst.*

TABLE 1—*Relative abundances of chromatographic peaks of sulfuric and nitric acid catalyzed TATP.*

	Relative Peak Areas (Sulfuric Acid: DADP 100%, Nitric Acid: TATP 100%)			
	Day 0	Day 2	Day 13	Day 27
Sulfuric acid catalyst	Acetone 12% TATP 60%	Acetone 26% TATP 58%	Acetone 34% TATP 60%	Acetone 68% TATP 59%
Nitric acid catalyst	Acetone 29%	Acetone 52%	Acetone 52%	Acetone 54%

acid catalyst, and the reaction products of the synthesis that utilized nitric acid catalyst, are included in Table 1. At day 0, the chromatogram of the sample synthesized utilizing sulfuric acid displayed peaks because of TATP (60%), DADP (100%), and acetone (12%). As the experiment progressed, there was little change in the relative peak areas of TATP to DADP; however, the relative peak areas of acetone increased [day 2: acetone 26%, day 13: acetone 34%, day 27: acetone 68%; compared to DADP in each chromatogram (100%)] consistent with degradation of the peroxide explosives for the duration of the experiment. There were no other peaks in the chromatograms of the sample synthesized utilizing sulfuric acid.

At day 0, the chromatogram measured of the filtered reaction products from the TATP synthesis that utilized nitric acid catalyst displayed peaks because of TATP (100%) and acetone (29%) (Table 1). At day 2, the relative peak area of acetone increased [52% compared to TATP (100%)]; however, there was little change for the remainder of the experiment. There were no other peaks in the chromatograms of the sample synthesized utilizing nitric acid.

Discussion and Conclusions

In a previous study at the same institute, it was demonstrated that rigorously purified TATP may, upon treatment with excess concentrated hydrochloric acid, degrade to form a series of chlorinated acetones, including chloroacetone, 1,1-dichloroacetone, 1,3-dichloroacetone, and 1,1,3-trichloroacetone (11). The current study was designed to determine whether reaction mixture contamination of rudimentarily purified (filtered) TATP, a more likely real-life scenario, may present a similar phenomenon. Emphasis was placed on determining whether residual acid from a hydrochloric acid catalyzed TATP reaction mixture may lead to the formation of chlorinated acetone degradation products as a means of elucidating a method by which that explosive could be distinguished from analogous material synthesized utilizing either sulfuric or nitric acid.

SPME GC/MS analyses measured at day 0 and at day 2 of TATP that was synthesized utilizing hydrochloric acid revealed the presence of TATP and acetone (see Fig. 2). The acetone is attributed to residual reaction mixture as there was no evidence at this stage of the experiment to suggest degradation of TATP had occurred. Additionally, at day 0 and day 2, there is no evidence of the presence of chlorinated acetones. This is consistent with the rudimentary filtration of TATP decreasing the amount of residual (from the reaction mixture) chloroacetone to below the limit of detection of the experiment (12). However, chromatograms measured at days 13 and 27 clearly identified the presence of chloroacetone and 1,1-dichloroacetone. This is consistent with residual hydrochloric acid, either coating the

TATP crystals or included within them, promoting the formation of chlorinated acetone degradation products for the duration of the experiment.

Chromatograms of the reaction products of the TATP synthesis that utilized sulfuric acid catalyst revealed relative peak areas of TATP and DADP that remained largely unchanged at days 0, 2, 13, and 27; however, the relative peak areas of acetone increased as the experiment proceeded. This was attributed to degradation of TATP and DADP for the duration of the experiment. There was no evidence of the presence of any additional degradation products. Similarly, chromatograms of the reaction products of the TATP synthesis that utilized nitric acid catalyst displayed an increase in the relative peak area of acetone from day 0 to day 2 consistent with some degradation of TATP; however, relative peak areas of TATP and acetone remained largely unchanged for the remainder of the experiment and it is unclear whether degradation persisted. Again, there was no evidence of the presence of any additional degradation products.

It has been demonstrated utilizing SPME GC/MS that the headspace analysis of aged, rudimentarily purified TATP that was synthesized utilizing hydrochloric acid may identify the presence of the degradation products chloroacetone and 1,1-dichloroacetone. The presence of chlorinated acetones may distinguish TATP synthesized utilizing hydrochloric acid catalyst from TATP produced utilizing either sulfuric or nitric acid catalysts.

References

1. Wolffenstein R. *Ueber die einwirkung von wasserstoffsuperoxyd auf aceton und mesiyloxyd.* Chem Ber 1895;28:2265–9.
2. Bellamy AJ. Triacetone triperoxide: its chemical destruction. J Forensic Sci 1999;44:603–8.
3. Oxley JC, Smith JL, Shinde K. Determination of the vapour density of triacetone triperoxide (TATP) using a gas chromatography headspace technique. Prop, Explos, Pyrotech 2005;30:127–30.
4. Matyas R, Pachman J, Ang H. Study of TATP: spontaneous transformation of TATP to DADP. Prop, Explos, Pyrotech 2008;33:89–91.
5. Duin ACT, Zeiri Y, Dubnikova F, Kosloff R, Goddard WA. Atomistic-scale simulations of the initial chemical events in the thermal initiation of triacteonetriperoxide. J Am Chem Soc 2005;127:11053–62.
6. Oxley JC, Smith JL, Chen H. Decomposition of a multi-peroxidic compound: triacetone triperoxide (TATP). Prop, Explos, Pyrotech 2002;27:209–16.
7. Muller D, Levy A, Shelef R, Abramovich-Bar S, Sonenfeld D, Tamiri T. Improved method for the detection of TATP after explosion. J Forensic Sci 2004;49:935–8.
8. Evans HK, Tulleners FAJ, Sanchez BL, Rasmussen CA. An unusual explosive, triacetone triperoxide (TATP). J Forensic Sci 1986;31:1119–25.
9. White GM. An explosives drug case. J Forensic Sci 1992;37:652–6.
10. Matyas R, Pachman J. Thermal stability of triacetone triperoxide. Sci Technol Energ Mat 2007;68:111–6.
11. Armitt D, Zimmermann P, Ellis-Steinborner S. Gas chromatography/mass spectrometry analysis of triacetone triperoxide (TATP) degradation products. Rapid Commun Mass Spectrom 2008;22:950–8.
12. Fitzgerald M, Bilusich D. Sulfuric, hydrochloric and nitric acid catalysed triacetone triperoxide (TATP) reaction mixtures: an aging study. J Forensic Sci 2011;56(5):1143–9.
13. Matyas R, Pachman J. Thermal stability of triacetone triperoxide, Propellants Explos. Pyrotech 2010;35:31–7.

14. Wilson PF, Prince BJ, McEwan MJ. Applications of selected-ion flow tube mass spectrometry to the real-time detection of triacetone triperoxide. Anal Chem 2006;78:575–9.

15. Dubnikova F, Kosloff R, Almog J, Zeiri Y, Boese R, Itzhaky H, et al. Decomposition of triacetone triperoxide is an entropic explosion. J Am Chem Soc 2006;127:1146–59.

16. Stein S, Mirokhin Y, Tchekhovskoi D, Mallard G. The NIST mass spectral search program for the NIST/NIH mass spectral library. Version 2.0 d. Washington, DC: National Institute of Standards and Technology, 2005.

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