Detection of triacetone triperoxide by thermal decomposition peroxy radical chemical
amplification coupled to cavity ring-down spectroscopy

Youssef M. Taha,¹ Matthew T. Saowapon,¹ and Hans D. Osthoff^{1*}

¹ Department of Chemistry, University of Calgary, 2500 University Drive N.W., Calgary,
Alberta, Canada T2N 1N4

*corresponding author; email hsthoff@ucalgary.ca; phone 403-220-8689; fax 403-289-9488

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Abstract

Triacetone triperoxide (TATP) is frequently used in improvised explosive devices because of its ease of manufacture and tremendous explosive force. In this paper, we describe a new method for detection of TATP, thermal decomposition peroxy radical chemical amplification cavity ring-down spectroscopy (TD-PERCA-CRDS). In this method, air is sampled through a heated inlet to which ~ 1 ppmv nitric oxide (NO) are added. To verify the purity of synthetic standards, the mid-infrared spectrum of TATP vapor was recorded. The thermal decomposition of TATP is shown to produce radicals which oxidize NO to nitrogen dioxide (NO_2), whose concentration increase is monitored by optical absorption at 405 nm using a blue diode laser CRDS. The sensitivity could be improved through addition of $\sim 1\%$ ethane (C_2H_6), which fuels catalytic conversion of NO to NO_2 . The limit of detection of TD-PERCA-CRDS with respect to TATP is 22 pptv (1 s data), approximately six orders of magnitude below TATP's saturation vapor pressure. Insights into the mechanism of TATP thermal decomposition, TD-PERCA-CRDS interferences, and the suitability of TD-PERCA-CRDS as a peroxy radical explosive detection method at security check points are discussed.

Keywords

Triacetone triperoxide (TATP), trace sensing, peroxy radical chemical amplification (PERCA), cavity ring-down spectroscopy (CRDS), mechanism of TATP thermal decomposition, mid-infrared spectrum

Introduction

Triacetone triperoxide (TATP; $C_9H_{18}O_6$) is frequently used in improvised explosive devices (IEDs) due to its ease of preparation from readily obtainable chemicals [1,2]. In spite of TATP's relatively high room temperature vapor pressure of ~ 50 mTorr [3,4], its detection at security check points is a challenge because it does not contain distinguishing features such as a nitro group, metallic elements, or characteristic UV-Vis or fluorescence spectra which are utilized to detect other classes of explosives [5]. Because of this need, a variety of instrumental techniques for detection of TATP vapors have been developed (Table S1). However, no single method has found widespread use for rapid and non-invasive screening (i.e., without having to invade people's personal space by collecting swab samples) with security agencies to date. Hence, the development of new and improved methods for real-time detection of TATP vapor continues to be of interest.

One approach that has not been explored in depth is indirect detection of TATP via its decomposition products. The thermal decomposition of TATP has been studied both theoretically [2] and experimentally [1,6,7] and yields acetone ($CH_3C(O)CH_3$), ozone (O_3), and carbon dioxide (CO_2) as stable products. These species are present in ambient air in high and variable concentrations, and it is hence difficult to detect enhancements relative to background concentrations.

The thermal decomposition of TATP produces methyl acetate and ethane as minor products whose formation suggests that methyl radical (CH_3) forms as an intermediate [1,2]. In air, CH_3 rapidly reacts with molecular oxygen to form the methyl peroxy radical (CH_3O_2):

The rate coefficient for this reaction at sea level and a temperature of $25^\circ C$ is $\sim 8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [8], such that the lifetime of CH_3 with respect to reaction with O_2 is $< 1 \mu s$.

Organic peroxy radicals such as CH_3O_2 are important atmospheric trace gas constituents and are involved in many important processes, such as the photochemical production of O_3 in the troposphere [9]. Hence, highly sensitive methods for their quantification have been developed. One such method is peroxy radical chemical amplification (PERCA) [10,11]. In this technique, peroxy radicals are amplified through a series of reactions (R2-R8, Table 1) involving high concentrations of nitric oxide (NO) and either carbon monoxide (CO) [10,11] or the less toxic ethane (C_2H_6) [12]; the peroxy radicals catalyze conversion of NO to NO_2 , and the amount of NO_2 produced is proportional to the amount of peroxy radicals originally present and is quantified [10-12]. Thus, TATP (and, by proxy, other peroxide explosives) could possibly be detected indirectly (in the form of NO_2) following TATP's thermal decomposition and amplification in a heated PERCA inlet.

Our research group has constructed blue diode laser cavity ring-down spectrometers (CRDS) for quantification of NO_2 at its optical absorption maximum at 405 nm [13,14] and has demonstrated detection of nitroaromatic explosives such as trinitrotoluene (TNT) vapor following its thermal decomposition (TD) in a heated inlet in the presence of PtO_2 or PdO [14].

In this paper, we describe a thermal dissociation peroxy radical chemical amplification cavity ring-down spectrometer (TD-PERCA-CRDS) for detection of TATP vapor, which was generated by synthesizing a solid TATP sample and sampling its head space. To verify the identity and purity of this sample, we measured the mid infrared spectrum of TATP vapor by Fourier Transform Infrared Spectroscopy (FTIR). The generation of radical species during the thermal decomposition of TATP is demonstrated and implications for the thermal decomposition mechanism of TATP are discussed. The suitability of TD-PERCA-CRDS as a TATP detection method is explored.

Materials and methods

Preparation of explosive samples

Because TATP is an explosive material that is shock- and heat-sensitive, care was used in its preparation, and only minute quantities were synthesized by amalgamating several literature procedures [1,2]. Briefly, hydrogen peroxide solution (50%), acetone (HPLC grade), and sulfuric acid (99.999%) were purchased from Sigma-Aldrich (Oakville, ON) and were used as received. All reagents and glassware were pre-cooled using an external ice-water bath. 0.5 mL acetone, 0.5 mL H₂O₂ and a drop of sulfuric acid were added to a 50 mL round bottom flask and allowed to warm up to room temperature. After 24 hours, a white solid had formed which was dissolved in 10 mL pentane, washed with 10 mL water in a 125 mL separatory funnel, dried by filtering through anhydrous MgSO₄ (Sigma-Aldrich), and allowed to evaporate to dryness in a 3-valve glass vessel (similar to the one shown in Fig. 1 of Furgeson et al. [15]), forming, a clear, colorless, and cubic crystal. Analysis of the head space vapor by FTIR (see below) revealed the presence of an impurity, which was removed by subsequent recrystallization from methanol [16].

Some experiments were replicated with a commercial TATP sample (Accustandard, New Haven, CT) shipped as a 100 µg mL⁻¹ solution in acetonitrile (ACN) contained in a sealed 1 mL ampule. This sample was transferred to a clean 3-valve glass vessel for sample delivery. Results with the commercial sample (not shown) were identical to those obtained with the material synthesized in house.

Fourier Transform Infrared Spectroscopy

The mid-infrared spectrum of TATP vapor was recorded on a Bruker Tensor 27 FTIR equipped with a multi-pass cell (Gemini Spectral Sciences, Garfield, NJ, Venus Series) with 6.4 m optical

path length. The resolution of the spectrometer was 0.5 cm^{-1} . Background spectra were acquired by flushing the multipass-cell with ultrapure, "zero" grade air (ZA; Praxair). The absorption cell was then filled with TATP vapor by flushing the head space above the TATP crystal with ~ 5 sccm of ZA through the cell. 16 sample and 16 background scans were averaged.

Thermal decomposition peroxy radical chemical amplification

The TD-PERCA-CRDS instrument is described in the S.I. Briefly, the instrument utilizes up to four parallel CRDS detection channels through which ambient air is sampled. To enable PERCA, a heated quartz inlet as shown in Fig. S1 was set up. Flows of ~ 20 standard cubic centimeters per minute (sccm) of high purity nitric oxide (NO) in N_2 (100.2 parts-per-million by volume, ppmv, Scott-Marrin) and ~ 50 sccm of ethane (99%, Matheson) were added to this inlet.

In the presence of NO and the absence of C_2H_6 , certain free radicals, e.g., CH_3O_2 , the hydroperoxyl radical (HO_2), the ethylperoxy radical ($\text{C}_2\text{H}_5\text{O}_2$), or the peroxyacetyl radical ($\text{CH}_3\text{C}(\text{O})\text{O}_2$) that are either present in trace amounts in ambient air or are generated by TD of certain thermally labile molecules, oxidize NO to NO_2 (whose concentrations are monitored by blue diode laser CRDS [13]):

The alkoxy radicals generated in R3 and R4 (CH_3O and $\text{C}_2\text{H}_5\text{O}$) dissociate to yield HO_2 :

The HO₂ then rapidly reacts with NO via R2. Hence, two NO₂ molecules are produced per alkyl peroxy radical.

In the presence of both NO and C₂H₆, the hydroxyl radical (HO), generated by R2, reacts with C₂H₆ to regenerate C₂H₅O₂:

The above reactions (i.e., R2, R4, R6-R8) constitute a catalytic cycle that result in an amount of NO, proportional to the initial radical concentration, being oxidized to NO₂ [12].

The amount of NO₂ generated is limited by the residence time of sampled in the inlet as well as by termination reactions, such as

and

or loss of radical species on the inner walls of the inlet. For PERCA measurements of radicals to be quantitative, it is therefore necessary to calibrate the amplification factor, or chain length.

Ambient air contains trace amounts of free radicals and much larger amounts of thermally labile radical reservoir species, the most important of which are the peroxy-carboxylic nitric anhydrides (RC(O)O₂NO₂, PANs) [17]. Their thermal dissociation generates peroxyacyl (PA) radicals, for example:

The PA radicals oxidize NO to NO₂:

In the presence of NO, the CH₃ radical generates two additional NO₂ molecules via R1, R3, R5 and R2, giving rise to a total of four NO₂ molecules generated per PAN molecule [13].

In the presence of NO and C₂H₆, additional amplification occurs as the HO radical generated from R2 feeds back into the chain reactions described above.

Using PAN as a radical source, we calibrated the chain length and found it depended on inlet temperature (typical values ranged from ~26 at ~120 °C to 695 at ~250 °C). However, this chain length decreased nonlinearly above ~ 0.5 ppbv radical abundance.

Generation of gas streams containing TATP

The explosive sample was placed in a 3-valve glass vessel, whose head space was purged with O₂ at a flow rate was controlled at 15 sccm using a 100 sccm mass flow controller (MFC). This flow was sent through the FTIR multipass cell and combined with a flow of ZA that was slightly greater than the sampling flow rate of the TD-PERCA-CRDS (~3 slpm).

Ambient air experiments were conducted in which the glass vessel containing the TATP sample was placed next to the TD-PERCA-CRDS inlet with the opening of the glass vessel at a distance of ~5 cm. The glass vessel was opened to ambient air and the contained vapor allowed to diffuse into the room for ~ 2 minutes as the TD-PERCA-CRDS sampled the air nearby. To reduce air currents generated by the lab's overhead ventilation system, the glass vessel was placed beneath a desk covered on all sides with a linen cloth. In addition to the TATP samples, blanks consisting of cleaned (empty) glass vessels were sampled showing no response.

Results

Mid-infrared spectrum of TATP vapor

Fig. 1 (Top) FTIR absorption spectra of TATP vapor before (gray color) and after recrystallization (red color). The strongest TATP transitions are labeled with the main atoms involved in and the type of vibrational motion (str = stretching motion, astr = asymmetric stretching motion). (Bottom) Reference spectra [18] of water (blue color), carbon dioxide (black color), hydrogen peroxide (red color) and acetone (green color) scaled to the mixing ratios indicated in the legend

The gas-phase FTIR spectrum of TATP is shown in Fig. 1. The observed frequencies and intensities are summarized in Table S2.

Prior to recrystallization, the spectrum contained a strong peak at 3442.5 cm⁻¹ (Fig. 1, gray trace). Recrystallization of TATP from methanol following the procedure by Oxley et al. [16] removed

this peak and several shoulders from the other transitions (plus many water and CO₂ lines present initially as impurities in the head space).

Even though there are 93 vibrational modes in TATP plus combination and overtone transitions, the mid-IR spectrum of TATP is relatively simple as many transitions overlap and are not resolved. There is agreement between the spectrum in Fig. 1 and the (literature average) transitions given by Brauer et al. [19] (Table S2) in that all expected transitions were present. Furthermore, transitions belonging to starting materials (i.e., of acetone and hydrogen peroxide) were not observed.

Assuming that TATP achieved saturation vapor pressure of $(6.3 \pm 2.8) \times 10^{-5}$ atm at 25 °C [3], the spectrum after recrystallization shown in Fig. 1 allows an estimation of the (upper limits of the) TATP absorption cross-sections. For the major peak in the spectrum at 1195 cm⁻¹, for example, the absorption cross section is $(3.7 \pm 1.6) \times 10^{-19}$ cm² molecule⁻¹. Cross-sections for the other peaks are summarized in Table S2.

TD-PERCA-CRDS measurements of background air and air spiked with TATP

A time series showing the response of TD-PERCA-CRDS, with its inlet heated to 250 °C, to reagent gases, background air, and TATP is presented in Fig. 2. In this example, the zero concentration level was established beforehand by sampling ZA (not shown).

At 20:38, ~655 ppbv of NO were added to the sampled air, producing a small offset (~3.3 ppbv in this example). At 20:39, the ZA flow was stopped and the instrument sampled indoor air.

Indoor air contains PAN and O₃ at concentrations that are smaller than found in outside air but can nevertheless be non-negligible [20,21]. The NO added to the inlet will react with O₃:

At 250 °C, the PANs fully dissociate, generating four equivalents of NO₂ [13]. In the example shown in Fig. 2, a total of ~20.6 ppbv of NO was oxidized to NO₂ by these pathways.

At 20:41, ~1.5% ethane was added to the inlet, initiating PERCA and raising the NO₂ level to ~275 ppbv. Most of this signal is due to chemical amplification of PA radicals generated from TD of PAN. In addition, we found that at 250 °C, a small fraction of O₃ (~17%) dissociates to O₂ and O, which then reacts with ethane [22], generating additional radicals that are amplified:

Though R14 is too slow to have atmospheric implications, it matters here because the high ethane content competes for the O radical with:

Attempts to titrate the O₃ by adding NO well ahead of the ethane addition point reduced but did not eliminate this interference (data not shown).

At 20:42 (Fig. 2), a TATP sample was placed in front of the inlet, and a sharp increase in signal, ~115 ppbv above the background level, was observed.

The atmospheric background drifts as mixing ratios of O₃ and peroxy radicals change throughout a typical day, though more slowly than perturbations due to placing TATP near the inlet (see next section).

Fig. 2 Time series showing the response of TD-PERCA-CRDS, with its inlet heated to 250 °C, to zero air plus 655 ± 3 ppbv NO (white background), ambient air plus NO (gray background), NO and $(1.5 \pm 0.1)\%$ ethane plus indoor air (blue background), and with additional TATP vapor (red background)

Optimization of TD-PERCA-CRDS response to TATP vapor

Fig. 3 summarizes the TD-PERCA-CRDS response to TATP in ZA as a function of inlet temperature.

Fig. 3 Mixing ratios of NO_2 observed by TD-PERCA-CRDS during headspace analysis of a TATP sample as a function of inlet temperature. (Left-hand axis): Black circles: reagent gases only. Red squares, green inverted triangles, and purple diamonds: TATP plus NO. Blue triangles: NO plus ethane. The error bars represent the standard deviation ($\pm 1 \sigma$) of consecutive measurements at a given temperature. (Right-hand axis; shaded areas) TATP mixing ratios expected for two trial runs with TATP at mixing ratios calculated from TATP's saturation vapor pressure multiplied by its expected extent of dissociation and flow dilution factor (see text). The shaded regions represent the uncertainty ($\pm 1 \sigma$) associated with the vapor pressure of TATP

In the absence of TATP and presence of NO and ethane, there was no response by TD-PERCA-CRDS regardless of sampling temperature (Fig. 3, black circles). Likewise, there was no response to TATP in the absence of PERCA gases (i.e., NO, or NO and ethane) over this temperature range (data not shown).

When sampling the TATP headspace in the presence of 0.7 ppmv NO (Fig. 3, red squares), a temperature dependent signal that increased up to 51 ± 5 ppbv at 250 °C was observed. A

qualitatively identical dissociation profile (Fig. 3, magenta diamonds and green triangles) was observed independent of TATP concentration. Upon addition of ethane, this signal was amplified further, up to 431 ± 33 ppbv of NO_2 at 250°C (Fig. 3, blue triangles).

Shown on the right-hand axis of Fig. 3 is the amount of TATP expected to decompose, which was calculated as follows: Assuming saturation vapor pressure $(6.3 \pm 2.8) \times 10^{-5}$ atm at 25°C [3] within the 3-neck flask, and applying a dilution factor the TATP mixing ratio reaching the inlet heater was calculated. For example, during run 1 (Fig. 3) the dilution factor was $(1.9 \pm 0.4) \times 10^{-3}$ (TATP sample flow/ total instrument flow = (5 ± 1) sccm / (2602 ± 100) sccm) and the TATP mixing ratio reaching the inlet was determined to be 138 ± 48 ppbv. For run 2, the dilution factor was $(6 \pm 4) \times 10^{-4}$, giving a TATP mixing ratio of 41 ± 30 ppbv. Of these amounts, only a fraction decomposes at temperatures $< \sim 325^\circ\text{C}$, as explained below.

The thermal decomposition of TATP follows first-order kinetics [1]. The amount that thermally decomposes in the heated inlet, $[\text{TATP}]_{\text{dec}}$, was estimated using [23]:

$$[\text{TATP}]_{\text{dec}} = (1 - e^{-kt}) [\text{TATP}]_0 \quad (1)$$

Here, $[\text{TATP}]_0$ is the amount of TATP present initially, and t is the residence of TATP in the inlet. The rate coefficient for thermal decomposition, k , is calculated using the Arrhenius equation ($A \times e^{(-E_a/(RT))}$) where R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and A and E_a are equal to $3.75 \times 10^{13} \text{ s}^{-1}$ and 151 kJ mol^{-1} , respectively [1].

The residence time in the converter, t , was calculated using the inner dimensions of the quartz heater and the flow rate and was $\sim 0.24 \text{ s}$. The expected thermal dissociation profiles were then calculated by multiplying equation (1), the equilibrium vapor pressure of TATP, and the flow

dilution factor for the conditions of runs 1 and 2 and are shown as underlays in Fig. 3. Even though some aspects of this calculation are only rough approximations (such as the assumption of uniform temperature within the heater), this approach nevertheless gives reasonable estimates of TD profiles in practice [23,24].

In the presence of NO, the shape of the experimental TD profiles matched those of the expected profiles. The ratio of observed NO₂ to expected TATP mixing ratios indicates an amplification factor of 2.6 ± 0.5 . This amplification factor was constant for NO mixing ratios above ~ 700 ppbv (Fig. S2).

Sampling TATP in the presence of both PERCA gases, i.e., NO and ethane, results in 431 ± 33 ppbv of NO₂ at 250 °C (Fig. 3, blue triangles). Higher inlet temperatures were not investigated as the amount of NO₂ that could be generated would have been limited by the amount of NO. This much larger response in the presence of ethane demonstrates that TD of TATP produces radicals that are chemically amplified to produce a large analytical signal.

Unlike the NO-only amplification, the amplification factor in the presence of ethane and NO is non-linear and scales roughly inversely with radical concentration, mainly due to radical – radical self-reactions at these large concentrations [12]. Nevertheless, an amplification factor of 22 ± 3 (temperature range 190 – 250 °C) was achieved, corresponding to a factor of ~ 9 per TATP decomposed.

Figures of Merit

When sampling ZA in the presence of ~ 2 ppmv NO, the CRDS has a minimum detectable NO₂ mixing ratio (calculated using equation 6 of [25]) of ~ 56 pptv for data averaged over 1 s. At ~ 325 °C in NO-only mode, the TATP detection limit (estimated based on detection of the amount

of NO₂ that is generated from it) is then ~22 pptv, more than six orders of magnitude below this compound's saturation vapor pressure. In the presence of ethane and NO at 250 °C, the minimum detectable NO₂ mixing ratio is ~100 pptv for 1 s data, corresponding to ~5 pptv of TATP. Both of these values are best-case scenarios since in practice, the limits of detection will be higher due to variability of the composition of indoor air.

Interference tests

A series of qualitative tests using chemicals found in our laboratory was conducted to evaluate the selectivity of this sensor (details are given in the S.I.). An inlet temperature of 250 °C was chosen as a compromise between sensitivity (i.e., T high enough to achieve a large TATP signal - Fig. 3) and likelihood of interferences (i.e., T low enough to avoid indiscriminate dissociation of non-target molecules). At 250 °C, all molecules tested produced a smaller response than TATP, except for peroxyacetic acid (CH₃C(O)O₂H, PAA) which produced a response of similar magnitude (Figure S12). This molecule is present in ambient air [26] and hence likely contributes to the indoor air background signal (Fig. 2). Positive responses were also observed for hydrogen peroxide (H₂O₂) and dinitrogen pentoxide (N₂O₅) (Figures S11 and S10). Both of these molecules are present in ambient air, but unlikely to be present in high concentration indoors.

There were negligible responses to the head space vapors above samples of acetone, water, acetic acid, 4-heptanone, iodine, nitrous acid, or sodium hypochlorite solution (Figures S3 – S8). Small negative signals were observed when sampling near surfaces such as human hand or from within an enclosed space (Figure S13), rationalized by dry deposition of O₃ and NO₂ to these surfaces [20].

When the inlet was operated at temperatures of 350 °C and 300 °C, a positive signal was observed when skin moisturizer cream or anti-perspirant was held up to the inlet; the signal intensity was less than observed for TATP when both were sampled at approximately equal distances to the inlet (Figures S14A and S14B). When the experiment was repeated at 250 °C, this interference was no longer present (Figure S14C).

Personal hygiene products contain numerous compounds, including pentamethyl-cyclopentasiloxane (D5), which mimics the structure TATP, though with Si rather than C and containing fewer O atoms. However, the head space above D5 did not produce a TD-PERCA-CRDS signal (Figure S15). It is hence not known which ingredients in these products cause this interference, though some possibilities are discussed below.

Discussion

Mid-infrared spectrum of TATP vapor

The mid-IR spectrum of TATP vapor reported here fills an important void in the current literature as there are few IR spectra of TATP reported, and most of those reported are in the solid state (and not of TATP vapor) or the description of the spectra is not comprehensive (e.g., cross-sections or tables of transitions not given, etc.). Knowledge of the TATP gas phase spectrum is needed to enable its detection by IR sensors.

Brauer and coworkers [19] provided a comprehensive summary of TATP infrared transitions on the basis of available solution and solid state spectra and their own theoretical predictions. Many of the transitions observed in this work are blue-shifted by a few cm^{-1} relative to those reported by Brauer et al. [19], possibly because of a lack of intermolecular interactions (such as hydrogen bond bridges) [2] that occur in the solid or liquid phase but not in the gas phase.

Our observations are consistent with other gas phase spectra reported in the literature such as the Raman transitions reported by Pacheco-Londono et al. [27] and the spectrum shown by Hildenbrand et al. [28], who unfortunately did not tabulate the IR frequencies they observed.

Recently, Guo and coworkers reported the gas-phase IR spectrum of diacetone diperoxide (DADP) [29]; several peaks that they reported for DADP were not present in Fig. 1, indicating the absence of DADP in our standards. Overall, the IR spectrum confirms that the head space above the synthesized TATP sample contained TATP in high purity.

We documented transitions of impurities prior to recrystallization as such transitions may be utilized for forensic "fingerprinting". The impurity peak at 3442.5 cm^{-1} observed originally (Fig. 1, gray trace) likely originated from an intermediate formed during TATP synthesis that co-precipitated. One potential candidate is $(\text{CH}_3)_2\text{C}(\text{OH})\text{-OO-C}(\text{CH}_3)_2\text{OOH}$, a molecule which was observed by Pacheco-Londono and coworkers during TATP synthesis [27].

Implications on the mechanism of TATP decomposition

The results presented here shows that peroxy radicals are formed during the thermal decomposition of TATP. A proposed mechanism is shown in Figure 4.

The main decomposition pathway for TATP follows a non-redox mechanism and involves several acetone elimination steps to yield O₃ (Fig. 4, top row) [2,1,6]. Upon formation of a first equivalent of acetone, an alkoxy peroxy diradical intermediate species (I) is formed. This diradical is believed to form a 7-membered ring (II) before further thermal decomposition yields a second equivalent of acetone and an alkoxy trioxyl diradical molecule (III). This molecule then forms a third equivalent of acetone and releases an O₃ molecule.

When sampling TATP in NO-only mode (e.g., Fig. 3, runs 1 and 2), an NO₂ signal that is a factor of 2.6 ± 0.5 larger than expected from TATP saturation vapor pressure and flow dilution was observed. This amplification factor is a lower limit since TATP may not have achieved saturation vapor pressure in the glass vessel, and some radicals may have been "lost" to radical – radical reactions or on the inner walls of the PERCA inlet. The observed amplification nevertheless indicates that the thermal dissociation does not exclusively proceed via pathway 1 as this pathway only generates 1 equivalent O₃ which reacts with NO to form 1 equivalent of NO₂. A plausible explanation is that radical intermediate (I) is sufficiently long-lived to react with NO rather than eliminating acetone.

Upon reaction of the alkoxy peroxy diradical (I) with NO, the dialkoxy diradical (IV) is likely formed. This molecule is the ring opening product of DADP and may proceed via a C-O cleavage reaction to stepwise eliminate two acetone molecules and an O₂ molecule. This pathway provides for 1 equivalent of NO₂ per TATP and is indistinguishable from the pathway shown at the top of

Figure 4. Neither one of these pathways is consistent with the observed amplification in the presence of NO and ethane which requires radicals that feed into the PERCA reaction sequence.

To explain the generation of such radicals, we proposed that (IV) proceeds via a C-C cleavage reaction to produce a methyl radical and intermediate (V). This molecule may then decompose via a C-C cleavage reaction to form two more methyl radicals. In NO-only mode, the methyl radical proceeds via reactions R1, R3, R5 and R2 to produce two equivalents of NO₂; thus, this pathway would yield 7 equivalents of NO₂. Alternatively, (V) could also eliminate acetone to form the PA radical which converts NO molecules to NO₂. On aggregate, this pathway yields 6 NO₂ molecules per molecule of TATP. Either pathway provides methyl radicals that initiate PERCA amplification in the presence of ethane.

However, no single pathway rationalizes the yield of 2.6 radicals per TATP. The most likely scenario, therefore, is that thermal decomposition of TATP in the presence of NO involves a combination of the above pathways.

Fig. 4 Proposed mechanism for TATP decomposition in the presence of NO

TD-PERCA-CRDS as a TATP detection method

The TD-PERCA-CRDS method developed enables highly sensitive (~ 5 pptv), rapid (1 Hz), continuous, and robust detection of TATP in ambient air. The figures of merit top most TATP detection methods reported in the recent literature (Table S1), all while deploying the easiest possible sample introduction method, direct gas analysis. The highest sensitivity (5 pptv; 0.5 pg equivalent) was achieved when the TD-PERCA-CRDS was operated with both ethane and NO. Though less sensitive by an order of magnitude, the NO only mode would be more attractive for routine screening applications as it requires fewer reagent gases and produces easier to handle

exhaust, though it would be straightforward to switch in ethane for boosted sensitivity if desired. The ultrahigh sensitivity of TD-PERCA-CRDS is a considerable advantage as it would help to overcome deliberate concealment of TATP (e.g., in a sealed plastic bag), which reduces the mixing ratios by a factor of $\sim 1,000$ or more [30].

The TD-PERCA-CRDS is robust as it builds on the now 30-year old CRDS technique, which has matured to a point that turn-key instruments have become commercially available from several manufacturers. Even though multiple detection channels are used in this work, a single CRDS channel would suffice for TD-PERCA-CRDS and enable a more compact instrument design.

One disadvantage of TD-PERCA-CRDS is the atmospheric background, which is considerably larger when operated in ethane-PERCA mode. While this background will drift over the course of a day (as indoor air is exchanged with outdoor air and O_3 is produced photochemically), it is not expected to change suddenly, certainly not on a time scale of a few seconds needed for screening. When present, TATP generated a large signal (e.g., Fig. 2) easily distinguishable from the slowly varying background. Furthermore, many buildings (e.g., hospitals) use scrubbers that condition intake air and remove a substantial portion of the molecules contributing to the atmospheric background signal, especially H_2O_2 , PAA, and N_2O_5 , whose indoor air concentrations are likely very small, and some of the PAN and O_3 .

The sensitivity of TD-PERCA-CRDS to PAA and N_2O_5 would not be an issue for security screening applications, since neither molecule is expected on people or luggage. On the other hand, H_2O_2 is a more commonly used household chemical, but it is also a common precursor for many homemade peroxide explosives, such that the false detection of H_2O_2 would not necessarily be a bad thing from a security viewpoint.

A disadvantage is the response to anti-perspirant and skin cream/moisturizer products at inlet temperatures $> 250\text{ }^{\circ}\text{C}$. These products contain numerous compounds, including D5. Organosiloxanes have become ubiquitous in the environment and are commonly used [31]. Cyclic siloxanes are slightly volatile and thermally decompose to release methyl radicals [32], though the Arrhenius parameters for decomposition [33] are such that this molecule is not expected to decompose at inlet temperatures used in this work, which was verified experimentally (Figure S15). However, recent studies [34] suggest that pyrolysis of impurities in polysiloxanes may occur at temperatures as low as $70\text{ }^{\circ}\text{C}$. TD of polysiloxanes is believed to generate dimethylsilane ($(\text{CH}_3)_2\text{SiO}$, D1) as an intermediate, whose further decomposition generates two CH_3 radicals [32] and, in the presence of excess NO , four equivalents of NO_2 . The potential response of TD-PERCA-CRDS to commonly used cosmetics somewhat compromises its utility at security checkpoints as it makes it prone to false positives, though TD-PERCA-CRDS may nevertheless be useful as a first screening tool.

On the other hand, it is likely (and an advantage) that this instrument would respond to peroxide explosives other than TATP: For instance, DADP also decomposes via a radical mechanism [1] similar to that of TATP and hence is expected to be detectable by the TD-PERCA-CRDS. Furthermore, the instrument would respond to the vapors of certain NO_2 -containing explosives (e.g., PETN) though only if these were present in very high concentration.

Table 1. List of chemical reactions and rate coefficients*

Number	Reaction	k (cm ³ molecule ⁻¹ s ⁻¹)	k _{298K} (cm ³ molecule ⁻¹ s ⁻¹)
R1	CH ₃ + O ₂ + M → CH ₃ O ₂ + M	$7.0 \times 10^{-31} \times (T/300)^{-3.0} \times [M]$	$7.8 \times 10^{-13}^{**}$
R2	HO ₂ + NO → HO + NO ₂	$3.45 \times 10^{-12} \times e^{(270/T)}$	8.5×10^{-12}
R3	CH ₃ O ₂ + NO → CH ₃ O + NO ₂	$2.3 \times 10^{-12} \times e^{(360/T)}$	7.7×10^{-12}
R4	C ₂ H ₅ O ₂ + NO → C ₂ H ₅ O + NO ₂	$2.55 \times 10^{-12} \times e^{(380/T)} \times 0.99^{***}$	9.1×10^{-12}
R5	CH ₃ O + O ₂ → HCHO + HO ₂	$7.2 \times 10^{-14} \times e^{(-1080/T)}$	1.9×10^{-15}
R6	C ₂ H ₅ O + O ₂ → CH ₃ CHO + HO ₂	$2.4 \times 10^{-14} \times e^{(-325/T)}$	8.1×10^{-15}
R7	HO + C ₂ H ₆ → C ₂ H ₅ + H ₂ O	$6.9 \times 10^{-12} \times e^{(-1000/T)}$	2.4×10^{-13}
R8	C ₂ H ₅ + O ₂ + M → C ₂ H ₅ O ₂ + M	$5.9 \times 10^{-29} \times (T/300)^{-3.8} \times [M]$	$7.8 \times 10^{-12}^{**}$
R9	HO + NO ₂ + M → HONO ₂ + M	$3.2 \times 10^{-30} \times (T/300)^{-4.5} \times [M]$	$9.8 \times 10^{-12}^{**}$
R10	HO + NO + M → HONO + M	$7.4 \times 10^{-31} \times (T/300)^{-2.4} \times [M]$	$9.7 \times 10^{-12}^{**}$
R11	CH ₃ C(O)O ₂ NO ₂ + M → CH ₃ C(O)O ₂ + NO ₂ + M		$4.4 \times 10^{-4} \text{ s}^{-1}$
R12	CH ₃ C(O)O ₂ + NO → NO ₂ + CH ₃ C(O)O → NO ₂ + CH ₃ + CO ₂	$7.5 \times 10^{-12} \times e^{(290/T)}$	2.0×10^{-11}
R13	NO + O ₃ → NO ₂ + O ₂	$2.07 \times 10^{-12} \times e^{(-1400/T)}$	1.9×10^{-14}
R14	O + C ₂ H ₆ → C ₂ H ₅ + HO	$1.66 \times 10^{-15} \times T^{1.5} \times e^{(-2920/T)}$	4.7×10^{-16}
R15	O + O ₂ + M → O ₃ + M	$6.4 \times 10^{-34} \times (T/300)^{-2.6} \times [M]$	1.4×10^{-14}

* Rate constant expressions are from the IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation.[35] Rate constants for R14 are from [22]. For simplicity, [N₂] is written as [M] in the above expressions.

** calculated assuming P = 1 bar

*** 1% proceeds to form C₂H₅ONO₂

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Compliance with Ethical Standards

The authors declare that they have no potential conflict of interest.

References

1. Oxley JC, Smith JL, Chen H (2002) Decomposition of a multi-peroxidic compound: Triacetone triperoxide (TATP). *Propellants Explos Pyrotech* 27 (4):209-216. doi:10.1002/1521-4087(200209)27:4<209::aid-prep209>3.0.co;2-j
2. Dubnikova F, Kosloff R, Almog J, Zeiri Y, Boese R, Itzhaky H, Alt A, Keinan E (2005) Decomposition of triacetone triperoxide is an entropic explosion. *J Am Chem Soc* 127 (4):1146-1159. doi:10.1021/ja0464903
3. Ewing RG, Waltman MJ, Atkinson DA, Grate JW, Hotchkiss PJ (2013) The vapor pressures of explosives. *TrAC Trends in Analytical Chemistry* 42 (0):35-48. doi:10.1016/j.trac.2012.09.010
4. Mbah J, Knott D, Steward S (2014) Thermogravimetric study of vapor pressure of TATP synthesized without recrystallization. *Talanta* 129:586-593. doi:10.1016/j.talanta.2014.06.031
5. Schulte-Ladbeck R, Vogel M, Karst U (2006) Recent methods for the determination of peroxide-based explosives. *Anal Bioanal Chem* 386 (3):559-565. doi:10.1007/s00216-006-0579-y
6. Bulatov V, Reany O, Grinko R, Schechter I, Keinan E (2013) Time-resolved, laser initiated detonation of TATP supports the previously predicted non-redox mechanism. *Phys Chem Chem Phys* 15 (16):6041-6048. doi:10.1039/c3cp44662j
7. Hiyoshi RI, Nakamura J, Brill TB (2007) Thermal Decomposition of Organic Peroxides TATP and HMTD by T-Jump/FTIR Spectroscopy. *Propellants, Explosives, Pyrotechnics* 32 (2):127-134. doi:10.1002/prep.200700002
8. Burkholder JB, Sander SP, Abbatt JPD, Barker JR, Huie RE, Kolb CE, Kurylo MJ, Orkin VL, Wilmouth DM, Wine PH (2015) Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation Number 18. National Aeronautics and Space Administration, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California
9. Lightfoot PD, Cox RA, Crowley JN, Destriau M, Hayman GD, Jenkin ME, Moortgat GK, Zabel F (1992) Organic Peroxy-Radicals - Kinetics, Spectroscopy And Tropospheric Chemistry. *Atmos Environm A* 26 (10):1805-1961. doi:10.1016/0960-1686(92)90423-l

10. Clemitshaw KC, Carpenter LJ, Penkett SA, Jenkin ME (1997) A calibrated peroxy radical chemical amplifier for ground-based tropospheric measurements. *J Geophys Res* 102 (D21):25405-25416. doi:10.1029/97JD01902
11. Cantrell CA, Shetter RE, Lind JA, McDaniel AH, Calvert JG, Parrish DD, Fehsenfeld FC, Buhr MP, Trainer M (1993) An Improved Chemical Amplifier Technique For Peroxy Radical Measurements. *J Geophys Res* 98 (D2):2897-2909. doi:10.1029/92JD02842
12. Wood EC, Deming BL, Kundu S (2016) Ethane-Based Chemical Amplification Measurement Technique for Atmospheric Peroxy Radicals. *Environmental Science & Technology Letters* 4 (1):15-19. doi:10.1021/acs.estlett.6b00438
13. Paul D, Osthoff HD (2010) Absolute Measurements of Total Peroxy Nitrate Mixing Ratios by Thermal Dissociation Blue Diode Laser Cavity Ring-Down Spectroscopy. *Anal Chem* 82 (15):6695-6703. doi:10.1021/ac101441z
14. Taha YM, Odame-Ankrah CA, Osthoff HD (2013) Real-time vapor detection of nitroaromatic explosives by catalytic thermal dissociation blue diode laser cavity ring-down spectroscopy. *Chem Phys Lett* 582 (0):15-20. doi:10.1016/j.cplett.2013.07.040
15. Furgeson A, Mielke LH, Paul D, Osthoff HD (2011) A photochemical source of peroxypropionic and peroxyisobutanoic nitric anhydride. *Atmos Environm* 45 (28):5025-5032. doi:10.1016/j.atmosenv.2011.03.072
16. Oxley JC, Smith JL, Bowden PR, Rettinger RC (2013) Factors Influencing Triacetone Triperoxide (TATP) and Diacetone Diperoxide (DADP) Formation: Part I. Propellants, Explosives, Pyrotechnics 38 (2):244-254. doi:10.1002/prep.201200116
17. Roberts JM (1990) The atmospheric chemistry of organic nitrates. *Atmos Environm A* 24 (2):243-287. doi:10.1016/0960-1686(90)90108-Y
18. Sharpe SW, Johnson TJ, Sams RL, Chu PM, Rhoderick GC, Johnson PA (2004) Gas-phase databases for quantitative infrared spectroscopy. *Appl Spectrosc* 58 (12):1452-1461
19. Brauer B, Dubnikova F, Zeiri Y, Kosloff R, Gerber RB (2008) Vibrational spectroscopy of triacetone triperoxide (TATP): Anharmonic fundamentals, overtones and combination bands. *Spectroc Acta Pt A-Molec Biomolec Spectr* 71 (4):1438-1445. doi:10.1016/j.saa.2008.04.022

20. Weschler CJ (2000) Ozone in Indoor Environments: Concentration and Chemistry. *Indoor Air* 10 (4):269-288. doi:10.1034/j.1600-0668.2000.010004269.x
21. Jakobi G, Fabian P (1997) Indoor/outdoor concentrations of ozone and peroxyacetyl nitrate (PAN). *International Journal of Biometeorology* 40 (3):162-165. doi:10.1007/s004840050037
22. Baulch DL, Cobos CJ, Cox RA, Frank P, Hayman G, Just T, Kerr JA, Murrells T, Pilling MJ, Troe J, Walker RW, Warnatz J (1994) Summary table of evaluated kinetic data for combustion modeling: Supplement 1. *Combustion and Flame* 98 (1):59-79. doi:10.1016/0010-2180(94)90198-8
23. Paul D, Furgeson A, Osthoff HD (2009) Measurement of total alkyl and peroxy nitrates by thermal decomposition cavity ring-down spectroscopy. *Rev Sci Instrum* 80:114101. doi:10.1063/1.3258204
24. Thaler RD, Mielke LH, Osthoff HD (2011) Quantification of Nitryl Chloride at Part Per Trillion Mixing Ratios by Thermal Dissociation Cavity Ring-Down Spectroscopy. *Anal Chem* 83 (7):2761-2766. doi:10.1021/ac200055z
25. Brown SS, Stark H, Ciciora SJ, McLaughlin RJ, Ravishankara AR (2002) Simultaneous in situ detection of atmospheric NO_3 and N_2O_5 via cavity ring-down spectroscopy. *Rev Sci Instrum* 73 (9):3291-3301. doi:10.1063/1.1499214
26. Phillips GJ, Pouvesle N, Thieser J, Schuster G, Axinte R, Fischer H, Williams J, Lelieveld J, Crowley JN (2013) Peroxyacetyl nitrate (PAN) and peroxyacetic acid (PAA) measurements by iodide chemical ionisation mass spectrometry: first analysis of results in the boreal forest and implications for the measurement of PAN fluxes. *Atmos Chem Phys* 13 (3):1129-1139. doi:10.5194/acp-13-1129-2013
27. Pacheco-Londono L, Pena AJ, Primera OM, Hernandez-Rivera SP, Mina N, Garcia R, Chamberlain RT, Lareau R (2004) An experimental and theoretical study of the synthesis and vibrational spectroscopy of triacetone triperoxide (TATP). In: Carapezza EM (ed) *Sensors, and Command, Control, Communications, and Intelligence(C31) Technologies for Homeland Security and Homeland Defense* lli, Pts 1 and 2, vol 5403. *Proceedings of the Society of Photo-Optical Instrumentation Engineers (Spie)*. Spie-Int Soc Optical Engineering, Bellingham, pp 279-287. doi:10.1117/12.542851
28. Hildenbrand J, Herbst J, Wollenstein J, Lambrecht A (2009) Explosive detection using infrared laser spectroscopy. In: Razeghi M, Sudharsanan R, Brown GJ (eds) *Quantum Sensing and Nanophotonic Devices Vi*, vol 7222. *Proceedings of SPIE*. Spie-Int Soc Optical Engineering, Bellingham, p 72220B. doi:10.1117/12.808976

29. Guo C, Persons J, Woodford JN, Harbison GS (2015) Gas-Phase Infrared and NMR Investigation of the Conformers of Diacetone Diperoxide (DADP). *J Phys Chem A* 119 (40):10221-10228. doi:10.1021/acs.jpca.5b07074
30. Kolla P (1997) The application of analytical methods to the detection of hidden explosives and explosive devices. *Angew Chem Int Ed* 36 (8):800-811. doi:10.1002/anie.199708001
31. Rücker C, Kümmerer K (2015) Environmental Chemistry of Organosiloxanes. *Chem Rev* 115 (1):466-524. doi:10.1021/cr500319v
32. Almond MJ, Becerra R, Bowes SJ, Cannady JP, Ogden JS, Walsh R (2008) A mechanistic study of cyclic siloxane pyrolyses at low pressures. *Phys Chem Chem Phys* 10 (45):6856-6861. doi:10.1039/b812535j
33. Davidson IMT, Thompson JF (1971) Dimethylsilanone from the pyrolysis of octamethylcyclotetrasiloxane. *Journal of the Chemical Society D: Chemical Communications* (6):251-252. doi:10.1039/c29710000251
34. Kulyk K, Zettergren H, Gatchell M, Alexander JD, Borysenko M, Palianytsia B, Larsson M, Kulik T (2016) Dimethylsilanone Generation from Pyrolysis of Polysiloxanes Filled with Nanosized Silica and Ceria/Silica. *ChemPlusChem* 81 (9):1003-1013. doi:10.1002/cplu.201600229
35. Atkinson R, Baulch DL, Cox RA, Crowley JN, Hampson RF, Hynes RG, Jenkin ME, Rossi MJ, Troe J (2004) Evaluated kinetic and photochemical data for atmospheric chemistry: Volume I - gas phase reactions of O_x, HO_x, NO_x and SO_x species. *Atmos Chem Phys* 4:1461-1738. doi:10.5194/acp-4-1461-2004