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# Factors Influencing Destruction of Triacetone Triperoxide (TATP)

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**Abstract**: Acid catalyzes the formation of triacetone triperoxide (TATP) from acetone and hydrogen peroxide, but acid also destroys TATP, and, under certain conditions, converts TATP to diacetone diperoxide (DADP). Addition of strong acids to TATP can cause an explosive reaction, while reaction with dilute acid reduces the decomposition rate so drastically that gentle destruction of TATP is impractical. However, combined use of dilute acid with slightly solvated TATP made gentle destruction of TATP feasible. Variables including acid type, concentration, solvent and ratios thereof have been explored, along with kinetics, in an attempt to provide a field-safe technique for gently destroying this homemade primary explosive. The preferred method is moistening TATP with an alcoholic solution (aqueous methanol, ethanol, or *iso*-propanol) followed by addition of 36 wt-% hydrochloric acid. Preliminary experiments have shown the technique to be safe and effective for destruction of hexamethylene triperoxide diamine (HMTD), as well.

## 1 Introduction

The hazardous nature of peroxides in general is well established. Those with multiple peroxide functionalities, such as triacetone triperoxide (TATP), diacetone diperoxide (DADP), or hexamethylene triperoxide diamine (HMTD), can be explosive. (Figure 1)

They are not used by legitimate military groups because they are highly sensitive to shock, friction, and heat. They are attractive to terrorist groups because synthesis is straightforward, requiring a few easily obtained ingredients. Peroxide explosives were used as initiators by would-be-bombers Ahmed Ressam (Dec. 1999), Richard Reid (Dec. 2001), and Umar Abdulmutallab (Dec. 2009). They were proven effective as main charges in Palestinian bombs and the July 2005 London bombings. The discovery of methods for the gentle chemical destruction of peroxide explosives, at room temperature, is the purpose of this study.

The oldest, most popular and safest approach to disposal of illegal explosives is blow-in-place. Direct handling and transporting of potentially sensitive materials by law enforcement and other qualified personnel is avoided. Since peroxide explosives are frequently found in high-population density areas, blow-in-place protocols are not always practical. There are documented examples, where law enforcement has taken extreme measures to destroy illicit explosives involving complete destruction of the premises. For example, in November 2010 a rented house in Escondido, CA was destroyed because, to quote law enforcement officers, the house contained "the largest amount of certain homemade explosives ever found in a single U.S. location. Nearly every room was packed with piles of explosive material…six mason jars with highly unstable hexamethylene triperoxide diamine, or HMTD…" Controlled burn of the house was deemed the only safe way to handle the disposal [1].

There are few publications that have addressed safe, effective, field-usable methods for destroying TATP; two have suggested copper and tin salts to effect destruction at elevated temperature [2,3]; one used mineral acids and elevated temperature [4]. These articles offered guidance in the search for a room-temperature answer for gentle chemical destruction of peroxides. Ideal protocols would involve a homogeneous liquid chemical solution to spray over
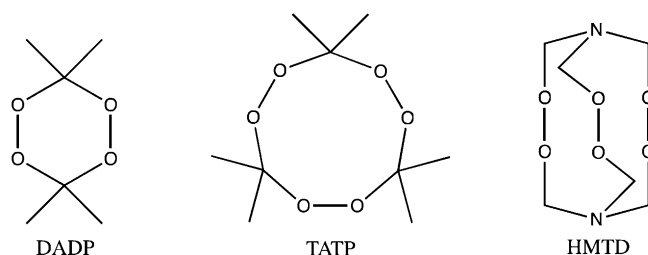


**Figure 1.** Chemical structures of TATP, DADP, and HMTD.

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solid peroxide stashes or a method involving immersion of peroxide saturated materials into a solution that would quiescently destroy the explosive in hours without further handling. Our first approach was to seek a general solution applicable to peroxide explosives with no prior characterization. Concentrated sulfuric acid was found to effectively destroy mg amounts of TATP; however, when scaled-up to even 1 g, the excessive heat release caused violent rapid release of energy, perhaps detonation [5].

This study follows extensive investigations of the formation of TATP, which is formed by reaction of acetone and hydrogen peroxide [6–8]. Under suitable conditions the two reagents can slowly form TATP at room temperature. However; the usual methods for synthesis of TATP involve controlled addition of acid. Excess acid and/or elevated temperature can favor the formation of DADP. If the heat of the reaction is substantial, it can initiate the peroxide mixture, causing detonation. Herein, we explore the region where acid can be used to affect quiescent decomposition of TATP. This work mainly focused on the destruction of 0.5 g or 3 g quantities of solid TATP, but it was helpful to obtain kinetics for the destruction of TATP in solution. Field tests were performed on 50, 100, and 460 g quantities of TATP.

## 2 Experimental Section

### 2.1 Synthesis of TATP and DADP

TATP and DADP were synthesized in our laboratory as previously reported [7–9]. TATP crude yields were typically 68%; recrystallization from hot methanol yielded a white, finely divided crystalline product, melting point 94–95 °C. The yield for DADP was 76% with a melting point of 131–132 °C after recrystallization from ethyl acetate.

### 2.2 Destruction of TATP

For the TATP destruction experiments, the recrystallized TATP (500 mg, 2.25 mmol) was placed in clear 40 mL glass vials and moistened with 0.5, 1, 2, or 4 mL ethanol, 2-propanol, acetone, ethyl acetate, diesel, iso-octane, or toluene. This was followed by addition of 0.5, 1, 2, 3, 4, 5, 9 mL of acids in varying concentrations. More than 600 individual experiments were performed. All mixtures were allowed to react at room temperature uncovered for 2–24 h before extraction with 10 mL dichloromethane (TATP solubility at room temperature $>1$ g/4 mL) and rinsing with distilled water (3 mL) followed by $Na_2CO_3$ (3 mL, 1%). The organic layer was dried with anhydrous magnesium sulfate and analyzed by gas chromatography with mass selective detector (GC/MS). Each analytical run began with a series of five or more authentic TATP samples ranging in concentration from 10–10,000 µg mL$^{-1}$. These samples were used to monitor instrument responses and plot calibration curves.

An Agilent 6890 GC with Agilent 5973i MSD detector was used (i.e electron impact). The inlet was operated with a 5:1 split at 150 °C. The column was an HP-5MS (30 m × 0.25 mm × 250 µm), operated in constant flow mode with a flow rate of 1.5 mL min$^{-1}$ and average velocity of 45 cm s$^{-1}$. The transfer line for GC to MS was held at 250 °C. The oven was programmed 50 °C for 2 min before ramping to 200 °C at 10 K min$^{-1}$. The MS had a solvent delay of 2 min and scanned from 14–500 *m/z*.

### 2.3 Kinetics for Destruction of TATP

Solutions of TATP (5 mL) were measured into 40 mL screw-top vials. Two vials were prepared; one with an acidic alcohol solution (5 mL) and the other with a TATP solution (5 mL). These solutions were equilibrated at specified temperatures in a water bath or GC oven. After equilibration, the 5 mL acid solution was poured into the 5 mL TATP solution, and the mixture was held at constant temperature for the duration of the experiment. At recorded time intervals, an aliquot of the reaction mixture was removed by syringe, placed in a separate 15 mL vial containing dichloromethane (DCM), rinsed with 2 to 3 mL of 3% NaHCO₃, followed by a rinse with distilled water, removing the aqueous layer each time. The organic layer was dried with a small amount of MgSO₄ (anhydrous) and transferred to a GC vial for quantification of remaining TATP. A parallel experiment with 5 mL of solvent (i.e. no acid) was used as a control.

For destruction of solid TATP with aqueous acid TATP (5 mg) was placed into a 16 mL screw cap vial and acid (1 mL) was added. At recorded intervals the reaction was quenched by addition of about 3 mL 3 wt-% sodium hydrogen carbonate followed by DCM (5 mL). The aqueous layer was discarded; a second rinse with sodium hydrogen carbonate was performed; and a third with distilled water. The organic layer was dried with anhydrous magnesium sulfate and analyzed by GC/MS.

To quantify TATP, an Agilent 6890 gas chromatograph with 5973i mass selective detector (GC/MS) was used. The inlet temperature was 110 °C and total flow was 24.1 mL min$^{-1}$ (helium carrier gas). The inlet was operated in splitless mode, with a purge flow of 20 mL min$^{-1}$ at 0.5 min. The column was a Varian VF-200MS (15 m × 0.25 mm × 250 µm), operated in constant flow mode with a flow rate of 1.5 mL min$^{-1}$. The oven program was initial temperature of 40 °C for 2 min followed by a 10 K min$^{-1}$ ramp to 70 °C, a 20 K min$^{-1}$ ramp to 220 °C and a post-run at 310 °C for 3 min. The transfer line temperature was 250 °C and the mass selective detector source and quadrupole temperatures were 230 °C and 150 °C, respectively. Electron impact ionization at 70 eV was used.

### 2.4 Large-Scale Decomposition

For all large-scale experiments addition of reagents was done remotely. A pumping apparatus was erected and an

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electronic means of actuating the pumps by remote control was assembled. TATP (460 g) was placed in a 4 L beaker with thermocouples and tubes from the output of the pumps already in place. A secondary means of adding acid was included in case of pump failure. This was accomplished by securing a Nalgene bottle with a spigot above the beaker containing the TATP. Tygon tubing attached to the spigot was placed in the beaker. The valve could be operated remotely by mechanical means ensuring that if some acid were added and the pump failed that more acid could be added without approaching the acidified TATP. Two thermocouples were used in this experiment. One was attached to the outside of the beaker and one submerged in the TATP. Alcohol solution (950 mL 50 wt-% 2-propanol/water) was pumped onto the TATP first at approximately 100 mL min$^{-1}$ using an aquarium pump. The TATP did not appear wet. The acid was then metered (120 mL min$^{-1}$) in the mixture using a peristaltic pump with acid resistant tubing; when the temperature rose to 70 °C the pump was stopped. A total of 425 mL of acid was added. Once the experiment was completed the products of the reaction were neutralized with sodium hydrogen carbonate and put into a 4 L glass waste container. A sample of the waste was extracted in DCM followed by GC/MS analysis.

## 2.5 Heat Release

Heat released during the reaction of acid with dissolved TATP was measured using a Thermal Hazards Technologies micro-calorimeter. To calibrate the instrument two amber GC vials containing 1 mL reagent alcohol were placed in the sample and reference positions of the instrument. In calibration mode, the number of pulses was set to 3; the pulse size to 300 mJ; the pulse interval to 300 s; and the lead time to 30 s; samples were stirred at 200 rpm. To determine the heat of mixing between sulfuric acid and reagent alcohol, the instrument was set to collection mode with an experimental duration of 1000 seconds. A modified acid injection method was designed to accommodate the corrosive nature of strong acids. A glass capillary syringe needle was attached to a 1 mL plastic syringe. The syringe was primed to remove excess air and reduce dead volume, and the desired mass of acid was pulled into the syringe.

Once a stable baseline was achieved, data collection began followed by manual injection of acid into alcohol. To determine heat released during the reaction between acid and TATP, the steps described above were followed using 1 mL of a 40 mg mL$^{-1}$ TATP/alcohol solution in the sample position and an experimental duration of 50,000 s.

## 2.6 Decomposition Product Identification

The type and concentration of acid used to destroy TATP determined reaction progress and products formed. Experiments, in duplicate, were conducted to examine the effect of acid type. TATP (500 mg) and water/alcohol (1 mL of 50 %) (either ethanol or 2-propanol) were combined. To this mixture was added 2 mL of one of the following: sulfuric acid (65 %), hydrochloric acid (36 %), nitric acid (70 %), phosphoric acid (85 %), methanesulfonic acid (99 %), boron trifluoride (48 % in diethyl ether), trifluoroacetic acid (99 %), or perchloric acid (99 %). WARNING: The addition of nitric acid resulted in violent fuming. Mixtures reacted for 3 h before extraction as described above. Products were identified by comparison of mass spectra to authentic samples of TATP, DADP, and various chlorinated acetones or by spectral matching to the NIST database. Relative amounts of each material in solution are expressed as percentage of the total chromatograph signal.

## 3 Results and Discussion

### 3.1 Relative Rates of TATP Decomposition with Acid

It was proposed that the application of mineral acid, an inexpensive and widely available liquid, applied as a spray or mist, could be a field approach to destruction of TATP. Addition of concentrated sulfuric acid (3 mL of 80 % or 90 %) to solid TATP (3 g) resulted in detonation. In an attempt to slow the reaction, solvents were added to the TATP (3 mL of diesel fuel, various alcohols). Addition of 98 % sulfuric to the TATP moistened with a solvent resulted in violent decomposition, but not detonation. To avoid violent reactions, experiments were designed to screen different solvent and acid combinations. TATP destruction did not occur with bases, but many acids, even BF$_3$, destroyed TATP to some

**Table 1.** Percent TATP remaining (0.5 g initial mass) after wetting with solvent and then adding acid.

| Ratio solvent:acid | Solvent | % Remaining | Acid (p$K_a$) | Ratio solvent:acid | Solvent | % Remaining |
|---|---|---|---|---|---|---|
| 1:2 | EtOH/*i*PrOH (3 h) | 0 | Methanesulfonic (−13) | 1:0.5 | Toluene (24 h) | 43 |
| 1:2 | | 0 | HClO$_4$ (−8) | 1:0.5 | | violent |
| 1:2 | | 0/9 | 36 % HCl (−6.3) | 0.5:2 | | 36 |
| 1:2 | | 30/37 | 65 % H$_2$SO$_4$ (−3) | 0.5:1 | | 73 |
| 1:2 | | 0 | 70 % HNO$_3$ (−1.6) | 1:0.5 | | 0 |
| 1:2 | | 0/1 | Trifluoroacetic (0.23) | – | | – |
| 1:2 | | 0 | BF$_3$ | – | | – |
| 1:2 | | 75/83 | H$_3$PO$_4$ (2.2) | – | | – |
| 2:2, 2:3 | | 100 | Acetic (4.8) | – | | – |

**Table 2.** First-order decomposition rate constant of solid TATP (5 mg) at 22 °C with aqueous acid (1 mL).

| $H_2SO_4$ | wt% | k(sec$^{-1}$) | HCl | wt% | k(sec$^{-1}$) | $HNO_3$ | wt% | k(sec$^{-1}$) | $HClO_4$ | wt% | k(sec$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 16M | 89 | 7.1E-03 | - | - | - | - | - | - | - | - | - |
| 14M | 82 | 1.9E-03 | - | - | - | 13M | 60 | 1.8E-02 | - | - | - |
| 12M | 74 | 8.8E-04 | 12M | 36 | 1.4E-03 | - | - | - | - | - | - |
| 10M | 64 | 1.9E-04 | 10M | 32 | 2.6E-04 | 10M | 49 | 2.4E-03 | 9.3M | 61 | 7.9E-03 |
| 8.1M | 54 | 9.8E-05 | 8.8M | 28 | 1.8E-04 | 8.1M | 41 | 1.5E-04 | 8.4M | 58 | 1.7E-03 |
| 4.7M | 34 | 2.7E-05 | 5.4M | 18 | 1.3E-05 | - | - | - | - | - | - |

with solvent wetted TATP (Table 1) and neat, solid TATP (Table 2). The results in Table 1 are expressed as percent TATP remaining after a specified time interval. The solid TATP was first moistened with the solvent followed by addition of the acid. Note that in Table 1 decomposition of TATP is more complete in the same time interval, when using 36 wt-% HCl than when using 65 wt-% $H_2SO_4$, though the molar concentrations of these acids were roughly the same. This may be explained by the higher $pK_a$ value for HCl. In Table 2, aqueous acid was added directly to the TATP and the amount remaining vs. time was determined

extent. Not every acid was compatible with the organic solvent used. The addition of methylsulfonic acid (MSA), $BF_3$, or $HClO_4$ resulted in instant and violent boiling of the solutions, and the solutions quickly turned from white to brownish-black. A survey of acids was accomplished, both

**Table 3.** First-order decomposition rate constant for dissolved TATP with aqueous acid rate (mg s$^{-1}$) = $k$*solubility.

| Temperature 22 °C | | | | | | Temperature 45 °C | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| TATP [mg] | Acid (3.7 mmol) | Solvent (10 mL) | $k$ [s$^{-1}$] | Solubility [mg mL$^{-1}$] | Rate [mmol s$^{-1}$] | TATP [mg] | Acid (3.7 mmol) | Solvent (10 mL) | $k$ [s$^{-1}$] | Solubility [mg mL$^{-1}$] | Rate [mmol s$^{-1}$] |
| 100 | 97%* | Acetonitrile (ACN) | 1.4E-01 | 125 | 1.8E+01 | 100 | 97% | Ethanol (EtOH) | 6.4E-04 | 143 | 9.2E-02 |
| 100 | 97% | 90:10 ACN:H$_2$O | 1.8E-04 | 105 | 1.9E-02 | 100 | 97% | 90:10 EtOH:H$_2$O | 8.6E-05 | 123 | 1.1E-02 |
| 100 | 97% | 80:20 ACN:H$_2$O | 4.7E-05 | 49 | 2.3E-03 | 100 | 97% | 80:20 EtOH:H$_2$O | 1.5E-04 | 76.9 | 1.1E-02 |
| 100 | 97% | 70:30 ACN:H$_2$O | 1.8E-05 | 44 | 8.0E-04 | 100 | 97% | 70:30 EtOH:H$_2$O | 2.0E-04 | 51.4 | 1.0E-02 |
| 7.5 | 97% | 50:50 ACN:H$_2$O | 7.4E-05 | 11.1 | 8.2E-04 | 7.5 | 97% | 50:50 EtOH:H$_2$O | 3.0E-04 | 13.2 | 4.0E-03 |
| 7.5 | 36% | Acetonitrile | 2.0E-04 | 125 | 2.5E-02 | 100 | 97% | n-Propanol (nPrOH) | 3.0E-04 | 188 | 5.6E-02 |
| 7.5 | 36% | 50:50 ACN:H$_2$O | 9.9E-05 | 11.1 | 1.1E-03 | 100 | 97% | 90:10 n-PrOH:H$_2$O | 1.7E-05 | 141 | 2.4E-03 |
| 7.5 | 18% | Acetonitrile | 4.8E-04 | 125 | 6.0E-02 | 100 | 97% | Isopropanol (iPrOH) | 8.9E-05 | 217 | 1.9E-02 |
| 7.5 | 18% | 50:50 ACN:H$_2$O | 1.1E-04 | 11.1 | 1.2E-03 | 100 | 97% | 90:10 iPrOH:H$_2$O | 2.9E-05 | 155 | 4.5E-03 |
| 7.5 | 97% | Methanol (MeOH) | 5.2E-04 | 35.7 | 1.9E-02 | 100 | 97% | 80:20 iPrOH:H$_2$O | 2.3E-05 | 109 | 2.5E-03 |
| 7.5 | 97% | 50:50 MeOH:H$_2$O | 5.6E-05 | 1.45 | 8.0E-05 | 100 | 97% | 70:30 iPrOH:H$_2$O | 7.0E-05 | 69 | 4.8E-03 |
| 7.5 | 65% | Methanol | 4.7E-05 | 35.7 | 1.7E-03 | 7.5 | 97% | 50:50 iPrOH:H$_2$O | 2.5E-04 | 24.0 | 6.0E-03 |
| 7.5 | 65% | 50:50 MeOH:H$_2$O | 5.3E-05 | 1.45 | 7.7E-05 | 100 | 97% | Methanol | 2.0E-03 | 80 | 1.6E-01 |
| 7.5 | 35% | Methanol | 6.7E-05 | 35.7 | 2.4E-03 | 100 | 97% | 90:10 MeOH:H$_2$O | 2.1E-04 | 57.6 | 1.2E-02 |
| 7.5 | 35% | 50:50 MeOH:H$_2$O | 3.7E-05 | 1.45 | 5.3E-05 | 100 | 97% | 80:20 MeOH:H$_2$O | 3.0E-04 | 33.3 | 9.9E-03 |
| 7.5 | 36% | Methanol | 1.7E-04 | 35.7 | 6.0E-03 | 7.5 | 97% | 60:40 MeOH:H$_2$O | 8.8E-04 | 12.7 | 1.1E-02 |
| 7.5 | 36% | 50:50 MeOH:H$_2$O | 5.8E-05 | 1.45 | 8.4E-05 | 7.5 | 97% | 50:50 MeOH:H$_2$O | 9.7E-04 | 5.99 | 5.8E-03 |
| 7.5 | 18% | Methanol | 2.4E-04 | 35.7 | 8.6E-03 | 100 | 97% | t-Butanol (tBuOH) | Acid reacts preferentially with t-butanol | | |
| 7.5 | 18% | 50:50 MeOH:H$_2$O | 6.3E-05 | 1.45 | 9.1E-05 | 100 | 97% | 90:10 tBuOH:H$_2$O | | | |

**Table 4.** Milliliters solvent required to dissolve 100 mg TATP at room temperature.

|         | Acetone | Diesel | EtAc | i-Octane | Toluene | EtOH (100%) | EtOH (50%) | i-PrOH | i-PrOH (50%) | Water       |
|---------|---------|--------|------|----------|---------|-------------|------------|--------|--------------|-------------|
| Average | 1.0     | 3.0    | 1.2  | 2.1      | 0.8     | 3.0         | 62.2       | 3.8    | 40.2         | 14–16 ppm [6] |
| sd      | 0.5     | 1.0    | 0.2  | 0.5      | 0.2     | 0.8         | 7.4        | 1.2    | 3.5          |             |
| rsd /%  | 44      | 33     | 14   | 23       | 20      | 26          | 12         | 33     | 9            |             |

by quenching the reaction at specified time intervals. The first-order rate constants from this data also indicated that HCl decomposed TATP more quickly than sulfuric acid at highest concentration (i.e. 12 M). Table 3 shows first-order rate constants for the decomposition of TATP dissolved in the solvent system indicated. Decomposition is much faster in solution than in solid so that lower concentrations of acid can decompose TATP relatively quickly (Table 3); again the effectiveness of HCl is noticeable.

We previously reported that in synthesis water content affected the ratio of TATP/DADP; high water favoring TATP [8]. Water also affects the rate of decomposition as well as the decomposition products. Water, entering the reaction with the acid, and in some cases with the solvent, slows the rate of TATP decomposition (Table 3). Solubility is part of the effect. TATP is soluble in the alcohols and acetonitrile but practically insoluble in water, yet the acid can more freely dissociate in water. The highest observed decomposition rate constant was for TATP in acetonitrile with no water, and in that solvent TATP converted to DADP. This conversion was not observed in alcohol solutions of TATP, nor when 10% or more water was added to the acetonitrile solutions of TATP. Furthermore, use of an alcohol solvent or addition of water slowed the decomposition of TATP. Similar observations were noted when using alcohols as co-solvents in TATP formation reactions [8]. Rates of TATP decomposition were dependent on the type of alcohol. TATP decomposition was faster in primary alcohols (MeOH > EtOH > n-PrOH) than in 2-propanol, a secondary alcohol. Tertiary butyl alcohol reacts preferentially with acid rather than TATP forming 2,2,4,6,6-pentamethyl-3-heptene, a condensation product of tert-butanol catalyzed by sulfuric acid.

The rate constants for TATP decomposition in alcohol are at a maximum in pure alcohol but pass through a minimum as the amount of water increases. The formation of alcohol/water complexes were shown to have a significant impact upon protonation of organic acids and bases and is attributed to preferential solubility by water or the organic solvent depending on the nature of the substance [10–12]. Table 4 shows the solubility of TATP in the various solvents. If rates (mg s$^{-1}$) were calculated from the product of the rate constant and solubility (assuming solvent-wetted solid TATP maintains a film of saturated solution), the decreased solubility negates (i.e. Table 3, far right columns) the effect of increasing rate constants with increasing water content.

We found that TATP reacted violently with concentrated sulfuric acid, but decomposed extremely slow when the concentration was reduced to 65 wt-%. As an alternative to using concentrated acid to decompose TATP, partial dissolution of TATP was used. TATP is soluble in most organic solvents, but complete dissolution of large quantities found in the field would be impractical. Instead of attempting to dissolve TATP, just enough solvent to wet the TATP was applied. The dissolved TATP surface layer was available for faster decomposition than the solid TATP suggesting that more dilute aqueous acid could cause its decomposition without instant explosion. In addition, the solvent might serve as a heat sink. Proposing a coating effect from the organic solvent suggest that volume of the organic liquid as
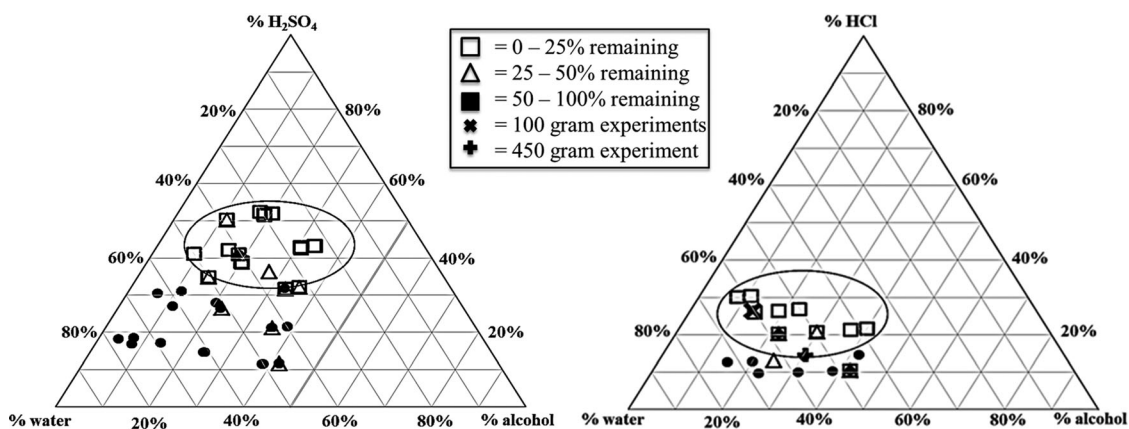


**Figure 2.** Ternary diagram of destruction of 500 mg TATP Wetted with alcohol (ethanol or *iso*-propanol), Water and acid [left H$_2$SO$_4$(17–24 h); right HCl (3–7 h) (□=0–25% remaining, △=25–50% remaining, ■=50–100% remaining)].

**Table 5.** Conversion of TATP (2.25 mmol, 500 mg) to DADP alcohol in 3 h at 25 °C.

| acid | pKa | conc M | mmol | TATP | DADP | R-OOH's peroxy | Other Products |
|------|-----|--------|------|------|------|----------------|----------------|
| conc HCl (36%) | -6 | 12 | 24 | 0-20% | 2-5% | 0.7-2% | chlorinated acetones (73-97%) |
| conc HNO₃ (70%) | -1.64 | 16 | 32 | 0.1-0.2% | 81-92% | 0.1-0.5% | R-ONO, R-ONO₂ (8-17%) |
| conc TFA (98%) | 0.23 | 13 | 26 | 0.1-1% | 99-100% | 0.1-0.2% | none identified |
| H₂SO₄ (65%) | -3.6 | 10 | 24 | 47-48% | 48-50% | 2-5% | none identified |
| H₃PO₄ | 2.15 | 15 | 29 | 83-87% | 13-17% | 0.2-2% | none identified |

well as surface area of the TATP must be considered in any attempt to scale-up these reactions.

Figure 2 summarizes attempts to decompose 500 mg TATP using the method outlined in section 2.2. The ternary diagrams express the percentage by weight of water, alcohol and acid present in the experiments. Note that the percentage does not represent the concentration of solvent nor acid added but is the percentage after all components in the composition are accounted for totaling 100%. Compositions, which successfully destroyed TATP are outlined by an oval in the ternary diagrams. Successful destruction was defined as 0–25% of TATP remaining following reaction (3–7 h for experiments with hydrochloric acid and 17 to 24 h for experiments with sulfuric acid). The trends revealed in these diagrams of wetted, solid TATP, is in agreement with observations made on TATP in solution (Table 3). HCl destroyed TATP significantly faster and at lower acid concentrations than did sulfuric acid. Increased amounts of water, and reduced amounts of acid slowed decomposition to an extent that decomposition was incomplete (i.e. more than 50% TATP remaining). When acetone, ethylene glycol, and ethyl acetate were used as the wetting agents, the acid decomposition of TATP proceeded but somewhat slower than it did with alcohol wetting agents. Interestingly, with 50 wt-% ethylene glycol/water wetting agent, 65% sulfuric acid did not destroy TATP in 24 h, while 36% HCl did. Although TATP was soluble in *iso*-octane, toluene, and diesel (Table 4), using these as wetting agents rendered acid treatment rather ineffective (65% sulfuric destroying 20–25% and 36% HCl destroying 40% of the TATP). This is likely due to the immiscibility of the aqueous acids with these solvents.

## 3.2 Decomposition Products

Minor amounts of peroxo-acetone species have been previously identified in the acid destruction of TATP [8]. Depend-

ing on the reaction conditions DADP could be a significant decomposition product. Table 3 reports that the highest decomposition rate constant for TATP was observed in dry acetonitrile and that in that solvent TATP converted to DADP. This conversion was not observed in alcohol solutions of TATP, nor when 10% or more water was added to the acetonitrile solutions of TATP. An important difference was also observed when TATP was moistened with alcohol rather than completely dissolved; some DADP formed with most acids used, but acid was applied in molar excess, which favors conversion of TATP to DADP [8,13,14]. When sulfuric and hydrochloric acids were at roughly the same molarity (65% and 36%, respectively); the decomposition of TATP occurred at about the same rate (Table 2). However, the sulfuric acid produced significant amounts of DADP from 500 mg TATP, whereas HCl did not (Table 5). This production of DADP was also noted when 35% (4.7 M) sulfuric acid was used to treat TATP at 50 °C, conditions meant to simulate the use of battery acid and the normal self-heating effect of the decomposition. To minimize DADP formation HCl was chosen for the field destruction of TATP. Decomposition of TATP using HCl produced a variety of chlorinated acetones as well as chloroacetic acid ester (Figure 2). The decomposition affected by 70% nitric acid formed primarily DADP as well as nitro- and nitroso-organics [15].

## 3.3 HMTD

Because it is likely that the user of the acid destruction technique might not have distinguished between the peroxides TATP and HMTD, the same technique was used on HMTD and found to be a safe and effective method of destruction [HMTD (1 g) was wetted with 2 mL 50 wt-% ethanol/water solution followed by remote injection of 2 mL 36 wt-% hydrochloric acid, and gentle decomposition occurred in 4 h]. Table 6 illustrates how the use of acids and organic solvents affect the rate of decomposition of HMTD compared to TATP.

Concentrated sulfuric acid causes both TATP and HMTD to detonate. Adding concentrated sulfuric acid to TATP wetted with alcohol solutions resulted in a violent reaction but this was not observed with HMTD. This is likely due to the insolubility of HMTD in most solvents, such as alcohols. The data suggests that hydrochloric acid is the acid of choice when attempting to decompose both peroxides. TATP and HMTD are effectively decomposed in similar amounts of time when

**Table 6.** Comparison of HMTD and TATP decomposition under similar conditions.

| | HMTD | | | | TATP | | |
|---|------|---|---|---|------|---|---|
| | HCl 36% | H2SO4 98% | H2SO4 65% | | HCl 36% | H2SO4 98% | H2SO4 65% |
| solid | no solid after 1 hour | Detonation | no solid after 1 hour | solid | no solid after 3 hours | Detonation | no solid after 8 hours |
| solid wetted with EtOH | no solid after 5 hours | no solid after 2 hours | no solid after 6 hours | solid wetted with EtOH | no solid after 4.5 hours | violent decomp | no solid after 13 hours |
| solid wetted with 50wt% EtOH/H₂O | no solid after 4 hours | no solid after 2 hours | no solid after 4 hours | solid wetted with 50wt% EtOH/H₂O | no solid after 4.5 hours | violent decomp | no solid after 12 hours |

using hydrochloric acid. Slightly dilute sulfuric acid was also effective at decomposing HMTD but not as effective at decomposing TATP. The data in Table 6 suggests that 50 wt-% ethanol/water solution with 36 wt-% hydrochloric acid was most effective.

In an attempt to understand violent reactions, even detonations, that concentrated sulfuric acid causes with TATP and HMTD, high-speed video was used to examine the reaction of a single drop of acid on each peroxide. A 5 cm line of TATP (200 mg) was placed onto a microscope slide. A drop of concentrated sulfuric acid was pipetted onto one end. Once initiation was observed, the TATP disappeared in linear progression in 17 ms. No immediate flame was produced. A 12 ms delay was observed before a blue flame formed in the air above the microscope slide. The flame transitioned from blue to yellow as a fireball grew. A similar experiment was conducted with HMTD. The first observation was a burst of smoke or fine particulate. In the same fashion as TATP the pile disappeared in linear progression, but before the entire pile of HMTD was gone a yellow flame was already forming above the HMTD. From initiation to the moment that the pile had disappeared 15 ms had elapsed. To determine the reactive species, the peroxides were treated with 80% sulfuric acid in a sealed GC vial. Subsequent GC/MS analysis of the TATP decomposition

gases showed acetone, TATP and DADP in the headspace. We believe minute hot particles are responsible for igniting this gaseous mixture. Similar analysis of the HMTD headspace showed one broad hump. When HMTD was moistened with ethanol and treated with HCl, carbon dioxide, esters of formic acid, and, possibly, tetramethyl hydrazine were found in the headspace vapors.

### 3.4 Decomposition Mechanism

All the strong acids decomposed TATP, but rates (Table 1, Table 2) and final products (Table 5) differed. If a protic solvent, e.g. water or alcohol, is used the carbocation formed when the TATP ring opens is stabilized and the intermediate will react more slowly and decompose into smaller molecules. If no water was present, the carbocation is not stabilized and the intermediate quickly cyclizes to DADP. In both cases acetone was formed. Figure 3 illustrates these alternate routes.

The chloroacetones and chlorinated esters observed during the decomposition of TATP in hydrochloric acid suggest an acid catalyzed haloform reaction (Figure 4). Multiple chloro substitutions are generally observed under basic conditions with the presence of hypochlorite [16] but the presence of organic peroxy groups can oxidize chloride to
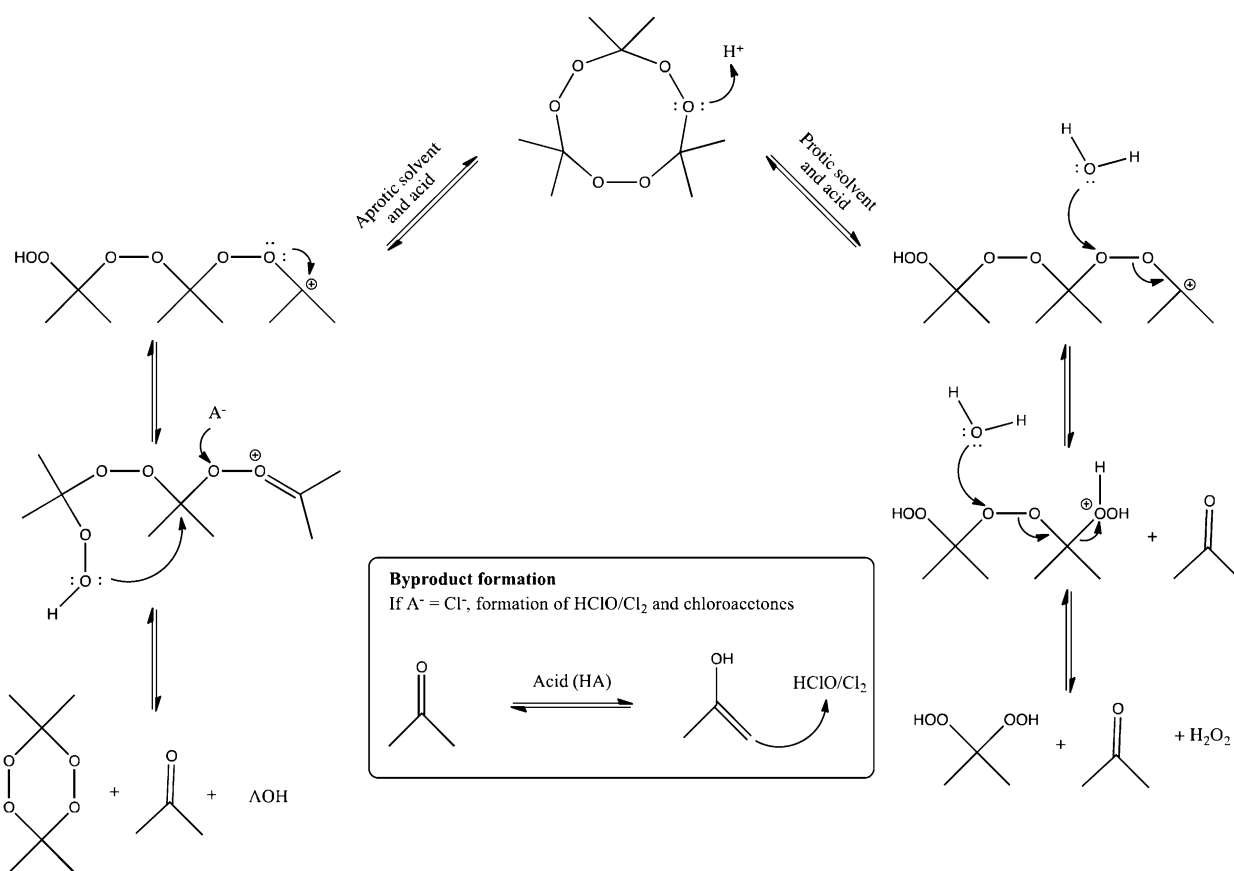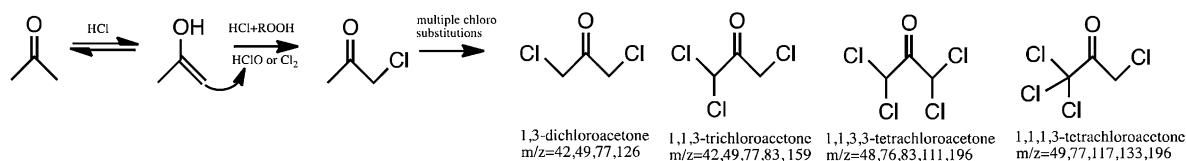


**Figure 3.** TATP decomposition by acid with and without water present.

Chloroacetone formation



| | | | |
|---|---|---|---|
| 1,3-dichloroacetone m/z=42,49,77,126 | 1,1,3-trichloroacetone m/z=42,49,77,83,159 | 1,1,3,3-tetrachloroacetone m/z=48,76,83,111,196 | 1,1,1,3-tetrachloroacetone m/z=49,77,117,133,196 |

Chloroacetic acid ester formation



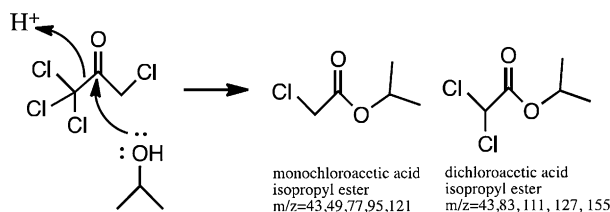| | |
|---|---|
| monochloroacetic acid isopropyl ester m/z=43,49,77,95,121 | dichloroacetic acid isopropyl ester m/z=43,83,111, 127, 155 |

**Figure 4.** Byproduct formation.

chlorine or hypochlorite facilitating this type of reaction under acidic conditions.

## 3.5 Calorimetry

During calorimetry experiments when 65 wt-% $H_2SO_4$ was added to 1 mL (40 mg mL$^{-1}$) alcohol solutions of TATP, no reaction was observed until the solution was raised to 50 °C. At 50 °C temperature the reaction started within minutes. The experiment was repeated using 80 wt-% sulfuric acid. Within minutes heat release was visible and after about 11 h it appeared to be complete. Duplicate experiments were run using sulfuric, hydrochloric and nitric acids taking care to deliver similar quantities of water while delivering the same number of moles of acid because previous work had shown that water affects the formation and destruction of TATP [8]. Under the same conditions hydrochloric acid resulted in a faster reaction rate but with less heat released overall than tests using nitric or sulfuric acid.
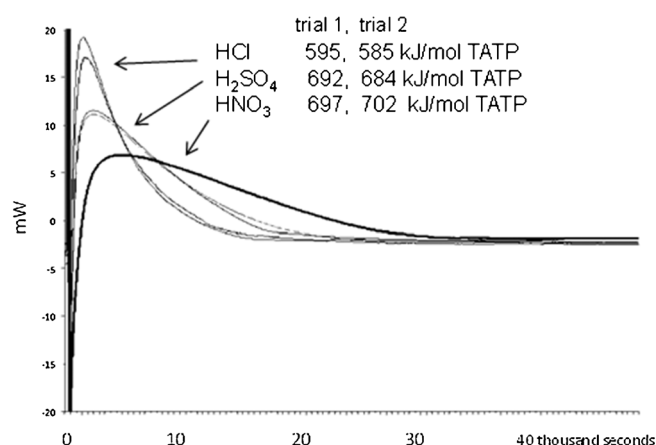


**Figure 5.** Calorimetry trace acid added to an ethanol (1 mL) solution of TATP (40 mg).

Figure 5 shows the calorimetry traces and the heat release observed for each of the duplicate experiments.

## 3.6 Scale up

When the 500 mg tests were scaled to TATP (3 g) wetted with alcohol (3 mL), the acid (3 mL) was added remotely. With concentrated HCl (36 %), the decomposition went quiescently; when it was 90 % sulfuric acid, the reaction was violent (see Figure 6). Outdoor field tests were conducted on 100 g and 460 g quantities of TATP. Quantities of acid and solvent are detailed in Table 7. Hydrochloric acid was chosen due to its ability to decompose TATP quickly without the formation of DADP and its reduced heat of reaction with TATP. Aqueous ethanol and 2-propanol (50/50 with water) were tested on the 100 g scale with similar results (Table 7). Aqueous 2-propanol was chosen for the 460 g experiment over the lower molecular weight alcohols due to its higher boiling point (82.5 °C); butanol was not considered due to its reactivity with acid. Data points for these experiments are also labeled on the ternary diagrams in Figure 1. For the 100 g experiments the solvent and acid were added rapidly via mechanical means.

Scaling up from 100 g to 460 g the alcohol and acid were pumped onto the TATP by a remote control pumping setup described in Section 2.4 and the mixing was monitored remotely by video and with thermocouples both inside and outside the mixing vessel. The Frank-Kamentskii model [17] (Equation (1)) was used to estimate temperature where runaway self-heating might occur. The temperature of thermal runaway was estimated to be between 113 and 116 °C, using input values for activation energy (E) and frequency factor (A) taken from the literature [18] (i.e. 151 kJ mol$^{-1}$ and 3.75 E13); estimating thermal conductivity ($\lambda$) as 0.0012 J s$^{-1}$ m$^{-1}$ deg$^{-1}$; density ($\rho$) as 1.2 g cm$^{-3}$; and using 7.8 cm radius; the shape factor $\delta$ for an infinite cylin-
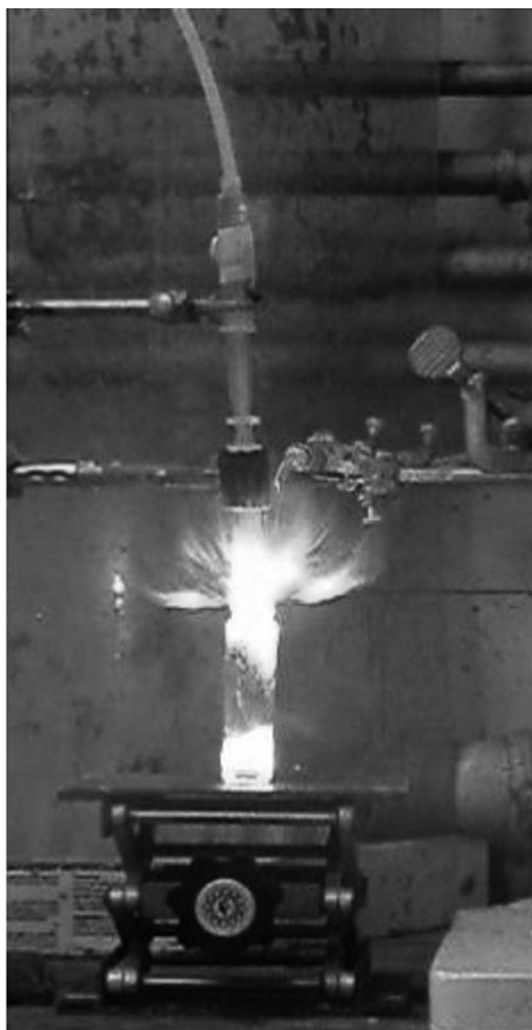
**Figure 6.** TATP (3 g) violently reacting with acid.

der (2.72) and heat release ($Q$) as either 2000 or 3000 J g$^{-1}$ (based on various differential scanning calorimetric runs).

$$E/Tc = R \ln \left[ (r2d\ \rho QAE)/(Tc^2\ \delta\ \lambda\ R) \right] \qquad (1)$$

Alcohol addition proceeded with no significant change in temperature. About 3 min after addition of hydrochloric acid had begun (ultimately 425 mL), the temperature rose rapidly to about 75 °C. Acid addition was terminated; temperature dropped to about 45 °C; and the mixture appeared to be swirling the solid TATP. Gradually, the temper-

ature rose again, and boiling and foaming became evident, while solid TATP disappeared. The mixture reached 75 °C again about 15 min after the commencement of acid addition. The solution was boiling vigorously, and all solid TATP had disappeared. Over the next 40 min boiling slowly subsided and temperature returned to ambient [the total elapsed time for the experiment was approximately 25 min from time of start of alcohol addition (10 min) until the TATP was no longer visible by visual inspection]. The acidic solution was neutralized, and products identified by GC/MS as reported above.

If the field decomposition had been a direct scale-up from the 0.5 g TATP destructions, 1.8 L of HCl would have been required and the complete reaction would have taken hours. The self-heating of the large-scale decomposition increased the decomposition rate to the point that significantly less acid and time were needed to complete the reaction. Thus, the effect of dilute acid was examined at slightly elevated temperature to simulate the bulk heating of a larger sample. TATP (500 mg) was treated with aqueous 2-propanol (1 mL, 50/50), heated to 50 °C, and sulfuric acid (2 mL, 35 %, 4.7 M) was added. As the reaction was monitored for 3 h, DADP was formed and decomposed, but the reaction at no time was vigorous. It appears likely that battery acid, which is 29 to 34 % sulfuric acid, could be used for an emergency field destruction of TATP.

## 4 Conclusions

TATP can be destroyed quiescently under certain conditions. The ternary diagrams (Figure 2) suggest that the optimum ratio of water, solvent, and acid may vary depending on the acid. TATP decomposes faster with hydrochloric acid than with sulfuric acid of about comparable molarity but sulfuric acid can lead to the formation of DADP on larger scales. The same decomposition mechanism is postulated (Figure 3), but different conjugate bases result in different decomposition products and different amounts of heat released.

Treating TATP with concentrated mineral acids may cause its detonation. Decreasing the concentration of the acid may results in decomposition that is far too slow. Initially, solvent was added to produce a thin layer of solvated TATP. This accelerated the decomposition of TATP sufficiently that its decomposition in dilute acid could be accomplished in a reasonable amount of time. Not surprising 10 M sulfuric

**Table 7.** TATP destruction field tests.

| Mass TATP [g] | Solvent | Solvent [mL] | Acid | Acid [mL] | Time to destruction |
|---|---|---|---|---|---|
| 100 | EtOH 50 % | 200 | HCl 36 % | 400 | 20 min |
| 100 | IPA 50 % | 200 | HCl 36 % | 400 | 20 min |
| 100 | IPA 50 % | 100 | HCl 36 % | 400 | 2 h 20 min |
| 460 | IPA 50 % | 900 | HCl 36 % | 425 | 25 min |

and 10 M hydrochloric decompose TATP at about the same rate (Table 2). The resulting products were different; and although HCl decomposed TATP slightly faster, it did so with slightly less heat output. In fact, there was so little difference in the rate and heat release of TATP decomposition by $H_2SO_4$ and by HCl, that it was initially puzzling that the concentrated sulfuric acid treatment was so much more violent than that of HCl. A possible key to controlling the acid destruction of TATP is mitigating the potential temperature rise due to exothermic decomposition by supplying a heat sink in the form of a solvent or wetting agent. Dropping concentrated sulfuric acid on TATP is violent because the exothermic decomposition results in a rapid rise in temperature, which is not mitigated by acid. This leads to detonation in the case of concentrated sulfuric acid, which has a specific heat of $1.5 \, J\,g^{-1}\,K^{-1}$, which is the lowest of the concentrated acids (32% HCl = $2.5 \, J\,g^{-1}\,K^{-1}$, 60% sulfuric = $2.2 \, J\,g^{-1}\,K^{-1}$, 95% nitric = $2.1 \, J\,g^{-1}\,K^{-1}$, 60% nitric = $2.7 \, J\,g^{-1}\,K^{-1}$). Wetting TATP with water ($4.184 \, J\,g^{-1}\,K^{-1}$) would provide a good heat sink, but TATP is so insoluble in water that the decomposition would proceed very slowly. Use of aqueous alcohols (50/50) as the wetting agent rather than water increases the solubility of TATP while ensuring acid dissociation and increased heat capacity of the system.

TATP and HMTD are effectively decomposed in similar amounts of time when using hydrochloric acid. We prefer concentrated hydrochloric acid for the gentle destruction of TATP because it reacts slightly faster than a comparable concentration of sulfuric acid; its heat release is lower; and it does not tend to create DADP. Hydrochloric acid and aqueous alcohol wetting agent have gently destroyed TATP on the 460 g scale.

This work serves as a guideline for decomposing TATP and HMTD in the lab or when blowing-in-place or transporting to a remote location is not an option. This study used TATP and HMTD made in our laboratory and carefully purified. Destruction of samples of unknown origin or contamination is significantly more hazardous than the studies reported herein. **There is significant uncertainty and danger associated with large-scale chemical destruction of these peroxides. In all cases addition of acids and solvents *must* be done remotely and preferably with temperature monitoring.**

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