Factors Influencing Triacetone Triperoxide (TATP) and Diacetone Diperoxide (DADP) Formation: Part I

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Abstract

Conditions which result in the formation of triacetone triperoxide (TATP) or diacetone diperoxide (DADP) from acetone and hydrogen peroxide (HP) have been studied for the purposes of inhibiting the reaction. Reaction of HP with acetone precipitates either DADP or TATP, but the overall yield and amount of each was found to depend on (1) reaction temperature; (2) the molar ratio of acid to HP/acetone; (3) initial concentrations of reactants, and (4) length of reaction. Controlling molar ratios and concentrations of starting materials was complicated because both sulfuric acid and hydrogen peroxide were aqueous solutions. Temperature exercised great control over the reaction outcome. Holding all molar concentrations constant and raising the temperature from 5 to 25°C showed an increase of DADP over TATP formation and a decrease in overall yield. At 25°C a good yield of TATP was obtained if the HP to acetone ratio was kept between 0.5-to-1 and 2-to-1. At constant temperature and HP-to-acetone held at one-to-one ratio, acid-to-HP molar ratios between 0.10:1 and 1.2:1 produced good yield of TATP. Plotting the molality of HP versus that of sulfuric acid revealed regions in which relatively pure DADP or pure TATP could be obtained. In addition to varying reaction conditions, adulterants placed into acetone were tested to inhibit the formation of TATP.

Because there is much speculation of the relative stability, sensitivity, including solvent wetting of crystals, and performance of DADP and TATP, standard tests (i.e. DSC, drop weight impact, and SSED) were performed.

1 Introduction

Triacetone triperoxide (3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexoxonane, TATP, CAS #17088-37-8), is a sensitive, moderately powerful energetic material first reported in 1895 [1]. The one-pot synthesis from readily available precursors can, if certain precautions are met, produce TATP in high yield. TATP, being highly volatile (odor similar to pepper) and sensitive to friction and shock, does not lend itself to military or commercial applications; however, it has been used successfully by foreign and domestic terrorists. Properties of the pure material are reported in Table 1 along with standard military explosives for comparison. Literature procedures abound for TATP synthesis, from peer-reviewed journals and the internet, but all are similar [1, 4-6, 9-22]. Furthermore, an internet search provides a plethora of videos and forums of individuals who candidly show and speak about making TATP. Beginning in Israel in the 1980's, terrorist attacks have used TATP, either as the main or initiating charge [23]. Some of those incidents are shown in Table 2. Recent papers have investigated TATP synthesis, including unintended synthesis when acetone and hydrogen peroxide are used in cleaning procedures [30]. The focus of this study was to observe how varying reaction conditions affected yield of the reaction products TATP and diacetone diperoxide (DADP) and the extent to which the reaction is reversible or preventable (Scheme 1).

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2 Experimental Section

2.1 Reagents and Chemicals

Acetone (HPLC-grade) and concentrated sulfuric acid (Certified ACS Plus) were obtained from Fisher Scientific. Hydrogen peroxide was obtained from Univar at 50% w/w in water and was diluted to 30% and 9wt% using distilled water. Higher concentrations of hydrogen peroxide were obtained by removal of water at elevated temperature. All concentrations of hydrogen peroxide were verified by refractometry to within +/- 1wt% [31]. Adulterants (102 compounds) were obtained from Fisher Scientific and Sigma-Aldrich with varying degrees of purity.

2.2 Preparation of Triacetone Triperoxide (TATP) with and without adulterants

Into a glass test tube (16mm x 150mm) containing a small stir bar, 1.53g +/- 0.01g (13.5 millimols, mmols) of 30wt% hydrogen peroxide was weighed. The test tube was capped with Parafilm and placed in a temperature-controlled water bath. Acetone, 0.78g +/- 0.01g (13.5mmols), neat or adulterated, was added to the hydrogen peroxide, and they were allowed to mix for a minimum of 15 minutes before sulfuric acid (40-96wt%, generally, 1.35 to 0.135 mmols) was added. If higher concentration of HP were used, i.e. $\geq$ 50wt%, optimum results (~100% yield) was achieved using a 1:1:1 mole ratio of sulfuric acid (65wt%): HP (50wt%) : acetone and holding the mixture at 5$^\text{o}$C for 24 hours.

The majority of the experiments were performed using a molar ratio of 0.01:1 or 0.10:1 of 46-50wt% sulfuric acid to hydrogen peroxide. The 1 mol% loading was achieved by using 1 drop, via pipet, of 40-50wt% sulfuric acid. The 10 mol % loading was achieved by using 0.276g of 48wt% sulfuric acid, delivered by pipette. The sulfuric acid concentration was verified by density. Acid addition was monitored for several reactions to determine temperature spike; a

maximum of 8°C rise was seen in samples that were run at 25°C. In one series of experiments, 90wt% sulfuric acid was added, drop wise, in varying amounts to make step-wise increases in catalyst loading.

The solution was allowed to stir, behind a blast shield, for a minimum of 24 hours before filtration. The theoretical yield was 1.00 gram (4.5mmols) TATP; at this scale, multiple batches were run simultaneously. Following reactions for the specified lengths of time, test tubes were removed and filtered under water aspiration using 4.25cm diameter Fisher P4 (4-8μm particle retention) filter paper. Each reaction was washed with 75 to 150mL distilled water at ambient temperature. Due to the high vapor pressure of TATP, the product was only allowed to dry only 15 minutes. If standing beads of water were removed by blotting, this length of time was sufficient to remove water without significant loss of TATP. Once mass of the solid product was obtained, each sample was placed into a glass vial with a plastic push-cap and placed into a -15°C freezer until analyses were performed. When analytically pure samples were required, the re-crystallization protocol cited below (Section 2.5) was employed. Melting point 94-96°C; ^{1}H NMR 1.46 ppm and ^{13}C NMR 21 and 107 ppm (CDCl$_3$); MS fragmentation pattern: m/z = 222 (Parent, very small), 117 [(CH$_3$)$_2$CO$_2$CCH$_3$O]$^{+}$, (medium), 101 [(CH$_3$)$_2$CO$_2$CH$_3$]$^{+}$ (medium), 91 [(CH$_3$)(CH$_2$)C(OH)(OOH)]$^{+}$ (very small), 89 [C$_3$H$_5$O$_3$]$^{+}$ (very small), 75 [C$_3$H$_7$O$_3$]$^{+}$ (large), 73 [C$_2$H$_5$O$_2$]$^{+}$ (small), 59 [(CH$_3$)$_2$COH]$^{+}$ (large), 58 [(CH$_3$)$_2$CO]$^{+}$ (large), 43 [CH$_3$CO]$^{+}$ (dominant), 29 [CH$_3$CH$_2$]$^{+}$ (medium), 15 [CH$_3$]$^{+}$ (medium).

2.3 Sample Preparation of Diacetone Diperoxide (DADP)

Similar to the TATP synthesis reactions, 13.5mmols of hydrogen peroxide was combined with 13.5mmols of acetone in a test tube in a temperature controlled bath. The hydrogen peroxide concentration varied from 30wt% to 65wt%; two concentrations of sulfuric acid,

55wt% and 63wt%, were used. The molar ratio of sulfuric acid to hydrogen peroxide was varied from 0.3:1 to 1.5:1 for 65wt% HP; 0.55:1 to 1.8:1 for 50% wt HP; and 1:1 to 2.5:1 for 30wt% HP. Reactions were run at 25°C and 5°C for 24 hours. Reactions were cooled in an ice bath while acid was added before being transferred to the 25°C bath; reactions at 5°C were not cooled further prior to acid addition. Filtration procedures were similar to that for TATP syntheses (Section 2.2), but more water (>200mL) was used to rinse precipitate since more acid was used in DADP preparation. When high sample purity was required, the re-crystallization protocol cited below (Section 2.5) was employed. Melting point 131-133°C; ^{1}H NMR 1.35 and 1.80 ppm and ^{13}C NMR 20, 22 and 108 ppm (CDCl$_3$); MS fragmentation pattern: m/z = 133 $[(CH_3)_2OCO_2C(CH_3)O]^+$ (small), 117 $[(CH_3)_2CO_2CCH_3O]^+$ (small), 101 $[(CH_3)_2CO_2CH_3]^+$ (large), 89 $[C_3H_5O_3]^+$ (very small), 75 $[C_3H_7O_3]^+$ (small), 73 $[C_2H_5O_2]^+$ (small), 59 $[(CH_3)_2COH]^+$ (large), 58 $[(CH_3)_2CO]^+$ (large), 43 $[CH_3CO]^+$ (dominant), 29 $[CH_3CH_2]^+$ (medium), 15 $[CH_3]^+$ (medium).

2.4 Preparation of TATP/DADP Mixtures

Mixtures of TATP and DADP were prepared by dissolving proportional masses of each into 25g acetone, e.g. 75/25, 50/50 and 25/75, with a total mass between 1.50-2.00 g. The acetone solution was poured onto 100g of distilled water with vigorous stirring. After 10-15 minutes of stirring, the mixture was filtered and washed with room temperature distilled water; organic solvents were not used as a wash due to differing solubilities of DADP and TATP. The solid was allowed to dry for 30 minutes before being weighed and placed into a glass vial with plastic push-cap.

2.5 Recycling of Samples

Samples of TATP and DADP no longer needed were recrystallized. Double recrystallization was used to prepare TATP for standards. The first recrystallization was from methanol, and the solution was allowed to cool slowly to room temperature before being placed into a freezer. After filtering and washing with cold (-15°C) methanol, the TATP was re-dissolved in pentane. The pentane solution was cooled rapidly in an ice water and salt bath with continued stirring. In this manner, a smaller particle size was obtained. Recrystallization of DADP was performed in methanol or ethyl acetate.

2.6 Adulterated TATP

Adulterated solutions of acetone were prepared by adding acetone to the desired mass of adulterant in a 15mL vial with a total mass of 10g. Over 100 adulterants were tested in a range of concentrations from 1wt% to 50wt%. Sparingly soluble adulterants were used as saturated solutions; for these adulterants, saturation was below 10wt%. In these cases, rather than determine solubility and adjust the mass of acetone solution to maintain a ratio of 1:1 between hydrogen peroxide and acetone, the standard mass of acetone, 0.78g, was used. For these solutions, the actual mass ratio of hydrogen peroxide to acetone fell between 1:1 and 1.12:1. Reactions using adulterated acetone were run in duplicate per concentration and specific reaction conditions; few were run only once. Reaction times were measured from the time of addition of acid to filtration of the solid precipitate.

2.7 Analytical Methods

Melting points were obtained on a Mel-Temp model 1001, without temperature corrections; samples containing DADP required sealing both ends of the capillary tubes to prevent sublimation. For multiple samples produced under the same conditions, the melting point range reported is an average of the onset of melting and completion of melting (i.e. low end of the range and the high end of the range) observed for all the samples.

Gas chromatograph (Agilent 6890) coupled to either a mass selective detector (Agilent 5793) (GC/MS) or a micro-electron capture detector (GC/μECD) was used to quantify TATP and DADP against pure samples in acetonitrile solutions. Most impurities present in samples could not be positively identified by GC/MS, nor were laborious attempts made to do so. Samples for GC analysis were prepared by weighing 9-11mg of sample into a 10mL volumetric flask and filling to mark with acetonitrile; for GC/μECD analysis, a further 1:10 dilution was performed.

The GC/MS inlet temperature was 150°C and a flow of 11.6mL/min (helium carrier gas). The inlet was operated in split mode, with a ratio of 5:1 and a split flow of 7.5mL/min. A 10m DB5-MS column (J&W) with a 0.25mm inner diameter and a 0.25μm film thickness was operated under a constant flow condition of 1.5mL/min. The oven program had an initial temperature of 50°C with a 4min hold followed by a 10°C/min ramp to 200°C and a post-run at 310°C for 1min. The transfer line temperature was 250°C and the mass selective detector source and quadrupole temperatures were 230°C and 150°C, respectively, and electron-impact ionization was used.

The GC/μECD inlet temperature was 170°C, a pressure of 2.36psi (helium carrier gas) and operated in splitless mode. The 6m RTX-TNT2 column (Restek, 0.53mm inner diameter,

1.5µm film thickness) was held to constant pressure. The oven program had an initial temperature of 40°C and a 2min hold followed by a 20°C/min ramp to 150°C, a 1min hold and a post-run at 250°C for 2mins. The detector was set to 280°C with 30mL/min nitrogen makeup gas flow.

Physical attributes, including density, impact sensitivity, explosivity, and thermal stability, were characterized for pure TATP and DADP and mixtures of TATP/DADP, following determination of approximate ratios of TATP to DADP using GC/µECD. Crystal densities were obtained on a Micromeritics Helium Pycnometer with barium chloride calibration. A single sample was analyzed ten times by the instrument and a density given with a standard deviation. Due to the high vapor pressure of DADP, an accurate density was not obtained for mixtures of TATP and DADP or neat DADP. Impact sensitivity, i.e. drop-weight impact, was performed using an apparatus modeled after Lawrence Livermore National Laboratories drop weight impact machine; the weight used was 1.91kg [32]. A small-scale explosivity device (SSED) was used, wherein a mass of material is placed inside a British 0.303 rifle cartridge (primer removed) and detonated with a Teledyne RISI RP-3 (29mg PETN) detonator. Typically the mass of material used was 2.0000g, unfortunately, due to the low tap density and inability to pack TATP or DADP into the cartridge, the mass was significantly less. Relative power output is correlated by finding the percentage of the base remaining versus the initial mass of the cartridge [33, 34].

A TA Instruments Q100 differential scanning calorimeter (DSC) was used to determine onset temperature of decomposition, heat release and exothermic maximum temperature. Calibration of the DSC consisted of sapphire disc T_{zero} calibration followed by 4 metal standards for heat release and temperature calibration: indium, tin, lead and zinc. Samples were sealed in glass capillary tubes using 0.1-0.2mg of material. Standard run conditions were: Equilibrate at -

10°C, ramp 20°C/min to 30°C, turn data storage on, ramp 20°C/min to 400°C. For mixtures of

TATP and DADP, the DSC was used for observing eutectic and non-eutectic melting.

In adulteration experiments, percent yield of white precipitate formed was the main

metric for determining if adulterants affected the reaction between hydrogen peroxide and

acetone. Neat reactions were run using similar reaction times, temperature and catalyst loading

for comparison. Percent yields were calculated based on either hydrogen peroxide or acetone,

whichever was the limiting reagent; the ratio between hydrogen peroxide and acetone was 1:1 for

the majority of the reactions. Purity/identity of the white precipitate was judged primarily by

melting point, but in some cases GC/MS or GC/μECD analysis was performed. While GC/MS

could not reveal inorganic salts or solvents which might decrease melting point, it would reveal

organic impurities. Use of TATP calibration standards allowed determination of whether the

solid was primarily TATP or whether a large percentage of its mass was some material invisible

to the GC detector. Hence, in several cases we report a decrease in melting point but a high level

of purity indicated by GC/MS or GC/μECD analysis.

3 Results and Discussion

3.1 Factors Affecting TATP Yield

3.1.1 Hydrogen Peroxide to Acetone Ratio

An optimum molar ratio of hydrogen peroxide (HP) to acetone was determined using two

different means of varying the ratio: the amount of HP was held constant at 13.5mmols and the

amount of acetone was varied, or the amount of acetone was held constant at 13.5mmols and the

amount of HP was varied. The HP-to-acetone molar ratio was varied between 0.25:1 to 4:1 with

two different sulfuric acid (48wt%) amounts, 0.14mmols (1mol%) or 1.35mmols (10mol%)

(Figure 1). Regardless of which reagent was held constant, a molar ratio between 0.5:1 and 2:1 resulted in good yield of TATP; outside this range, the yield decreased.

<figr1>

3.1.2 Concentration of HP and Reaction Length

Yield of TATP increased with increasing concentration of HP even though the molar ratios of HP to acetone of 1:1 and sulfuric acid (48wt%) to HP of 0.01:1 were held constant (Figure 2). In a 48 hour reaction, 84wt% HP yielded 84wt% TATP, while 30wt% HP yielded 30% TATP. At low amounts of acid (1mol%), an increase in reaction length increased yield; with 30wt% HP, the yield more than doubled between 24 hours (16%) and 72 hours (35%) (Figure 2).

<figr2>

<figr3>

3.1.3 Reaction Temperature

The temperature of the reaction was varied from 5°C to 40°C. While concentrations of sulfuric acid (48wt%) and HP (30wt%) were not varied, their molar ratio was (Figure 3). At temperatures less than 25°C, molar ratios of acid to HP higher than 0.1:1 increased yield; above 25°C, increasing the molar ratio of acid to HP above 0.1:1 resulted in decreased yield of solid peroxide. With 0.1:1 acid to HP molar ratio, a maximum yield was obtained at 25°C. By GC/µECD analysis, the reactions ran at 40°C with a molar ratio of acid to HP of 0.2:1 yielded 1-3wt% DADP; all other reactions yielded TATP only.

3.1.4 Acid to HP/Acetone Ratio

Two reaction temperatures, 5°C and 25°C, were used to observe product distribution over a wide range of concentrations and amounts of sulfuric acid (48wt%-96wt%) and HP (30wt% - 84wt%); molar ratios ranged from 0.002:1 to 2.5:1 (Figure 4). HP to acetone molar ratio was set as 1:1 and was not varied. At 5°C, an increase in yield was observed with increased acid amount, reaching nearly 100% at an acid to HP molar ratio of 0.8:1, before declining. At 25°C, overall yield reached a maximum at an acid to HP molar ratio of 0.4:1 before declining. Above a molar ratio of acid to HP of 0.5:1, reactions ran at 5°C had greater overall yields than identical reactions ran at 25°C. Presumably, at higher temperatures, the use of larger amounts of acid resulted in decomposition of the peroxides. Figure 4 is expressed as total yield because analysis was of total precipitate formed, both TATP and DADP.

<figr4>

3.2 Conditions Affecting DADP Formation

In order to assign percentages of TATP and DADP of the overall mixtures (shown in Figure 4), GC/µECD analysis was performed against standards. Figures 5 and 6 illustrate that high temperature (25°C vs. 5°C) and high acid content favored DADP formation. Temperature affected overall yield (Figure 4) and product distribution; for example, under the same conditions, 1:1 molar ratio of sulfuric acid (63wt%) to HP (65wt%), samples ran at 5°C yielded over 80% TATP, while samples ran at 25°C were almost 100% DADP.

<figr5>
<figr6>

Both Hernandez and Matyas discussed some aspects of the TATP/DADP conversion. Hernandez reported that the reaction of acetone and hydrogen peroxide at temperatures below 0°C gave exclusively TATP, but at 20°C a mixture of TATP and DADP was obtained (amount

of acid was not reported) [17]. Matyas noted a dependence on acid concentration. He found that when an acetone and hydrogen peroxide (30wt%) mixture was treated with 1 molar equivalent of 96wt% sulfuric acid, DADP formed; when 65wt% sulfuric acid was used, 2.5 molar equivalents of acid were necessary to form DADP [15].

In the present experiments, the concentration of hydrogen peroxide was found to dictate the amount of acid necessary to convert TATP to DADP. As the initial concentration of HP was increased (concentration of sulfuric acid held constant), the amount of acid necessary for complete conversion of TATP to DADP decreased. For example, with 30wt% HP and 63wt% sulfuric acid, a 1.5:1 acid to HP mol ratio yielded only DADP; when the initial concentration of HP was increased to 65wt%, a smaller molar ratio, 0.8:1, induced complete conversion to DADP (Figure 7). Raw data collected at 5°C and 25°C is provided in supplemental data.

<figr7>

While the importance of acidity on the HP/acetone reaction has long been acknowledged, it appears the volume of water in reaction mixture plays an important role. Since both HP and acid were aqueous, the relative ratios of reactants were complex. Figure 8 illustrate that water-to-sulfuric acid molar ratio alone is insufficient to determine the resultant product mix. As the total volume of the reaction mixture decreased with increasing HP concentration, the volume occupied by the precipitated solid peroxide remained nearly constant. The result was that less TATP transformed into DADP at conditions where similar water-to-sulfuric-acid molar ratios achieved by high acid concentration and low HP concentration yielded strictly DADP. Figure 9 plots the reaction products at 25°C as a function of HP moles per kg of water and sulfuric acid moles per kg of water, where water comes into the reaction with both the HP and the acid. This allows select synthesis of TATP or DADP. If the desired product is TATP then high

concentration of HP and low acid must be used (black diamonds, Figure 9); for high yield of DADP, lower concentration of HP and higher concentration acid are required (black circles, Figure 9).

<figr8>

<figr9>

3.3 Physical Properties

3.3.1 TATP/DADP Mixture

On do-it-yourself synthesis web sites there is often speculation on the effect of forming DADP rather than TATP in improvised syntheses. The concern is which peroxide is more sensitive or unstable. The fact that TATP exhibits a lower DSC exotherm (239°C) than DADP (251°C) indicates it is somewhat less thermally stable (Table 3). The DSC thermograms indicated that a low melting eutectic was formed when a small amount of DADP contaminated TATP. Analysis of crude samples showed significant destabilization if quantities of acid exceeded 10mol% or impurities were present caused from adulteration of the acetone with 20wt% 2-butanone or 2-pentanone (Table 3). Mixtures of TATP and DADP were found to be more impact sensitive than either pure chemical. Impact sensitivity was only slightly decreased for crude samples (Table 4). Also in Table 4 are the results of the Small Scale Explosivity Device (SSED) tests; which measures the explosive power of 2 gram samples initiated with small detonators. Both TATP and DADP perform poorer than TNT, leaving 42% of the cartridge case attached to the base, but this result was achieved with considerably less TATP (~0.8g) than DADP (~1.3g).

<tabr3>

<tabr4>

3.3.2 Wetted TATP

While do-it-yourself "chemists" speculate on the effect of DADP contamination of their TATP, explosive disposal personnel speculate on methods to "desensitize" TATP sufficiently so that it can be safely moved from a domestic location. To illustrate the potential associated hazards, a 4.3kg weight was used in the impact device against 20mg TATP. Pure TATP produced a "go" response at a drop height of 5cm. Wetting it with ethanol (EtOH), a 50/50 mixture of ethanol/water or diesel resulted in a mixture that usually did not "go" even when the weight was raised to 100 cm (Table 5). A popular remedy, WD-40, did not show reproducible desensitization, and water, alone, showed none. We attribute the "desensitizing" effect of certain liquids and the failure of others to their relative tendency to dissolve TATP. Even though the amount of ethanol was too little to dissolve the TATP and the material did not appear to be dissolving, we believe the outer coating was sufficiently softened to reduce sensitivity to impact. Water, in which TATP has little solubility, did not reduce its sensitivity to impact.

<tabr5>

When the entire test series was repeated with a different batch of TATP; less favorable results were obtained (Table 5). Mixtures which showed reduced sensitivity, e.g. EOH/water, now produced a "go". Particle size distinctions (i.e. fine versus coarse) were based on visual observations. This suggested that morphology of different batches might influence sensitivity. Factors such as particle size, factors which influence aggregation and product purity can be influenced by subtle details associated with synthesis such and temperature, solvent composition and ionic strength. Factors facilitating aggregation would likely increase sensitivity of TATP to shock and friction.

3.4 Adulterated Reactions

To inhibit the reaction between acetone and hydrogen peroxide we sought chemicals to adulterate the precursors without interfering with their desired usage. The ideal adulterant would be kept at a few percent loading, be relatively non-toxic and completely inhibit formation of TATP under most conditions. Our approach was to seek out additives that destroyed hydrogen peroxide, diverted hydrogen peroxide (by reacting with it), quenched the acid catalyst, or made isolation of TATP cumbersome. Over one hundred adulterants, chosen from eight classes of reagents were tested: (1) antioxidants; (2) radical initiators; (3) metal salts; (4) molecules containing reactive bonds; (5) ketones other than acetone; (6) organic solvents to prevent TATP precipitation; (7) amines and inorganic bases; (8) halides and halogenated organics. Reactions involving adulterated solutions of acetone used a molar ratio of 1:1 hydrogen peroxide (30wt%) to acetone and either 1) 25°C with 1 mol% sulfuric acid for 48 hours or 2) 5°C with 10 mol% sulfuric acid for 24 hours. DADP was not observed by GC/MS or GC/µECD for any of these reactions. Most of the adulterants failed to retard TATP formation. Adulterants and rational for choosing them is as follows:

(1) Antioxidants were added in an attempt to quench hydroxyl and hydroperoxy radicals should they be formed during synthesis of TATP. However, butylated hydroxytoluene, vanillic acid, butylated hydroxyanisole, diethyl phthalate, benzoquinone, tannic acid, pyrogallol, 4-hydroxyphenylacetic acid, resorcinol, p-hydroxyphenylacetic acid, gallic acid, butylated hydroxytoluene, vitamin E, dioctyl phthalate, and pyrogallol failed to reduce TATP production even when they were present in up to 30wt% concentration.

(2) Radical initiators (t-butyl peroxide, benzoyl peroxide, sodium persulfate, sodium bisulfite, ammonium bisulfite, glycol sulfite, acetone sodium bisulfate) were added in an attempt to destroy hydrogen peroxide before it reacted with acetone. None were successful.

(3) Catalytic decomposition of hydrogen peroxide and TATP can be achieved by some metal salts; however, copper salts of nitrate, sulfate, acetate, and iodide; iron salts of acetylacetonate, phosphate, chloride, phthalocyanine, and ferrocene; tin chloride; and zinc sulfate and chloride did not reduce TATP formation, while cooper chloride and bromide did.

(4) Molecules containing reactive bonds were added to offer hydrogen peroxide an alternative site for reaction. Terephthalaldehyde, benzaldehyde, furfural, formaldehyde, ethyl propiolate, 2-pentyn-1-ol, propargyl alcohol, methyl methacrylate, styrene, 5-vinyl-2-norbornene methacrylic acid, isoprene, t, t-1,4-diphenyl-1,3-butadiene, isobutylene, 7,7,8,8-tetracyanoquino-dimethane failed to effectively compete with acetone when added at the 20wt% level. Only at 40wt% to 50wt% did these adulterants become effective.

(5) To compete with acetone for oxidation formamide, cyclohexanone, cyclopentanone, 2- and 3-pentanone, 2-butanone, 2,3- and 2,4-butanedione, benzil, 1,4-cyclohexanedione, and 2-nonanone were added. At 20wt% they were slightly effective; to eliminate TATP formation they needed to be present at 50wt%.

(6) Organic solvents (methanol, carbitol, ethylene glycol, diethyl ether, ethyl acetate, toluene, and t-butanol) added to acetone at up to 50wt% did not prevent precipitation of TATP from solution.

(7) Amines and other bases ammonium or potassium hydroxide, trimethyl- or triethyl-amine, aniline, diaminopropane, diethylamine, diethylene triamine, ethylenediamine, hydrazine monohydrate, phenyl hydrazine, diethyl- or diisopropyl-amine, piperidine, or pyridine neutralized the acid catalyst [35]. They were effective at the 1wt% level in preventing TATP formation. However, their effect was readily overcome by the addition of excess acid.

Furthermore, many amines are toxic and on a time-scale of months, react with acetone, even when kept cold (-15°C).

Two type of adulterants were effective at reducing TATP formation—bases and iodide species. Iodide is known to decompose hydrogen peroxide (Eq. 1) with iodide consumed at a molar ratio of 3:1 (I^- : HP); bromide was known to react similarly [36,37]. Therefore, halide salts [ammonium iodide (NH$_4$I), tetrabutylammonium iodide (TBAI), methyltriphenylphosphonium iodide (MTPPI), potassium iodide (KI) and tetrabutylphosphonium bromide (TBPBr)] and organic halides [diatrizoic acid ($C_{11}H_9N_2O_4I_3$), and N-bromosuccinimide (NBS)] were used. Due to the high formula weight of iodine compounds, the molar ratio was low. For example, with a 10wt% NH$_4$I solution, the molar ratio of I^- : HP was 1:29; however, this was sufficient to disrupt the formation of TATP. Similar to amine adulterants, use of increased acid catalyst could overcome the inhibitory effect of iodide on TATP production. Furthermore, acetone solutions containing iodide salts, especially NH$_4$I, darken after a few months storage, but the inhibiting effect of iodide was not diminished.

4 Conclusion

The reaction between hydrogen peroxide and acetone was investigated to identify conditions that affect yield and purity of TATP and/or DADP. The molar ratio of HP to acetone was able to be varied between 0.5:1 and 2:1 without yield being drastically affected. Reaction temperature, reactant ratios to each other, and initial reactant concentrations affected overall yield as well as the ratio of TATP to DADP produced. Analysis of reaction conditions was complicated by the fact that both HP and sulfuric acid were aqueous. Some volume of solution was required for TATP conversion to DADP. Figure 9 outlines reaction conditions to be selected toward the desired product. Adulterating acetone to inhibit TATP formation was difficult to

achieve at low levels of adulterant. Some materials - amines, iodide salts, ketones, and metal

salts - showed promise, but either their toxicity or their adverse effect on solution stability would

be hindrances to their use, e.g. amines, iodide and metal salts. Low molecular weight ketones,

i.e. methyl ethyl ketone and 2-pentanone at relatively high adulterant concentration (≥20wt%)

proved most effective, with no loss in stability and minimal increase in toxicity.

5 References

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Table 1. TATP Characteristics

| | Sensitivity | | Power | | Vap. Pr. at 25°C (torr) |
	Impact (J)	Friction (N)	Trauzl	Ballistic Mortar	
TATP	0.2 [2], 0.3 [3], 0.8 [4], 1.0[a]	0.1 [3], 0.015 [4]	80% [3]	62% [5]	5x10^{-2} [6]
DADP	0.4 [2], 2.3[a]	--	--	--	1.3x10^{-1} [7]
PETN	3 [3], 6[a]	60 [3]	--	--	--
TNT	--	--	100%	100%	5.8x10^{-6} [8]

a This Work

Table 2. Terrorist Use of Peroxide Explosives

Where:	Who:	What:	When:	Ref:
Flight to US	Reid	TATP initiator in "Shoe Bomb"	12/01	[24]
NY/Denver	Zazi	Collected HP as a precursor	~9/09	[25]
London	Group of 6	Subway attempt, TATP & HP/Fuel	7/05	[26]
Denmark	Dukayev	Attempted letter bomb, TATP	9/10	[27]
MA	Robison Jr.	Amateur Chemist, home-made TATP + Other Explosives seized	'07-'08	[28]
TX	Rugo	Killed while grinding TATP + metals	7/06	[29]

Table 3. DSC Data (ramp rate 20deg/min from 50 to 400°C)

| | | | | DSC Events | | | | | | | | |
| | | | | TATP Melt | | | DADP Melt | | | Exotherm | | |
Sample	% wt TATP	% wt DADP	# of Runs	Onset (°C)	Heat Absorbed (J/g)	Max Endo (°C)	Onset (°C)	Heat Absorbed (J/g)	Max Endo (°C)	Onset (°C)	Heat Released (J/g)	Max Exo (°C)
TATP	100	0	7	95	85	97	--	--	--	202	2511	239
75/25 TATP/DADP	82-86	14-18	2	77	93	81	--	--	--	207	2775	240
50/50 TATP/DADP	53-61	39-47	2	78	55	81	96	49	105	207	2809	242
25/75 TATP/DADP	37-59	41-63	3	82	98	85	--	62	112	197	3128	243
DADP	0	100	4	--	--	--	130	200	132	219	3253	251
0.1 : 1 (30wt%), 5°C	100	0	2	93	63	98	--	--	--	184	2904	228
0.1 : 1 (30wt%), 5°C	91	0	3	--	37	94	--	--	--	175	2669	235
0.4 : 1 (65wt%), 25°C	98	3	2	88	48	90	--	--	--	96	2822	108
0.8 : 1 (50wt%), 25°C	50	47	3	75	68	80	--	--	--	93	2594	133
0.8 : 1 (50wt%), 25°C	44	47	3	78	28	81	104	61	114	128	2905	147
1.0 : 1 (65wt%), 25°C	0.6	94	2	--	--	--	125	72	128	133	2564	142
1.2 : 1 (50wt%), 25°C	0.5	96	3	--	--	--	124	99	128	149	2844	154
1.8 : 1 (50wt%), 25°C	0.1	91	2	--	--	--	125	90	127	137	2947	141
20wt% 2-Pentanone	84	--	2	88	28	94	--	--	--	139	1220	153
20wt% 2-Butanone	68	--	3	76	42	83	--	--	--	123	1698	143
10wt% Formamide	97	--	2	87	61	98	--	--	--	209	1952	242

Table 4. Drop Weight Impact (1.91 kg) & SSED Data

Sample:	% TATP / % DADP by GC/μECD	Melting Point °C	Impact h_{50} (cm)	SSED Data Charge Wt (g)	% Base Rem.
Recrystallized TATP	98 / 0	95-96	5.3	0.7580	42%
75/25 TATP/DADP	86 / 18	74-87	6.0	--	--
50/50 TATP/DADP	53 / 39	77-106	3.4	--	--
25/75 TATP/DADP	37 / 41	83-122	7.6	--	--
Recrystallized DADP	0 / 84	131-133	12.5	1.2989	42%
TNT	--	--	--	2.0000	37%
PETN	--	--	33.7	2.0000	26%
HMTD	--	--	4.7	--	--
0.6:1 (65wt%), 5°C	94 / 0.3	79-82	4.6	--	--
0.8:1 (50wt%), 5°C	85 / 0.4	88-89	4.0	--	--
1.8:1 (50wt%), 25°C	0.1 / 85	108-111	7.3	--	--

Table 5. Impact (4.3 kg) Sensitivity of Wetted TATP

Drop Weight (cm)	5	100	100	100	100	100	100
Additive	None	EtOH	EtOH/H_2O		Diesel	WD-40	Water
Additive (μL)	--	200	200	100	200	200	200
Trial			FINE PARTICLES				
1	G/NG	G/NG	NG	NG	NG	G?	G
2	G	NG	NG	NG	NG	NG	G
3	G	NG	NG	NG	NG	G?	G
4	NG	NG					
5	G	NG					
6	G	NG					
			COARSE PARTICLES				
Conditions	(a)	(a)	(c)	(b)	(c)	(c)	
(a) - wetted	G	G		G	G	G	
(b) - soaked 12h & wet	NG?	G		G	G	G	
(c) - soaked 12h & dry	G	G		G	G	G	

Figure Captions

Figure 1. % TATP Yield vs. molar ratio of HP (30wt%) to acetone; 1 or 10mol% Acid (48wt%); 48hr; 25°C
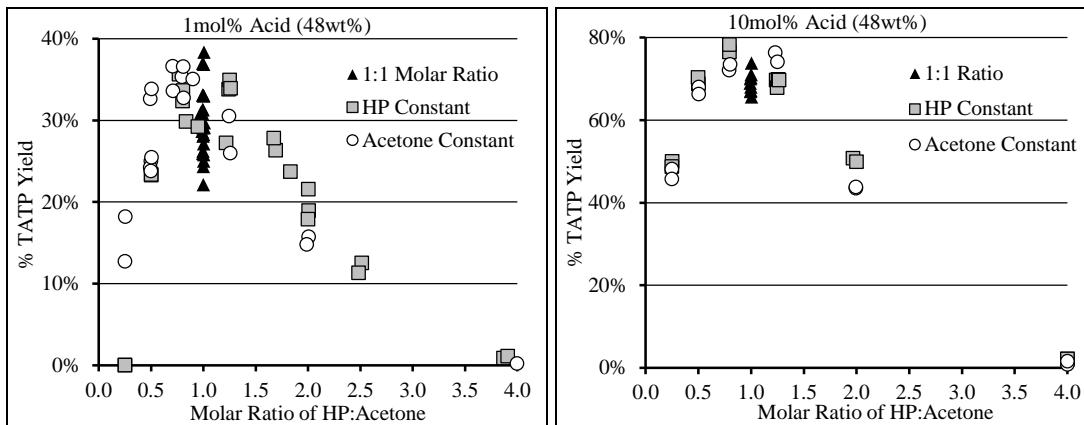
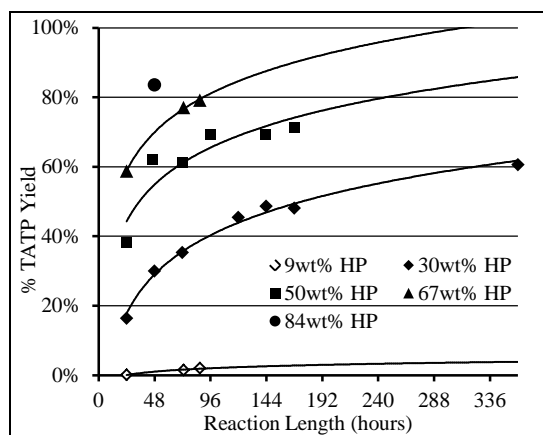**Figure 2.** % TATP Yield vs. RXN Length (hr) for varying [HP]; 13.5mmols HP/Acetone; 1 mol% Acid (48wt%)

Figure 3. % Total Peroxide Yield vs. RXN Temperature for varying molar ratios of acid (48wt%) to HP (30wt%); 13.5mmol HP /Acetone; 24hr

Figure 4. % Total Peroxide Yield vs. Molar Ratio of Acid to 13.5mmols HP/Acetone

Figure 5. % TATP (by GC) vs. Molar Ratio of Acid:HP; 13.5mmols HP/Acetone; 24hr; varying temp

Figure 6. % DADP (by GC) vs. Molar Ratio of Acid (varying wt%) to HP (varying wt%); 13.5mmols HP/Acetone; 24hr; varying temp

Figure 7. % DADP and % Total Peroxide Yield vs. Molar Ratio of Acid (63wt%) to HP (wt% HP indicated); 13.5mmols HP/Acetone; 25°C; 24hr

Figure 8. % DADP & % Total Peroxide Yield vs. Water to Acid (63wt%) molar ratio; wt% HP indicated; 13.5mmols HP/Acetone; 25°C; 24hr

Figure 9. Sulfuric Acid moles/kg water vs. HP moles/kg water – regions of DADP vs. TATP formation at 25°C; 13.5mmols HP/Acetone; 24hr

Scheme 1. Triacetone Triperoxide (TATP) and Diacetone Diperoxide (DADP)

Figure 1. % TATP Yield vs. molar ratio of HP (30wt%) to acetone; 1 or 10mol% Acid (48wt%); 48hr; 25°C

Figure 2. % TATP Yield vs. RXN Length (hr) for varying [HP]; 13.5mmols HP/Acetone; 1 mol% Acid (48wt%)

Figure 3. % Total Peroxide Yield vs. RXN Temperature for varying molar ratios of acid
(48wt%) to HP (30wt%); 13.5mmol HP /Acetone; 24hr
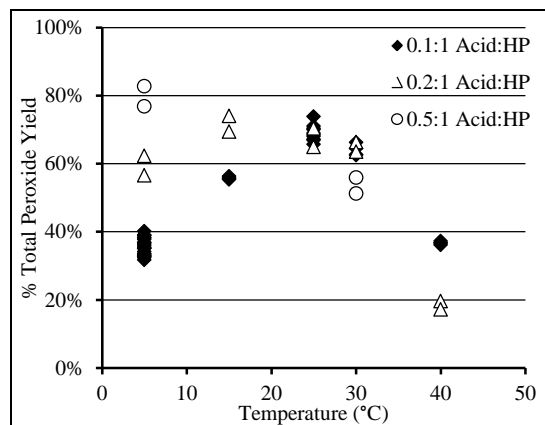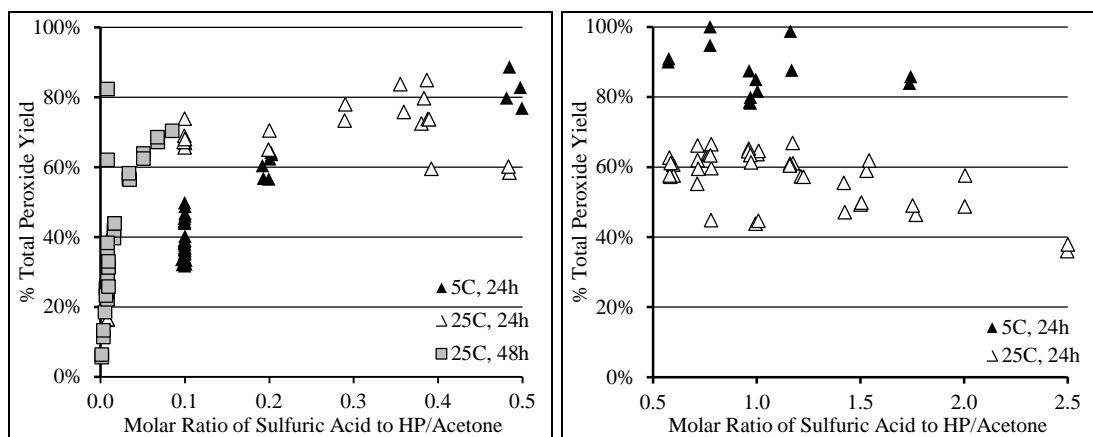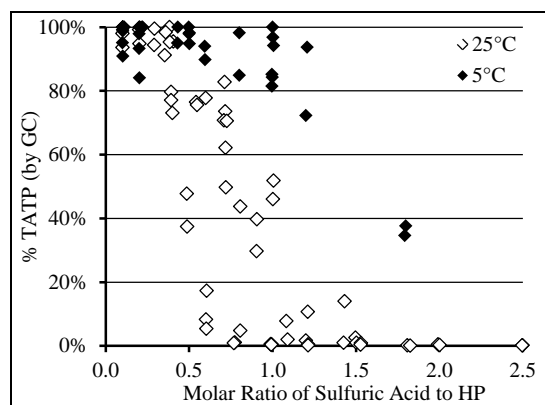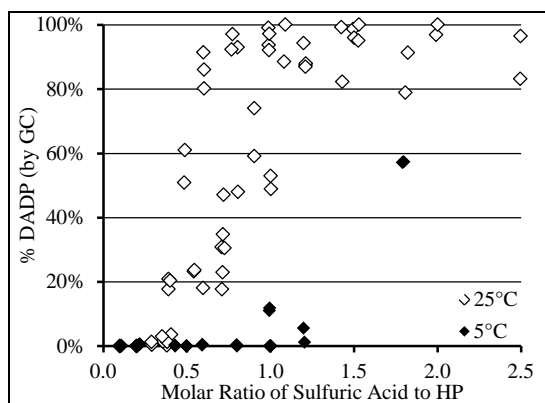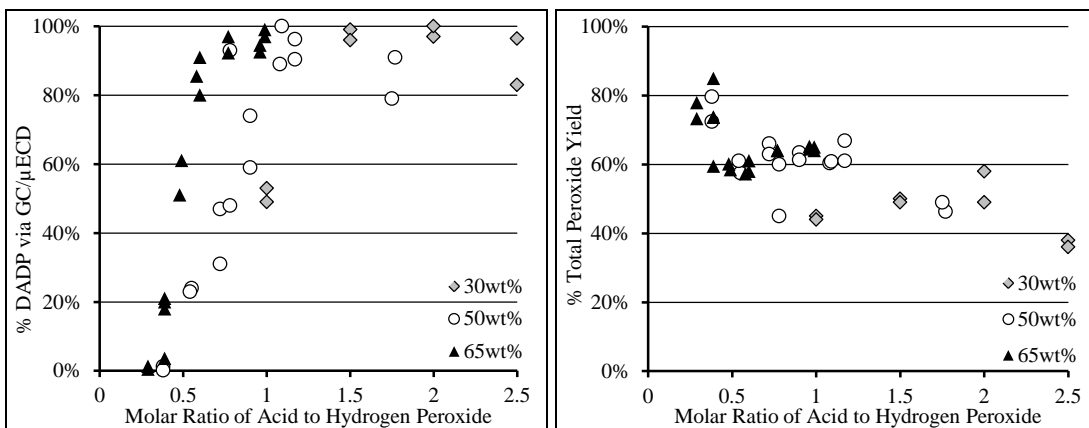* - at 40°C, 3wt% of the yield was DADP

Figure 4. % Total Peroxide Yield vs. Molar Ratio of Acid to 13.5mmols HP/Acetone
* - Left graph is an expanded view of 0-0.5 ratio region

Figure 5. % TATP (by GC) vs. Molar Ratio of Acid:HP; 13.5mmols HP/Acetone; 24hr; varying temp

Figure 6. % DADP (by GC) vs. Molar Ratio of Acid (varying wt%) to HP (varying wt%); 13.5mmols HP/Acetone; 24hr; varying temp

Figure 7. % DADP and % Total Peroxide Yield vs. Molar Ratio of Acid (63wt%) to HP (wt% HP indicated); 13.5mmols HP/Acetone; 25°C; 24hr

Figure 8. % DADP & % Total Peroxide Yield vs. Water to Acid (63wt%) molar ratio; wt% HP indicated; 13.5mmols HP/Acetone; 25°C; 24hr

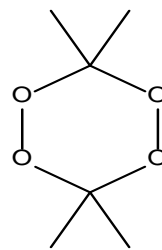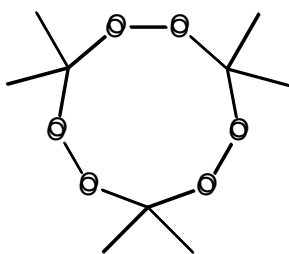**Figure 9.** Sulfuric Acid moles/kg water vs. HP moles/kg water – regions of DADP vs. TATP formation at 25°C; 13.5mmols HP/Acetone; 24hr

Scheme 1. Triacetone Triperoxide (TATP) and Diacetone Diperoxide (DADP)