Factors Influencing Triacetone Triperoxide (TATP) and Diacetone Diperoxide (DADP) Formation: Part 2

Jimmie C. Oxley[*]; James L. Smith; Lucus Steinkamp; Guang Zhang

[a]*University of Rhode Island,*
Chemistry Department
51 Lower College Road
Kingston, RI 02881
**joxley@chm.uri.edu*

Abstract

A comprehensive mechanistic study regarding acetone peroxides reveals that water has a profound effect on the formation of the solid cyclic peroxides, TATP and DADP. The identification and rate of occurrence of reaction intermediates as well as compositions of the final products offer explanation for previously reported results indicating that acid type and hydrogen peroxide concentration affect the acid catalyzed reaction between acetone and hydrogen peroxide. A kinetics study of the decomposition of TATP revealed the effects of water and alcohols. They generally retard conversion of TATP to DADP and leads complete decomposition of TATP by acid. A mechanism is proposed for the production of TATP and DADP.

Keywords: Triacetone triperoxide (TATP), Diacetone diperoxide (DADP), Product Formation, Product Decomposition, Mechanism, Kinetics

1. Introduction

Organic peroxides are often used as polymerization catalysts or bleaching agents [1-3]. However, a few with high ratios of peroxide functionality to ketone have found use as illicit explosives [4]. We have previously reported attempts to prevent synthesis of TATP in improvised settings [5]. That work pointed out a need for a detailed mechanistic study. Some of the questions of interest in TATP formation/destruction were conditions under which TATP and DADP form, mechanisms of formation and destruction and whether DADP could be formed directly or only through a TATP intermediate. These questions were addressed by identifying intermediates by gas chromatography/mass spectrometry (GC/MS), liquid chromatography/mass spectrometry (LC/MS) at high mass resolution and $^{1}H/^{13}C$ nuclear magnetic resonance spectroscopy (NMR). Intermediates were monitored during formation and destruction experiments to elucidate mechanisms.

2. Experimental Section

2.1 Reagents and Chemicals

HPLC-Grade acetone, acetonitrile, methylene chloride, methanol, 2-propanol, n-propanol, chloroform (0.75 wt% ethanol), trifluoroacetic acid (99 wt%), deuterated acetone (99.8 wt% D), 70 wt% nitric acid, 37 wt% hydrochloric acid and concentrated sulfuric acid (Certified ACS Plus) were obtained from Fisher Scientific. Deuterated acetonitrile was obtained from Cambridge Isotopes Lab.. Syntheses of TATP and DADP as catalyzed by sulfuric acid were previously reported [5]. In these experiments a higher melting crude product was obtained using 1:1:0.1 mole ratio of hydrogen peroxide to acetone to hydrochloric acid (18%). * For synthesis of deuterium-labeled TATP d^6 acetone was used. Precipitates were filtered, rinsed with water, and dried under aspiration for 30 minutes. Crude products were re-crystallized in methanol.

Final products were analyzed by GC/MS, GC/uECD, ^{1}H NMR and ^{13}C NMR. Anhydrous hydrogen peroxide was prepared by dissolving 20 g of L-serine in 20 mL 65 wt% hydrogen peroxide and following procedure given in reference 6. The anhydrous hydrogen peroxide was dissolved in acetonitrile and concentration checked by titration with 0.25N potassium permanaganate.

2.2 GC/MS Method

An Agilent 6890 gas chromatograph with 5973 mass selective detector (GC/MS) was used. The inlet temperature was 110°C and total flow of 24.1 mL/min (helium carrier gas). Inlet was operated in splitless mode, with a purge flow of 20 mL/min at 0.5 minutes. A 15 m Varian VF-200MS column with 0.25 mm inner diameter and 0.25 µm film thickness was operated under constant flow condition at 1.5 mL/min. The oven program was initial temperature of 40°C with a 2 minutes hold followed by a 10°C/min ramp to 70°C, a 20°C/min ramp to 220°C and a post-run at 310°C for 3 minutes. The transfer line temperature was 150°C and the mass selective detector source and quadrupole temperatures were 150°C and 106°C, respectively. Chemical ionization with anhydrous ammonia was used.

2.2.1 TATP Formation (GC/MS)

All reagents were chilled to 0^{o}C. Hydrogen peroxide (67 wt%, 0.47 g, 9.3 mmol) in 10 mL acetonitrile was placed in a round bottom flask equipped with stir bar. To this was added 2.6 mmoles sulfuric acid (0.267 g 96.5 wt%) and then 9.3 mmoles acetone (0.54 g) was added drop-wise. Periodically, aliquots of 100 uL of the reaction solution were removed, placed in 1 mL methylene chloride, and rinsed with 3 wt% sodium bicarbonate and water. The organic layer was dried over anhydrous magnesium sulfate and placed in 2 mL screw cap GC vials for GC/MS analysis..

2.2.2 Effect of water (GC/MS)

Acetone and hydrogen peroxide were mixed and chilled to 0°C. Water was pre-mixed with sulfuric or hydrochloric acid, chilled to 0°C, and added drop-wise to acetone/peroxide mixture keeping the temperature below 5°C. The ratios of reagents were maintained at 1:1:1 hydrogen peroxide:acetone:acid (8.6 mmoles) for each reaction. Once all acid was added the mixtures were removed from the ice water bath and allowed to stir at room temperature for 24 hours. The resulting products were analyzed using GC/MS.

2.2.3 TATP Destruction (GC/MS)

Into a 40 mL vial 100 mg TATP was measured. To the TATP 5 mL of solvent was added. In a second 40 mL vial solvent and any additional water were added totaling 5 mL. To the solvent and water solution 200 uL 96.5 wt% sulfuric acid were added. These solutions were allowed to equilibrate in an oven at 45°C. Once equilibrated, the two solutions were mixed and a timer was started. At recorded intervals 100 uL aliquots were removed and quenched by addition to 5 mL methylene chloride which was rinsed once with 3 wt% sodium bicarbonate and once with water followed by drying with anhydrous magnesium sulfate. Analysis for TATP and DADP was by GC/MS. Quantification of TATP and DADP was via external standard calibration curves.

2.2.4 Acetone Exchange Reactions (GC/MS)

TATP was stirred at room temperature with 5.4 mmol concentrated sulfuric in aqueous ethanol spiked with d^6 acetone (16.4 mmol). After 24 hours the TATP had not completely dissolved, but small aliquot of solution were analyzed by GC/MS for acetone exchange by identification of

presence or absence of deuterium containing fragments. Similar experiments involving acetonitrile, methanol or chloroform/TFA as solvent were conducted.

2.3 LC/MS Method

Certain experiments identified intermediates by liquid chromatography/mass spectrometry at high mass resolution (LC/MS). The mass spectrometer, a Thermo Scientific Exactive orbitrap mass spectrometer, was operated in positive ion mode using atmospheric pressure chemical ionization (APCI). Decomposition was minimized during analysis by setting the vaporizer at 175°C and capillary at 125°C. Discharge current was 5 μA and the sheath gas and auxiliary gas were operated at 25 and 10 arbitrary units, respectively. The LC ramped from 70/30 methanol/4 mM ammonium acetate in water mixture to a 15/85 methanol/4 mM ammonium acetate in water mixture in 5.5 minutes followed by a 30 second hold. The eluent was returned to a 70/30 methanol/4 mM ammonium acetate in water mixture and held for 4 minutes. MS resolution was set to high (50,000 at 2 Hz), and the maximum injection time was 250 ms.

2.3.1 TATP Formation (LC/MS)

Mixtures of acetone and 67 wt% hydrogen peroxide were prepared as molar ratios of 1:1, 2:1 and 1:2 and kept at room temperature without stirring. For LC/MS analysis 100 uL of each mixture was diluted to 1 mL with methanol.

2.3.2 d^6-Acetone Insertion into Proteo-TATP (LC/MS)

In a 25mL round bottom flask, 222mg TATP (1.0 mmols) and 75μL d^6-acetone (1.0 mmols) was added to 10 mL acetonitrile (ACN), methanol or chloroform. Trifluoroacetic acid (TFA, 150μL, 2.0 mmols) was added while stirring at room temperature. Samples for LC/MS analysis were prepared every 24hrs by diluting 0.5mL of the reaction mixture to a 1.5mL total volume.

2.4 Nuclear Magnetic Resonance (NMR) Method

A Bruker Avance III nuclear magnetic resonance (NMR) spectrometer with 7.1 Tesla magnet was used for all NMR experiments. Kinetic experiments, at 15°C (288K), monitored ^{1}H-spectra every 5 minutes (including scanning time) for up to 17 hours or daily for up to four days. Following the kinetics experiments, the samples were neutralized with excess sodium bicarbonate and either diluted by the identical solvent, sans-deuterium, and analyzed by GC/MS or returned to an NMR tube for subsequent analysis. 2-D NMR experiments: HSQC (hetero-nuclear single quantum coherence) and HMBC (heteronuclear multi-bond coherence) were performed. The ^{1}H (300 MHz) and ^{13}C (75 MHz) chemical shifts corresponding to all species present in the formation and decomposition of TATP reaction mixtures were obtained. NMR samples were then analyzed by GC/MS.

2.4.1 Formation of TATP/DADP (NMR)

In a 10 mL vial, 1 mL of 65 wt% hydrogen peroxide was mixed (24.6 mmols) with 1.9 mL of acetone (25.8 mmols) and 100 µL (0.92 mM hydrogen peroxide/acetone) of the mixture was transferred into an NMR tube with 1.2 mL deuterated acetonitrile. Trifluoroacetic acid (TFA) (20-80 µL, 0.26-1.04 mmols) and small amounts of tetramethylsilane (TMS), for calibration, were added. Quantification was relative to TMS.

2.4.2 Decomposition of TATP or DADP (NMR)

In a 10 mL vial, 45 mg TATP (0.2 mmols) was dissolved in deuterated solvent (0.6 mL CD_2Cl_2, 1.0 mL $CDCl_3$ or 1.2 mL CD_3CN) and transferred to a 5 mm NMR tube. The type and quantity

of acid added was varied: TFA (20-100 µL, 0.26-1.3 mmols), concentrated (96.5 wt%) sulfuric acid (10-20 µL, 0.18-0.36 mmols) or concentrated (37 wt%) hydrochloric acid (10 µL, 0.12 mmols). DADP (29 mg, 0.2 mmols) was dissolved in 1.0 mL of $CDCl_3$ and decomposed by addition of either TFA (60-100 µL, 0.78-1.3 mmols) or concentrated (96.5 wt%) sulfuric acid (10 µL, 0.18 mmols).

2.4.3 Acetone Exchange Without Acid (NMR)

TATP (111 mg, 0.5 mM) added to a 5 mm NMR tube with 1 mL d^6 acetone and 100 µL dichloromethane, sealed, and stored at room temperature. d^{18} TATP (120 mg, 0.5 mM) added to a 5 mm NMR tube with 0.9 mL acetone, 100 µL d^6 acetone (for locking) and 100 µL dichloromethane, sealed, and stored at room temperature.

2.4.4 Acetone Exchange Reactions (NMR)

In a 10 mL vial, 48 mg d^{18}-TATP (0.2 mmols) was dissolved in 1.2 mL CD_3CN or 1.0 mL $CDCl_3$. To this, either 50 µL acetone (0.68 mmols) for CD_3CN or 40 µL acetone (0.55 mmols) for $CDCl_3$ were added and the solution transferred to a 5 mm NMR tube. To the NMR tube, varying amounts (20-40 µL, 0.26-0.52 mmols) of TFA were added.

2.4.5 1,3-Dichloroacetone insertion into Proteo-TATP and d^{18}-TATP (NMR)

In a 10 mL vial, 22 mg TATP or 25 mg d^{18}-TATP (0.1 mmols) was dissolved in 1.2 mL CD_3CN. To this 42 mg of 1,3-dichloroacetone (0.3 mmols) was added before being transferred to a standard NMR tube. The amount of TFA added was 40 µL (0.52 mmols).

3.0 Results and Discussion

3.1 Formation of TATP with acid

Previous studies have shown that the best yield of TATP is obtained from a 1:1 mole ratio of acetone and hydrogen peroxide [5,7]. When using an acid catalyst such as hydrochloric or

sulfuric acid a white precipitate is quickly formed that can be washed and re-crystallized yielding high purity TATP, DADP or a mixture of the two [5,8]. To fully understand the mechanism of TATP and DADP formation it was necessary to conduct experiments using a co-solvent that would prevent precipitates in solution and not interfere with the analysis of the products and intermediates. Using GC/MS and NMR, TATP, DADP and intermediate species were observed and monitored over time. Figure 1 shows the progress of a typical reaction under highly acidic conditions by monitoring TATP and DADP by GC/MS. Initially the concentration of TATP rises sharply while that of DADP rises more gradually and levels off. The newly formed TATP undergoes decomposition in the presence of 1 molar equivalent of acid while DADP does not. Under less acidic conditions (3.5:3.5:1 HP:acetone:sulfuric acid) the concentration of TATP reached a maximum, remained constant for several days, and then gradually decreased as the concentration of DADP continually increased throughout the entire experiment. Eventually DADP is the final product if TATP cannot precipitate out of solution. In agreement with NMR data, upon increasing the amount of acid added, a faster rise to equilibrium was observed as well as a higher equilibrium concentration of TATP in solution. The decomposition of TATP also occurred more rapidly with increased amounts of acid, and water, itself, has an effect. Figure 2 shows that when the molar ratios of acetone, hydrogen peroxide and acid are kept constant (9.3 mmol) added water and reduced acid slows the rate of formation of both TATP and DADP and appears to suppress DADP formation more significantly. With minimal water present the rate of formation for TATP and DADP are at a maximum although TATP is still the major product observed.

<Figure 1>

<Figure 2>

3.2 Formation of TATP with no acid

A GC/MS screening of the products when 70 wt% hydrogen peroxide (HP) and acetone were mixed highlighted the importance of the ratios of each. When HP was in excess 5:1 over acetone more TATP was produced than DADP. When the ratio of HP to acetone was adjusted down from 5:1 to 1:1 and then to 1:5, the total amount of solid product decreased and the amount of DADP increased relative to TATP. Using NMR, the reaction between 70 wt% hydrogen peroxide and acetone without acid was monitored for up to 14 days and there was evolution of a number of peaks in both ^{1}H NMR and ^{13}C spectra as well as GC/MS chromatogram/spectra. Assignments of intermediates from NMR and GC/MS are given in Tables 1 and 2, respectively. Acetone and 70% HP were combined in ratios 1:1, 1:10 (excess acetone) and 10:1 (mostly HP) in 0.6 mL d^3 acetonitrile and monitored by ^{1}H NMR and ^{13}C NMR for 14 days. The relative progress of formation of proton resonances (as large, medium, small or tiny peaks) during synthesis of TATP/DADP is given at the far right columns of Table 1. On day zero there were two prominent methyl resonances in the ^{1}H NMR of each sample (Table 1); one at 2.1 ppm, assigned to the methyl protons of acetone, and the other at1.38 ppm attributed to the previously reported 2-hydroxy-2-hydroperoxypropane (I) intermediate (see Figure 7 for structure of intermediates) [9]. The acetone resonance shifted to slightly higher ppm with moderate to excessive amounts of HP. This was taken as evidence for protonation of acetone by HP. By day 4 the 1:1 and 10:1 HP:acetone (i.e. moderate to large amounts of HP) samples exhibited an additional methyl resonance at 1.44 ppm in ^{1}H NMR. This was assigned to a dimeric species where two molecules of acetone are linked by a peroxide functionality. Also by that time the protonated acetone species had decreased substantially at the expense of increasing reaction intermediates.

The larger chemical shift range of the ^{13}C NMR spectrum offered better peak separation with changes in carbon functionality. On day zero for the sample with excess acetone, resonances were observed at 24 ppm in the methyl region and 102 ppm in the carbonyl region. These were assigned to species with hydroxy terminal groups. On day zero of the samples with excess HP, peaks were seen at 20 ppm in the methyl region and at 109 ppm in the carbonyl region. These were assigned to species with terminal hydroperoxy groups. In the ^{13}C NMR spectrum of the sample of the 1:1 HP:acetone, the resonance associated with the methyl groups of 2-hydroxy-2-hydroperoxypropane (I) and the 2,2-dihydroperoxypropane (II) were observed at 20 and 24 ppm, respectively, as well as in the carbonyl region at 102 and 109, respectively. With daily monitoring, new ^{13}C resonances were observed in the methyl region: four between 20-21 ppm and three between 24-25 ppm. One at ~21 ppm is known to be TATP. On day zero 2-hydroxy-2-hydroperoxypropane (I) was at a maximum but diminished in size over time. The ^{13}C resonances of TATP (107.8 ppm CO) and DADP (108.7 ppm CO) did not become discernible until day 5 although their presence was detected on day 1 using GC/MS (Table 2).

In order to validate proton and carbon assignments, 2D NMR experiments were performed: HSQC (heteronuclear single quantum coherence) correlated to methyl and heteronuclear multi-bond coherence (HMBC) correlated to carbonyls. Chemical ionization GC/MS analyses, with ammonia reagent gas, were performed on the aged NMR solutions to confirm assignments of NMR resonances. Reasonable NMR resonances with corresponding masses, relative abundance of species, and chemical intuition were used to formulate assignments shown in Table 1.

<Table 1>

We had shown that solutions of acetone/HP without added acid contained several intermediates, and LC/MS confirmed the presence of longer chain oligomers and cyclic species (Figure 3) [10]. Species with terminal peroxide functionalities are favored, and increasing amount of hydrogen peroxide serves to enhance their formation. Only TATP and DADP precipitated under reaction conditions where acid, but no co-solvent, was present. In the absence of acid, solid TATP precipitated when the samples were aged at room temperature for up to two months. The asymmetric peroxides and longer chain oligomers were not observed by GC/MS, but using LC/MS they were observed in trace amounts.

<Figure 3>

3.3 Acetone Exchange in TATP

Experiments were conducted to determine if a new molecule of acetone could insert into an intact TATP ring. Deuterated acetone (d^6-acetone) was stirred with h^{18}-TATP and monitored daily for seven days by GC/MS. Similarly, d^{18}-TATP was monitored in h^6-acetone by ^{1}H NMR, typically for days; afterwards the solution was examined by GC/MS. GC/MS results indicated 1, 2, and 3 molecules of d^6-acetone were incorporated into h^{18}-TATP and 1 or 2 molecules of d^6-acetone into h^{12}-DADP in the presence of acid (Table 2). However, when no acid was added, ^{1}H NMR indicated no insertion of acetone; the proton resonances of the methyl groups in h^{18}-TATP (1.43 ppm) showed no decrease in intensity though followed for 7 days in d^6-acetone. Likewise the resonance of h^6-acetone (2.1 ppm) containing dissolved d^{18}- TATP indicated no decrease in intensity over a 7 day period. Without acid, neither exchange nor synthesis of fresh TATP nor DADP was observed.

<Table2>

Exchanges studies with chlorinated acetone were performed. d^{18}-Substituted TATP or proteo-TATP was stirred with 1,3-dichloroacetone in ACN with a five-fold excess of TFA. GC/MS analysis after d^{18} TATP and TFA had been stirred with dichloroacetone in ACN 17 hr showed d^{12} DADP, 1,3-dichloroacetone, and dichloro-TATP. While d^{12}-DADP was formed, presumably from opening of the d^{18} TATP-ring, no chloro-substitution into DADP was observed. Furthermore, the GC/MS fragmentation pattern as well as the quartet in the ^{1}H NMR spectrum suggested only singly substituted TATP(i.e.1,3-dichloroacetone) was formed. Neither tetrachloro-DADP nor hexachloro-TATP was observed, suggesting their formation may be sterically hindered. Interestingly, no incorporation of 1,1 dichloroacetone nor monochloro-acetone was observed (^{1}H, ^{13}C, GC/MS) even in the presence of acid (Table 3). Nevertheless, the observation of dichloro-substituted TATP indicates ring opening and re-closing does occur.

<Table 3>

3.4 Rate of TATP Formation

^{1}H NMR was used to monitor the one–to-one reaction of acetone and HP (0.88 mmol each) at 15^{o}C using 20, 40 or 80 uL of trifluoroacetic acid (TFA) (0.27, 0.54, 1.07 mmol). The reaction was monitored by taking spectra every 5 minutes (including scan time) for up to 17 hours (1020 min) (Figure 4 shows typical NMR data). After 200 minutes the methyl protons of TATP were clearly visible (as opposed to three days without acid). DADP protons only were barely visible after 800 minutes and were still faint at 1.35 and 1.79 ppm in the 1020 minute spectrum. The most abundant intermediates in the acid catalyzed reactions observed by NMR and GC/MS were 2,2-dihydroperoxy-propane (II) and 2,2'-dihydroperoxy-2,2'-diisopropylperoxide (V). Although 2-hydroxy-2-hydroperoxypropane (I) was most abundant when there was no acid catalyst, formation of 2,2-dihydroperoxypropane (II) was favored under acidic conditions [7,11]. TATP

formation was greatly accelerated by addition of acid; yet acid also caused TATP decomposition, as evident from following ^{1}H NMR resonance of TATP (1.42 ppm) when treated with various volumes of TFA (Figure 5). Monitoring TATP formation reactions by GC/MS showed the effect of the strength of acid as well as type of acid used. Compared to a mixture of acetone and HP with no added acid, concentrated sulfuric acid greatly enhanced the rate of formation of TATP as well as its decomposition to DADP. Reducing the concentration of the sulfuric acid, while maintaining a 1 molar equivalent acid, slowed TATP formation and significantly inhibited its decomposition to DADP. This observation suggested that water played a role. Concentrated HCl contains significantly more water than concentrated H_2SO_4. When water was added to sulfuric acid so that the water content in the acetone/HP mix was the same as when HCl was used, the rates of TATP formation with either acid were comparable. Use of nitric acid did not result in the same observed rate of formation, but nitric acid is the weakest of the strong acids used in these experiments. Use of weak acids such as citric acid and TFA resulted in dramatically slower rates of TATP formation (Fig. 6), although TFA was still capable of decomposing TATP.

<Figure 4>

<Figure 5>

3.5 Effect of Water

Previously reported results indicate that a change in the concentration of acid and hydrogen peroxide can dramatically affect the outcome of TATP syntheses [5]. Dilute reagents result in poor yield of solid products, and concentrated reagents in the presence of higher acid loadings result in increased DADP formation. Water appears to play an important role in the synthesis. In an attempt to understand how water affects DADP versus TATP formation, several syntheses were attempted using 30 wt% and 50 wt% HP, acetone and concentrated sulfuric or hydrochloric

acid. The ratios of the three reagents were maintained at 1:1:1 (8.6 mmol scale), but excess water, over that contributed by the reagents, was added (Table 3, Fig. 6). At the lowest levels of added water, the white solid formed was 100% DADP. At the highest levels of added water, the white solid precipitating was 100% TATP [12]. When the acid added was HCl, only a small amount of DADP was observed; this is attributed to the large amount of water (63wt%) in HCl. This phenomenon can be explained by the tendency of 2-hydroxy-2-hydroperoxypropane to disproportionate to 2,2-dihydroperoxypropane (II) and acetone in aqueous media [9]. The formation of the dihydroperoxy species appears to be a key step in TATP formation.

<Table 3>

<Figure 6>

3.6 Effect of Solvent and Temperature

To probe whether order of reactant addition had an effect on formation of TATP vs. DADP, it was varied (Table 4). The final precipitates, as well as in-situ products, were monitored by quenching the reaction at intervals during reagent addition and analyzing by GC/MS. There were no notable differences in the final products obtained regardless of whether the acid was added first to the acetone, to the HP, or to both together (cf. exp. 1 to 3, Table 4) [8]. Only when acid was the last reagent added did the reaction proceed slow enough for an intermediate, 2,2'-dihydroperoxy-2,2'-diisopropylperoxide (V) to be observed along with both cyclic peroxides (exp. 3); otherwise, only the cyclic peroxide(s) were seen. The final product of the hydrogen peroxide/acetone mixture varied markedly with solvent; acetonitrile favored formation of DADP at 0^{o}C, while alcohols favored TATP (cf. exp.1 with 1*, Table 4). The effect of temperature has been discussed by others without agreement [8,11,13]. Generally, TATP is favored at lower temperatures, but the effect of temperature can be manipulated by other factors such as solvent.

While DADP was the major solid product in ACN at 0^{o}C, at lower temperatures even in ACN, TATP was favored (cf. 1 to 1' and 3 to 3', Table 4). When TFA was substituted for sulfuric acid (exp 1") no precipitate formed within the same time interval as previous reactions (~30 minutes).

<Table 4>

3.7 Rate of TATP Decomposition

The decomposition of TATP by acid in CD_3CN or $CDCl_3$ was monitored by ^{1}H NMR. In ACN and $CDCl_3$ decomposition of TATP was pseudo-first order and formed DADP and acetone (Table 5). Quantifying TATP formation kinetics was more difficult due to formation of a number of intermediates, but initial formation rates of TATP in ACN are estimated in Table 5. Data suggests that at very high concentrations of acid, TATP is destroyed as fast as it is formed, and destruction of TATP in ACN leads to the formation of DADP (Tables 4 & 6). As TATP decomposed to DADP and acetone, other intermediates could be observed by ^{1}H NMR in d^3-ACN. In ACN, 2,2'-dihydroperoxy-2,2'-diisopropylperoxide (V) and 2,2-dihydroperoxy-propane (II) were observed as intermediates, whereas in $CDCl_3$ only 2,2'-dihydroperoxy-2,2'-diisoproylperoxide (V) was observed. NMR and MS data suggests these intermediates are identical to those observed in formation experiments (Table 1).

<Table 5>

Table 6 emphasizes the effect of water and solvent on TATP decomposition. Not only did water slow the decomposition, but it also appeared to retard conversion of TATP to DADP. Table 6 shows the pseudo first-order rate constants for TATP destruction in ACN and various alcohols. When concentrated sulfuric acid was added to a TATP ACN solution, the rate of disappearance of TATP was very high, and DADP was the end product. With added water the reaction was slowed significantly, and only trace amounts of DADP were observed. When concentrated

sulfuric acid was added to a TATP alcohol solution, the destruction of TATP was slower than in neat ACN, and only trace amounts of DADP were observed. Destruction of TATP was slower in alcohols with greater reactivity towards concentrated sulfuric acid, i.e. isopropanol or t-butanol. Methanol showed the highest rate of TATP destruction followed by ethanol, n-propanol and isopropanol. When t-butanol was used, an anomalous effect was observed. The reaction proceeded very quickly to a mixture of TATP and DADP and ceased. The decomposition of TATP by 37 wt% HCl generated some DADP, but the amount was very small compared with other acids (TFA SA) and chlorinated acetone species were detected [16].

<Table 6>

3.8 Mechanism

A proposed mechanism for the production of TATP and DADP is given in Figure 7. In a reaction between hydrogen peroxide and acetone without acid catalyst, 2-hydroxy-2-hydroperoxypropane (I) was observed in high quantities soon after mixing. When acid catalyst was added 2,2-dihydroperoxypropane (II) was the primary species observed shortly after mixing [11]. Symmetric species, where two acetones are linked by a peroxide linkage, 2,2'-dihydroxy-2,2'-diisopropylperoxide (III) and 2,2'-dihydroperoxy-2,2'-diisopropylperoxide (V) were also observed, but at later reaction times. The asymmetric species similar to 2-hydroxy-2'-hydroperoxy-2,2'-diisopropylperoxide (IV) were not directly observed by NMR or GC/MS and only trace amounts were observed using LC/MS. We speculate that when these are formed the hydroxyl group exchanges with a hydroperoxy group, or they rapidly convert to DADP and TATP, respectively [7]. The effect of water is apparent at this point.

When water content is low, 2-hydroxy-2-hydroperoxypropane (I) can be protonated facilitating formation of (IV) and a pathway to cyclization forming DADP. When water content

is high, disproportionation of (I) becomes favored resulting in the formation of the dihydroperoxy species (II) and, ultimately, the formation of TATP [9]. Under high water conditions water, itself, is protonated, and the overall reaction proceeds more slowly. Alcohol solvents also become involved in this competition for protonation. Formation reactions performed in methanol or ethanol under highly acidic conditions produced almost 100% TATP versus the same reactions performed in acetonitrile which produced 90 to 98% DADP (Table 5 entries 11 and 12 vs entry 1, 2, or 6).

Destruction of TATP results in the formation of 2,2'-dihydroperoxy-2,2'-diisopropyl peroxide (V) and acetone [14]. Depending upon the solvent used 2,2-dihydroperoxypropane (II) may also be observed. Under destruction conditions, the presence of water as well as alcohol retards TATP loss and prevents the formation of DADP. The presence of water and alcohol slowing the reaction can be attributed to the intermediate species competing with the solvent for protonation and the lack of formation of DADP can be attributed to the solubility of the intermediates in more polar and protic solvents. Under mildly acidic conditions the opening of the TATP ring is reversible and incorporation of a new acetone molecule is possible or decomposition to DADP may occur, explaining the presence of deuterated DADP in addition to deuterated TATP.

<Figure 7>

4.0 Conclusions

Previous work concluded that when solid TATP is the desired product, a 1:1 ratio of concentrated hydrogen peroxide (~70 wt%) and acetone with a modest amount of acid catalyst is optimal [5]. This work identified reaction intermediates and showed that the reaction between acetone and hydrogen peroxide proceeds, with or without acid. In the absence of acid 2-

hydroxy-2-hydroperoxypropane (I) forms as soon as hydrogen peroxide and acetone are mixed; with time other intermediates appear. Given sufficient time (weeks to months at room temperature) the cyclic peroxide TATP will precipitate without added acid [15]. In the presence of an acid catalyst the reaction proceeds faster resulting in solid TATP, DADP or a mixture of the two [5,8]. Under all conditions used in this study, TATP was the primary cyclic species formed initially. It has been established that decomposition of TATP to DADP is a pseudo first order process. The creation of DADP along with TATP under formation conditions was not a first order process. It can be concluded that DADP can be made directly via the linear peroxide intermediates, but the rate is slower than that of TATP formation, especially in the presence of water. DADP can also be formed via decomposition of TATP. TATP appears to be the kinetic product of the oxidation of acetone by hydrogen peroxide, while DADP is the thermodynamic product [11]. Water significantly affects the rate of formation of both cyclic peroxides, but suppression of DADP formation by water is much more marked.

The interaction of hydrogen peroxide and acetone, with or without acid, results in a variety of organic peroxides. TATP is sufficiently insoluble in water that it precipitates from HP/acetone solutions. If an organic solvent is present, which holds TATP in solution, then TATP may, with acid, undergo decomposition to the thermodynamic product, DADP. Nevertheless, both TATP and DADP are sufficiently insoluble in water that they are generally observed as the oxidation products of the hydrogen peroxide-acetone reaction rather than more soluble linear peroxide intermediates. With or without acid in the reaction mix, the same linear peroxides intermediates are formed, but without acid all the peroxides are formed more slowly; precipitation of TATP/DADP takes weeks or even months.

TATP formation is catalyzed by various acids. The differences observed between concentrated sulfuric and hydrochloric acids, forced us to consider the role of water. High water content in the reaction favored the formation of TATP; and less water, the formation of DADP [5]. Excessive amounts of water greatly retard the yield of solid product. Under near anhydrous conditions the formation of TATP and DADP were very rapid. In the presence of water, the formation of both was slow but the formation of DADP was suppressed to a greater extent than TATP. We postulate that low water content allows direct protonation of 2-hydroxy-2-hydroperoxypropane (I) converting it to 2-hydroxy-2'-hydroperoxy-2,2'-diisopropylperoxide (IV) that allows it to proceed to DADP. When water content is high, water is protonated and 2-hydroxy-2-hydroperoxypropane (I) disproportionates to acetone and 2,2-dihydroperoxypropane (II) (9). Species II can undergo further reactions to form TATP.

Insertion experiments suggest that mild acid conditions catalyze the opening of the TATP ring to form 2,2'-dihydroperoxy-2,2'-diisopropylperoxide (V), allowing a new acetone molecule to take its place or subsequent decomposition if the conditions are more severe. This point is important for the formation and destruction of TATP. Under destruction conditions it confirms that the process does not proceed to any appreciable extent via radical intermediates. The presence of the dihydroperoxy intermediates observed during destruction or under milder insertion conditions can only be rationalized by an ionic mechanism where acetone is removed leaving hydroperoxy species [14]. The presence of completely substituted TATP also implies one of two things: the TATP molecule opens and equilibrium with the intermediates is reestablished or the ring continually opens and recloses allowing all acetone molecules to be replaced with their deuterated counterparts. Both of these possibilities seem reasonable but which one dominates may depend upon the solvent used. Regarding formation, the insertion of

acetone seems to indicate that 2,2'-dihydroperoxy-2,2'-diisopropyl peroxide (V) will react with an acetone molecule to form the asymmetric hydroxy, hydroperoxy trimeric species prior to cyclizing to TATP. This supports the claim that the asymmetric species are short-lived intermediates leading to the cyclic peroxide products.

The destruction of TATP can also occur when using strong acids [16]. Water and alcohols show an effect in this process as well retarding the destruction of TATP but limiting the amount of conversion to DADP. Similar to the explanation for the effect of alcohols on formation of TATP the alcohols can participate in the reaction with concentrated acids reducing the amount of available acid to facilitate the reactions. The intermediates observed in the destruction reactions are also more soluble in the polar protic solvents stabilizing them against further reactions which could lead to the formation of DADP.

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List of Figures

Figure 1

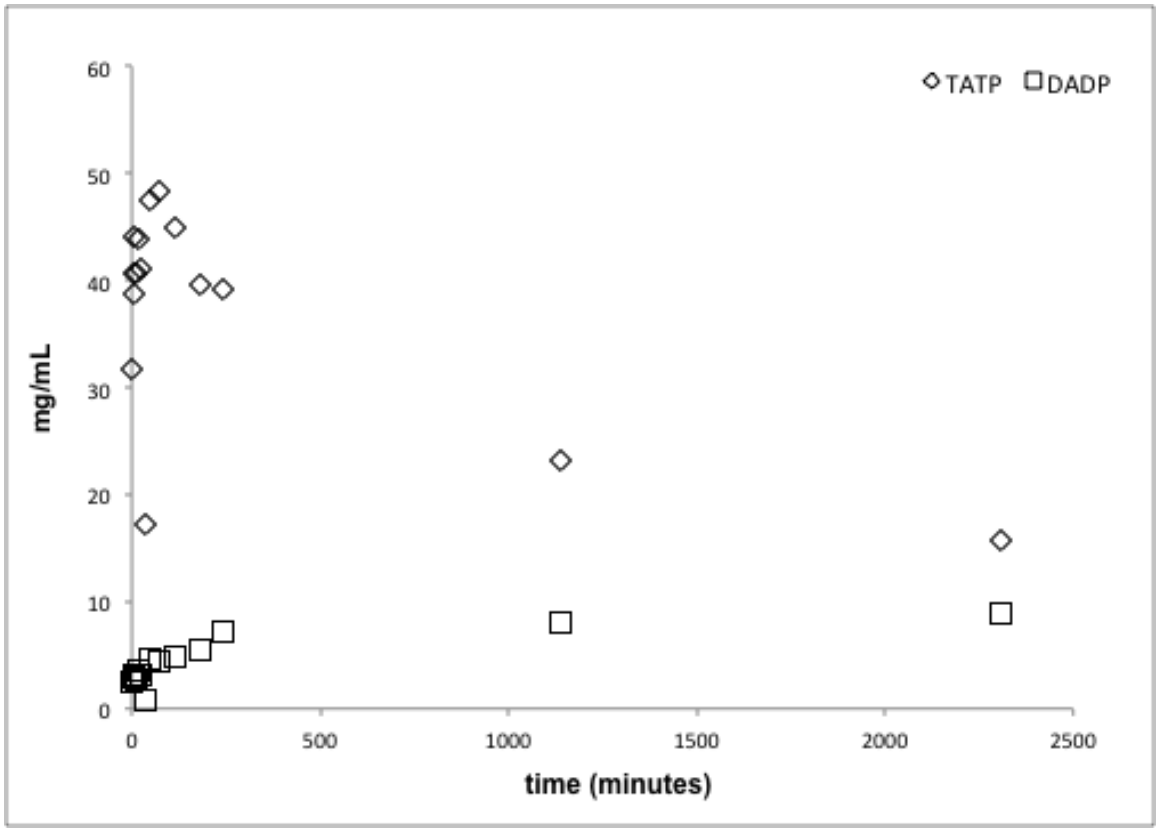

Fig. 1. Rate of Peroxide Formation with 1:1:1 (9.3 mmol) 65%HP:acetone: 96.5% sulfuric acid at 0^{o}C followed by GC/MS

Figure 2

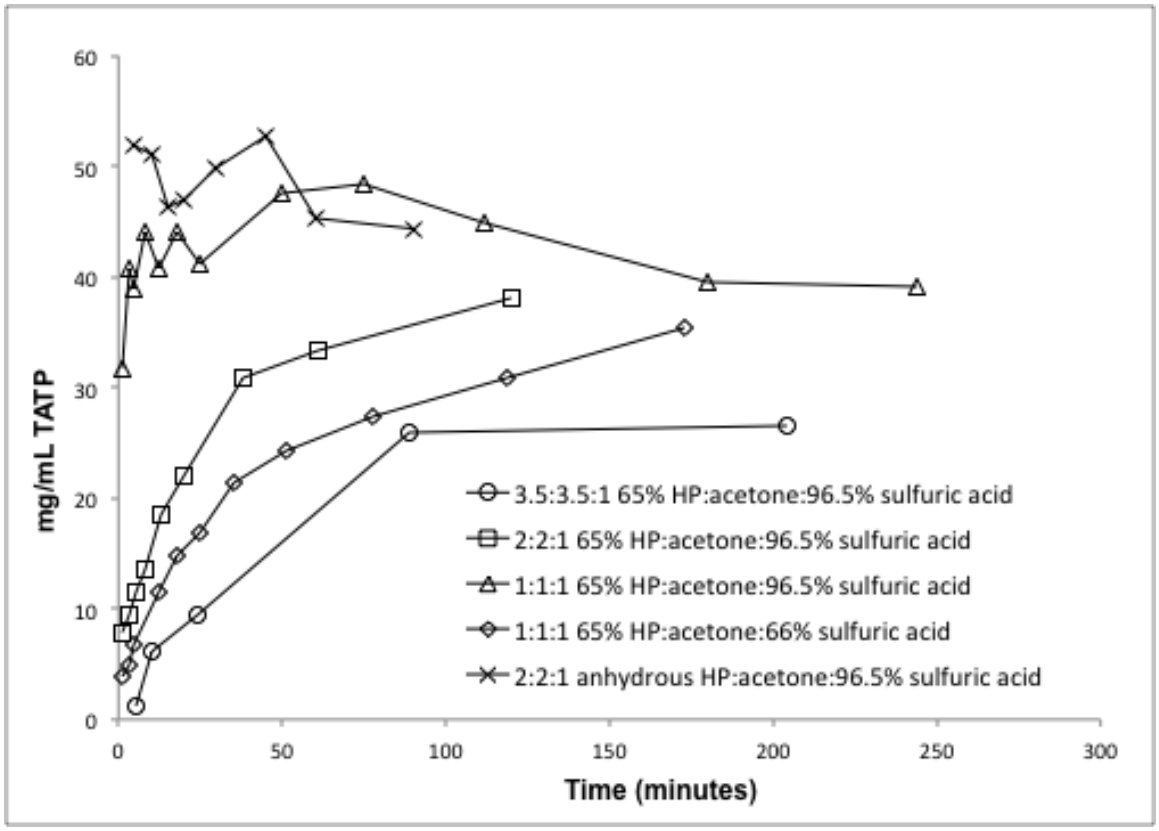

Fig. 2. Rate of TATP Formation followed by GC/MS: effect of varying the mole ratio of acid-to-HP, acid concentration, and water content.

Figure 3

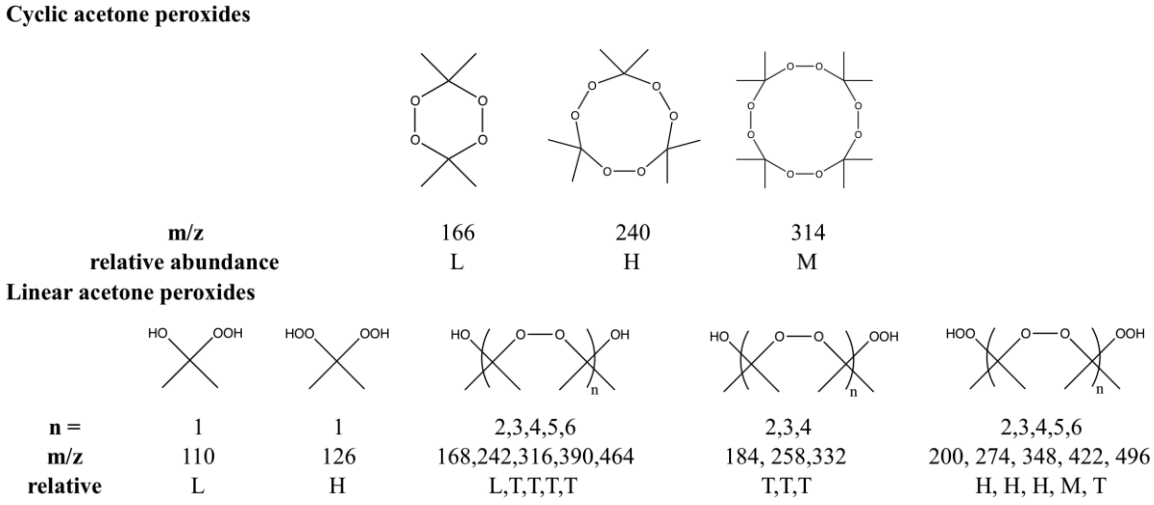

Figure 3. Products of HP/acetone reaction as observed by LC/MS

Figure 4

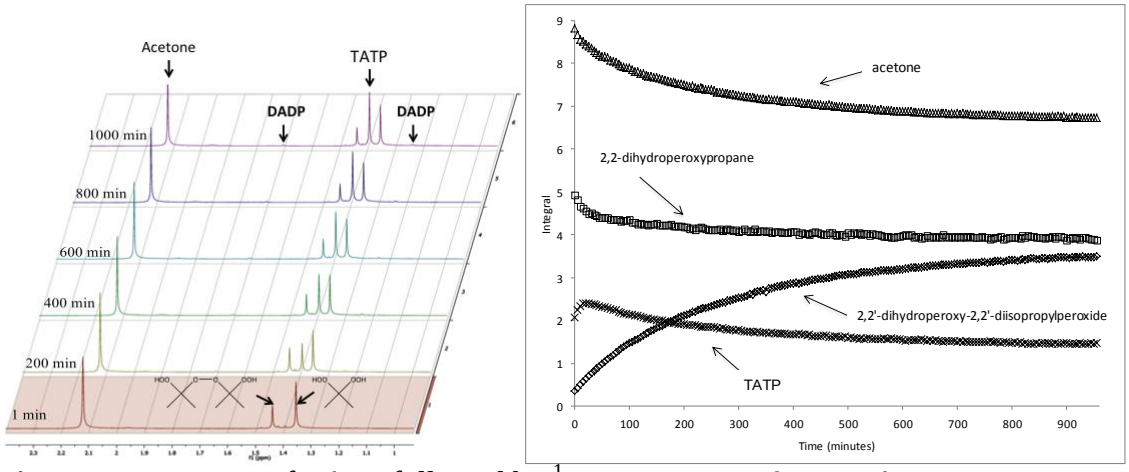

Figure 4. Formation of TATP followed by ^{1}H NMR using 40 uL TFA

Figure 5

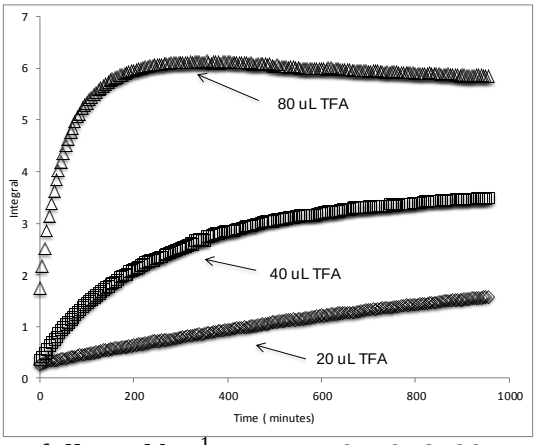

Figure 5. Formation of TATP followed by ^{1}H NMR 20, 40, & 80 uL TFA

Figure 6

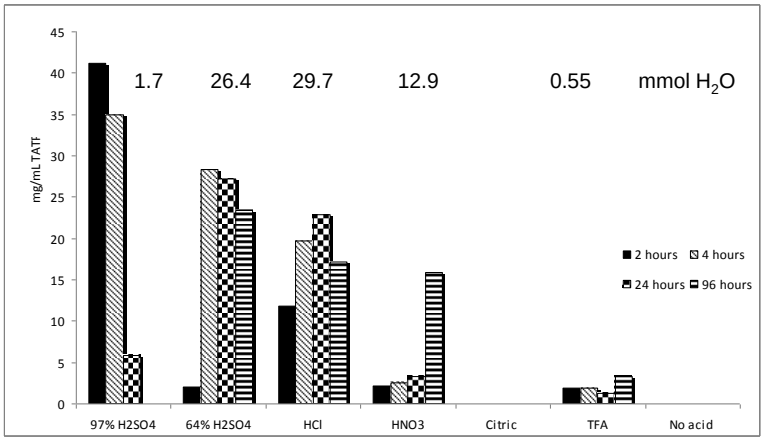

Figure 6. Rate of TATP Formation with 8.6 mmol each HP-Acetone-Acid vs Water

Figure 7

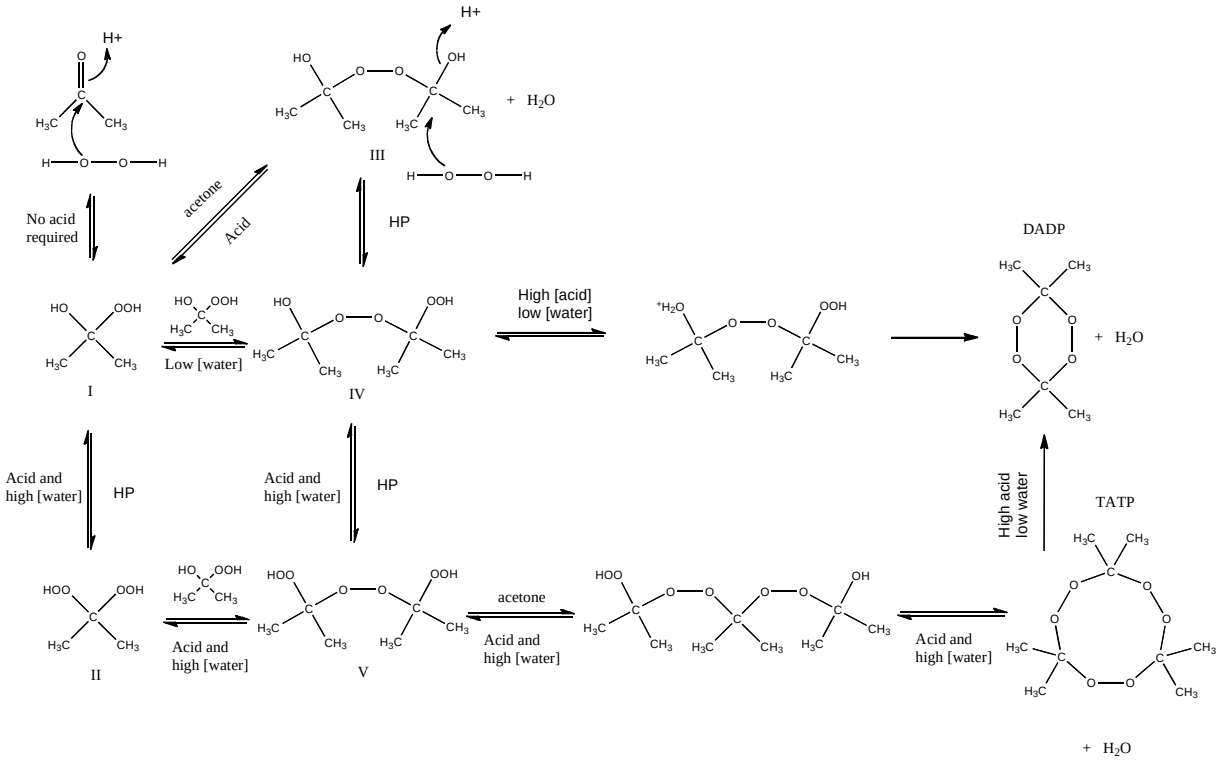

Figure 7. Mechanism for Synthesis of TATP and DADP

List of Tables

Table 1: NMR Resonance Assignments & Relative Abundance by Days of Reaction

1:1 HP:acetone no acid, in acetonitrile	^{1}H NMR (CH_3) ppm	^{13}C NMR (CH_3) ppm	^{13}C NMR (CO) ppm	Relative ^{1}H NMR abundance on day							
				0	1	3	5	7	10	12	14
2,2-hydroxy hydroperoxy propane (I)	1.38	24.2	102.37	L	L	M	M	S	S	S	S
2,2-dihydroperoxy propane (II)	1.38	20.2	109.41	M	L	L	L	L	L	L	L
2,2'-dihydroxy-2,2'-diisopropyl peroxide (III)	1.44	24.66	102.45	T	S	S	S	S	S	S	S
2,2'-hydroxy hydroperoxy-2,2'-diisopropyl peroxide (IV)	Uncertain	Uncertain	Uncertain								
2,2'-dihydroperoxy-2,2'-diisopropyl peroxide (V)	1.44	20.5	109.24	T	M	M	M	L	L	L	L
TATP (3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexoxonane)	1.42	20.97	107.77				T	T	T	S	S
DADP (3,3,6,6-tetramethyl-1,2,4,5-tetroxonane)	1.35, 1.79	20.8, 21.11	108.73	T	S	S	S	S	S	S	S
acetone	2.1	31	209	L	L	L	L	L	L	L	L

L = large; M = medium; S= small; T= tiny

Table 2: GC/MS Assignments for Various Products of Acetone/HP reaction

1:1 HP:acetone no acid, in acetonitrile	CI Mass spectrum (NH_3)				
	amount	mass	mass+1	mass+18	mass+18
2,2-hydroxy hydroperoxy propane (I)	s	92.1	93.1	110.1	127.1(+35)
2,2-dihydroperoxy propane (II)	m	108.1	109.1	126.1	126.1
2,2'-dihydroxy-2,2'-diisopropyl peroxide (III)	m	150.2	151.2	168.2	168.2
2,2'-hydroxy hydroperoxy-2,2'-diisopropyl peroxide (IV)	--	166.2	167.2	184.2	184.2
2,2'-dihydroperoxy-2,2'-diisopropyl peroxide (V)	l	182.2	183.2	200.2	200.2
dihydroxy trimer	s	224.3	225.3	242.3	242.3
hydroxy hydroperoxy trimer	--	240.3	241.3	258.3	258.3
dihydroperoxy trimer	m	256.3	257.3	274.3	274.3
TATP (3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexoxonane)	variable	222.2	223.2	240.2	240.2
DADP (3,3,6,6-tetramethyl-1,2,4,5-tetroxonane)	variable	148.2	149.2	166.2	166.2

L = large; M = medium; S= small; T= tiny

Table 3: Acid catalyzed insertion of labeled acetone into TATP

Labeled Acetone Insertion of TATP at 15°C for 17 hours

Exp. #	Experiment	Temperature (K)	Solvent	mL Solvent	Acid	µL Acid	mmols Acid	mg TATP	mmols TATP	Ratio Acid : TATP	Acetone	µL Acetone	mmols Acetone	Ratio of Acetone : TATP	Analysis	TATP	DADP
h^6-Acetone + d^{18}-TATP																	
1	h^0-acetone + d^{18}-TATP	288	CD3CN	1.20	TFA	30.0	0.403	48.0	0.200	2.01	d^0	50.0	0.680	3.40	^{1}H-NMR	insertion	insertion
2	h^0-acetone + d^{18}-TATP	288	CD3CN	1.20	TFA	40.0	0.537	48.0	0.200	2.68	d^0	50.0	0.680	3.40	^{1}H-NMR	insertion	insertion
3	h^0-acetone + d^{18}-TATP	288	CDCl3	1.00	TFA	20.0	0.268	48.0	0.200	1.34	d^0	40.0	0.544	2.72	^{1}H-NMR	insertion	insertion
4	h^0-acetone + d^{18}-TATP	288	CDCl3	1.00	TFA	30.0	0.403	48.0	0.200	2.01	d^0	40.0	0.544	2.72	^{1}H-NMR	insertion	insertion
5	h^0-acetone + d^{18}-TATP	288	(CH3)2CO+(CD3)2CO	1.00	none	0.0	0.000	120.0	0.500	--	d^0	900.0	12.242	24.49	^{1}H-NMR LC/MS	no insertion 7 days	no insertion 7 days
d^6-Acetone + h^{18}-TATP Reaction for 7 days																	
6	d^0-acetone + h^{18}-TATP	288	(CD3)2CO	1.00	none	0.0	0.000	111.0	0.500	--	d^6	1000.0	13.602	27.22	^{1}H-NMR LC/MS	no insertion 7 days	no insertion 7 days
7	d^6-Acetone + h^{18}-TATP	298	acetone+water		sulfuric		2.400	222.0	1.000	2.40	d^6		17.800	17.80	GC/MS	d^6TATP, TATP after 24 hr	d^{12} DADP, d^6 DADP & DADP + other in 48 hr
8	d^6-Acetone + h^{18}-TATP	298	EtOH		sulfuric						d^6		16.200		GC/MS	d^{18}TATP, TATP after 72 hr	d^{12} DADP, d^6 DADP & DADP + d-12 major
9	d^6-Acetone + h^{18}-TATP	298	ACN	10.00	TFA	150.0	2.013	222.0	0.925	2.18	d^6	75.0	1.021	1.10	GC/MS	both d^6, d^{12}, d^{18} TATP were observed	insertion observed, but no parent ion
10	d^6-Acetone + h^{18}-TATP	298	MeOH	10.00	TFA	150.0	2.013	222.0	0.925	2.18	d^6	75.0	1.021	1.10	GC/MS	both d^6, d^{12}, d^{18} TATP were observed	insertion observed, but no parent ion
11	d^6-Acetone + h^{18}-TATP	298	CHCl3	10.00	TFA	150.0	2.013	222.0	0.925	2.18	d^6	75.0	1.021	1.10	GC/MS	both d^6, d^{12}, d^{18} TATP were observed	insertion observed, but no parent ion
Chloro Acetone + d^{18} & h^{18}-TATP																	
12	1,3 dichloro acetone + d^{18}-TATP	288	CD3CN	1.20	TFA	40.0	0.537	24.0	0.100	5.40	dichloro	42.0 mg (S)	0.331	3.30	^{1}H-NMR & GC/MS	1 dichloro in TATP	no insertion
13	1,3 dichloro acetone + h^{18}-TATP	288	CD3CN	1.20	TFA	40.0	0.537	22.0	0.100	5.40	dichloro	42.0 mg (S)	0.331	3.30	^{1}H-NMR & GC/MS	1 dichloro in TATP	no insertion
14	1,1 dichloro acetone + h^{18}-TATP	288	CD3CN	1.20	TFA	40.0	0.537	22.0	0.100	5.40	dichloro	42.0 mg (S)	0.331	3.30	GC/MS	no insertion	no insertion
15	monochloro acetone + h^{18} TATP	288	CD3CN	1.20	TFA	40.0	0.537	22.0	0.100	5.40	dichloro	27.0	0.331	3.30	GC/MS	no insertion	no insertion
16	1,3 dichloro acetone + h^{18}-TATP	288	CD3CN	1.20	none	0.0	0.000	22.0	0.100	0.00	dichloro	42.0 mg (S)	0.331	3.30	GC/MS	no insertion	no insertion

Table 4: Acetone, HP, Acid, 1:1:1 (8.6 mmol each) & Varied H_2O

acetone (g)	50% HP (g)	water (mL)	96.5% sulfuric acid (g)	yield (mg)	% yield	% TATP	% DADP
0.5	0.586	0.25	0.876	308	48.3		100
0.5	0.586	0.5	0.876	246	38.6	7.6	92
0.5	0.586	0.75	0.876	348	54.6	81	19
0.5	0.586	1	0.876	378	59.3	100	
acetone (g)	**30% HP (g)**	**water (mL)**	**96.5% sulfuric acid (g)**	**yield (mg)**	**% yield**	**% TATP**	**% DADP**
0.5	0.976		0.876	218	34	11	89
0.5	0.976	0.25	0.876	140	22	72	28
0.5	0.976	0.5	0.876	265	42	72	28
0.5	0.976	0.75	0.876	161	25	89	11
acetone (g)	**30% HP (g)**	**water (mL)**	**37% HCl (g)**	**yield (mg)**	**% yield**	**% TATP**	**% DADP**
0.5	0.976		0.85	92.1	14	81	0
0.5	0.976	0.25	0.85	98.7	15	83	0
0.5	0.976	0.5	0.85	92.2	14	87	0
0.5	0.976	0.75	0.85	99.3	16	94	0

Table 5: GC/MS Analysis of Cyclic Peroxide Products vs HP/Acetone Reaction Conditions

	hydrogen peroxide grams, 66.8		acetone		sulfuric acid		acid:H_2O				crude	in situ	final	analysis
Line	wt%	mmol	gram	mmol	grams, 96.5 wt%	mmol	molar	order of addition	solvent	temperature	yield (g)	products	product	GC
1	2.73	54	2.96	51	10.4	102	1.450	HP/H_2SO_4/acetone	30 mL ACN	0C	2.93	n/a	98% DADP	uECD
2	2.73	54	2.97	51	10.5	103	1.460	HP/H_2SO_4/acetone	30 mL ACN	0C	2.6	n/a	98% DADP	uECD
3	2.74	54	2.90	50	10.3	101	1.436	acetone/H_2SO_4/HP	30 mL ACN	0C	3.11	n/a	100% DADP	uECD
4	2.74	54	2.96	51	10.34	102	1.440	acetone/HP/H_2SO_4	30 mL ACN	0C	3.1	TATP/dimer/DADP	87% DADP	MS
5	2.7	53	2.93	50	10.3	101	1.451	acetone/H_2SO_4/HP	30 mL ACN	0C	3.58	DADP	98% DADP	MS
6	1.6	31	1.8	31	5.16	51	1.284	HP/H_2SO_4/acetone	15 mL ACN	0C	1.37	TATP/DADP	90% DADP	MS
7	2.74	54	2.92	50	10.34	102	1.440	acetone/H_2SO_4/HP	30 mL ACN	-20C	3.01	TATP/DADP	77%DADP/7% TATP	MS
8	2.77	54	2.93	50	10.33	102	1.428	HP/H_2SO_4/acetone	30 mL ACN	-25C	3.34	TATP/dimer/DADP	22% DADP/67% TATP	MS
9	1.4	27	1.48	25	5.18	51	1.420	acetone/H_2SO_4/HP	15 mL ACN	-40C	1.71	TATP/dimer/DADP	93% TATP/1% DADP	MS
10	1.39	27	1.48	25	5.16	51	1.423	HP/H_2SO_4/acetone	15 mL ACN	-40C	1.75	TATP/DADP	90% TATP/1% DADP	MS
11	1.4	27	1.50	26	5.23	51	1.430	HP/H_2SO_4/acetone	15 mL EtOH	0C	0.96	n/a	98% TATP	uECD
12	1.39	27	1.5	26	5.24	52	1.439	HP/H_2SO_4/acetone	15 mL MeOH	0C	0.771	n/a	100% TATP	MS
13	1.36	26	1.48	25	5.83g >99% TFA	51	1.915	HP/TFA/acetone	15 mL ACN	0C		dimer->TATP, DADP		

Table 6: First order rate constants obtained from ^{1}H NMR at 288K following destruction of 45mg (0.203 mmol) TATP with acid or TATP formation from 100 uL acetone & HP (1.36mmol; 1:1 ratio) & TFA in 1.2mL d^{3}-CH_3CN

Reaction Type	Material Destroyed or Formed	Solvent	Acid	Volume (uL)	mmol acid	Rate Constant (1/min)	Rate Constant (1/sec)
Decomposition	TATP	Chloroform	TFA	30	0.392	0.0009	1.50E-05
Decomposition	TATP	Chloroform	TFA	40	0.522	0.0011	1.83E-05
Decomposition	TATP	Chloroform	TFA	60	0.784	0.004	6.67E-05
Decomposition	TATP	Chloroform	TFA	80	1.045	0.0149	2.48E-04
Decomposition	TATP	Chloroform	SA	10	0.188	0.0013	2.17E-05
Decomposition	TATP	Chloroform	SA	15	0.281	0.0018	3.00E-05
Decomposition	TATP	Chloroform	SA	20	0.375	0.0037	6.17E-05
Formation	TATP	Acetonitrile	TFA	20	0.261	0.0105	1.75E-04
Formation	TATP	Acetonitrile	TFA	40	0.522	0.029	4.83E-04
Decomposition	TATP	Acetonitrile	TFA	60	0.784	0.0007	1.17E-05
Formation	TATP	Acetonitrile	TFA	80	1.045	0.029	4.83E-04
Decomposition	TATP	Acetonitrile	TFA	100	1.306	0.0021	3.50E-05
Decomposition	DADP (30 mg)	Chloroform	SA	10	0.188	0.0022	3.67E-05

Table7

GC/MS monitoring of TATP (100 mg, 045 mmol) + H2SO4 (96.5wt%, 200 uL, 3.6 mmol)

Solvent (10 mL)	k (sec^{-1})	Result	Solvent (10 mL)	k (sec^{-1})	Result
Acetonitrile	2.41E-03	DADP			
25°C			90:10 acetonitrile:water	1.81E-04	no DADP
			80:20 acetonitrile:water	4.74E-05	no DADP
			70:30 acetonitrile:water	1.82E-05	no DADP
Methanol	1.98E-03	no DADP			
45°C			90:10 methnaol:water	2.13E-04	no DADP
			80:20 methanol:water	2.96E-04	no DADP
Ethanol	6.43E-04	no DADP			
45°C			90:10 ethanol:water	8.63E-05	no DADP
			80:20 ethanol:water	1.46E-04	no DADP
			70:30 ethanol:water	2.00E-04	no DADP
n-propanol	2.96E-04	no DADP			
45°C			90:10 n-propanol:water	1.72E-05	no DADP
isopropanol	8.86E-05	no DADP			
45°C			90:10 isopropanol:water	2.88E-05	no DADP
			80:20 isopropanol:water	1.01E-04	no DADP
			70:30 isopropanol:water	6.96E-05	no DADP
t-butanol	n/a	DADP/TATP			
45°C			90:10 t-butanol:water	n/a	DADP/TATP

*Reaction in t- butanol quickly converted some of the TATP to DADP but further change in concentrations was not observed. **Reaction in neat ACN used only 20 uL acid