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Ultrasonic Activation of Triacetone Triperoxide

By

LaTravia R. Dobson

A Thesis

Presented to the Faculty of

The Graduate College at the University of Nebraska

In Partial Fulfillment of Requirements

For the Degree of Master of Science

Major: Chemistry

Under the Supervision of Professor Patrick H. Dussault

Lincoln, Nebraska

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ULTRASONIC ACTIVATION OF TRIACETONE TRIPEROXIDE

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University of Nebraska, 2010

Adviser: Patrick Dussault

Triacetone triperoxide (TATP) is an organic peroxide that has received widespread attention in recent years. TATP is a ketone peroxide with a high active oxygen content. It is relatively shock sensitive, with explosive decomposition easily initiated, and is therefore considered a primary explosive. However, TATP is also a powerful explosive possessing about 83 % of the power of TNT. TATP can be prepared quickly and easily from inexpensive household chemicals in the absence of any specialized facilities, making it the explosive of choice for modern day terrorists.

TATP poses a major challenge for security and law enforcement services around the world. TATP and related peroxides do not include any of the functional groups commonly found in military or commercial explosives, making it difficult to detect. Furthermore, the sensitivity of TATP to shock, heat, friction and electrostatic discharge, characteristics which make it simple to trigger detonation, make the explosive extremely dangerous to handle in any quantity. In addition, there is currently no easy way to destroy bulk quantities of the explosive without detonating it in place. This poses a problem when/if the peroxide is found inside public places such as airports and train stations. In this thesis, we report investigations of a novel approach to the detection and/or deactivation of TATP based upon ultrasonication.

The views expressed in this article are those of the author and do not reflect the official policy or position of the United States Air Force, Department of Defense, or the U.S. Government.

To my family and friends

For your support and patience throughout the writing of this thesis,

THANK YOU!

-Tré

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1.0 Triacetone Triperoxide (TATP)

Triacetone triperoxide is a peroxide explosive that has seen a significant increase in recent use. Commonly known by the abbreviation TATP, triacetone triperoxide is also referred to as tri-cyclo acetone peroxide (TCAP) or Mother of Satan¹ in other parts of the world. Though very descriptive, these names do not reveal a great deal about the peroxide. However, breaking down the structure based on its chemical name, 3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexaoxacyclononane, provides the best insight into the properties of the peroxide. Triacetone triperoxide is an organic peroxide, a class of molecules containing an oxygen-oxygen bond as part of a C-O-O-C linkage. TATP belongs to a family of cyclic peroxides derived from the peroxyacetalization of ketones, termed “ketone peroxides”. The presence of a weak O-O bond, combined with the tendency of oxygen to form strong bonds to hydrogen (O-H) and carbon (C-O), results in many organic peroxides being thermochemically unstable² with regards to fragmentations or rearrangements to form nonperoxidic products. However, for many organic peroxides, the activation energy necessary to begin decomposition is sufficiently high that decomposition is not easily triggered. However, TATP and a number of other dimeric or trimeric ketone peroxides are highly dangerous materials at the other end of this reactivity spectrum. They not only have a high active oxygen content, defined as the fraction of peroxide oxygen relative to the molecular mass, but they are often relatively shock sensitive, with explosive decomposition easily initiated.²

Acetone, a simple ketone, is one of the most used and readily available chemicals in the U.S. It is a staple to most chemistry labs and a common industrial chemical (e.g.

cleaning agents, polymer precursor). When acetone is reacted with hydrogen peroxide and an acid, a mixture of acetone peroxides is made (Figure 1). These acetone peroxides include the dimer, diacetone diperoxide (DADP) and the trimer, triacetone triperoxide (TATP). A tetrameric acetone peroxide has reportedly been synthesized.³ However, the existence of the tetramer has been questioned due to the lack of a crystal structure or other unambiguous characterization. In particular, the structure as the tetramer⁴ has been characterized by others as an alternate and stable conformer of TATP.⁵ The chemistry involved in the formation of the acetone peroxides will be described in section 1.2.1.

Many peroxides are thermochemically unstable, but few have the combination of thermochemical instability and shock sensitivity found in TATP and DADP. Moreover, in contrast to traditional military and commercial high explosives, the acetone peroxides can be prepared quickly and easily from inexpensive household chemicals in the absence of any specialized facilities. As a result, TATP and related molecules have become known as the explosives of choice for terrorism. It is therefore of great importance to find improved methods for detection and controlled destruction of TATP and related acetone peroxides. Our research focused on two approaches to this challenge. The first approach investigated ultrasonication of TATP, with a goal of achieving controlled decomposition of this shock-sensitive material. The second approach investigated Brønsted and Lewis acid activation of TATP, with a goal of inducing heterolytic skeletal fragmentations which would enhance detectability and facilitate the chemical breakdown of the explosive material.

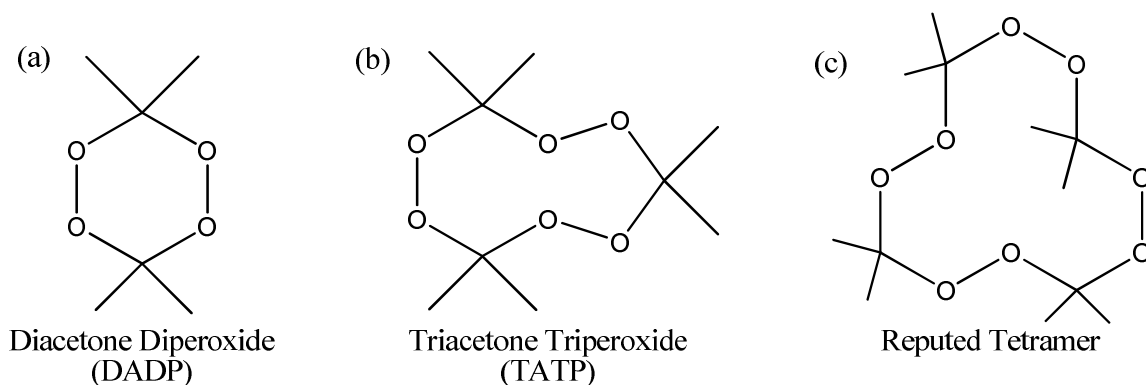


Figure 1: Structures of acetone peroxides. a) dimer, b) trimer, c) tetramer

1.1 History of TATP

TATP was first discovered by Richard Wolffenstein in 1895. While investigating coniine, the active principle in poisonous hemlock, Wolffenstein oxidized the plant extracts with hydrogen peroxide in a solution of acetone. After several weeks of reaction a precipitate began to form. Wolffenstein filtered off the precipitate and recrystallized it. He discovered the resulting crystals exploded upon heating, and he patented the product as an explosive.⁶ In the early 1900s, Adolf Baeyer and Victor Villiger revisited Wolffenstein's work and reported the syntheses of DADP and TATP with an acid catalyst.⁷ After Baeyer and Villiger's paper was published in 1900, there were very few reports on TATP for the next half century. During the 1950's, Milas and Golubovic, in the course of studies on organic peroxides, began investigating the products derived from reactions of hydrogen peroxide with ketones, and TATP was once again in the spotlight. Milas published three papers on TATP and other related organic peroxides.⁸⁻¹⁰ After Milas' work concluded, the topic of TATP became dormant again. From time to time it would reemerge in the science community when it or another peroxide was made by accident and caused a lab fire or explosion.¹¹⁻¹² Today, TATP has regained notoriety due

to its use by terrorists around the world. In 2001, TATP was used in combination with a secondary explosive in an attempt to blow up a plane in midflight by Richard Reid, the “shoe” bomber.¹³ A related compound, hexamethylene triperoxide diamine (HMTD) was employed in the 2005 bombings on the London train and bus systems.¹⁴

There are four main factors why TATP is so alluring to terrorists; 1) it is cheap and easy to make in large quantities from non-controlled materials; 2) it has a high explosive yield, possessing about 83 % of the power of TNT; 3) in contrast to other commercial explosives such as TNT or RDX, it can be detonated without a blasting cap or similar detonator; and 4) it is difficult to detect by traditional methods.

Although TATP is a cost efficient and powerful explosive, there is one very important reason why it has never been used in civil engineering or as a military munition; TATP is extremely sensitive to detonation by shock, friction, heat and electrostatic charge. Many people, ranging from the novice garage scientist to the professional chemist, have been injured in the manufacture and/or use of this explosive.¹⁵⁻

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1.2 TATP Formation, Characterization & Decomposition

1.2.1 The Chemistry of Formation

The formation of triperoxides has been studied by many peroxide chemists, the foremost being Nicholas Milas⁸⁻¹⁰. Overall, the formation of TATP can be summarized as the repeated nucleophilic addition of hydrogen peroxide to acetone followed by the acid-catalyzed condensation/dehydration of peroxy/hydroxyl acetal intermediates. Two primary pathways to forming TATP are described below, with the most notable difference between the routes being the point of acid addition. Story’s approach begins

with the formation of 1,1'-Dihydroxypropyl peroxide(I).¹⁷ To form the dihydroxypropyl peroxide, two molecules of acetone are reacted with one molecule of hydrogen peroxide. Though this intermediate was not isolated by Story et al, its formation during this reaction was confirmed by Antonovskii et al who synthesized intermediate I solely by reacting the ketone with hydrogen peroxide in a neutral solution.¹⁸

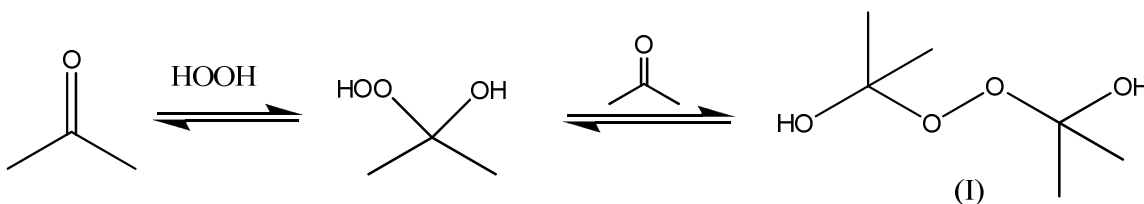


Figure 2: Formation of 1,1'-Dihydroxypropyl peroxide

The next step involves the conversion of one of the hydroxyl groups to a hydroperoxy group to form 2-hydroperoxy-2'-hydroxy diisopropylperoxide(II). Intermediate II is created in an acid-catalyzed condensation involving reaction of intermediate I with one molecule of hydrogen peroxide. Story confirmed that even with a large excess of hydrogen peroxide, intermediate I cannot convert to the hydroperoxy peroxide (II) without the addition of acid. Story referenced two separate procedures, one by Kharasch & Sosnovsky and the other by Ledaal, for the synthesis of intermediate (II)¹⁹⁻²⁰, resulting in yields of 65 % and 53% respectively.

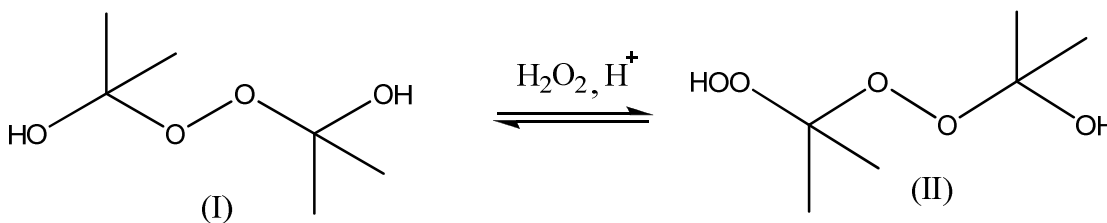


Figure 3: Formation of 2-Hydroperoxy-2'-hydroxy diisopropylperoxide

The same conversion of the hydroxyl group to a hydroperoxide is repeated to form 2,2'-dihydroperoxy-2,2'-diisopropylperoxide (III) in step three. For this synthesis,

Story referenced a procedure originally reported by Criegee²¹. No yield was given for the reaction.

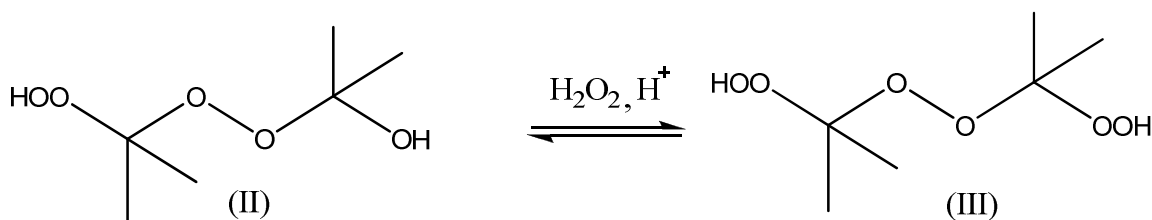


Figure 4: Formation of 2,2'-Dihydroperoxy-2,2'-diisopropylperoxide

The final step is the most intriguing in the Story synthesis pathway. To form TATP, intermediate III is dissolved in methanol in the presence of a trace amount of acid, which is present throughout the reaction. Story describes the reaction as “very exothermic” with the solution heating up so rapidly as to come to reflux.¹⁷ Based upon the stoichiometry of the reaction, it seems most likely that intermediate III undergoes disproportionation with three dihydroperoxy peroxides required to generate two molecules of TATP. After the reaction subsides and the solution is cooled, TATP is retrieved in 81% yield. Before settling on a method to be used throughout his experimentation Story tested synthesis methods for TATP by Kharasch-Sosnovsky and Ledaal. The one-pot synthesis of TATP by the Kharasch-Sosnovsky method gives the product in 72% yield while the Ledaal method results in an 83% yield.

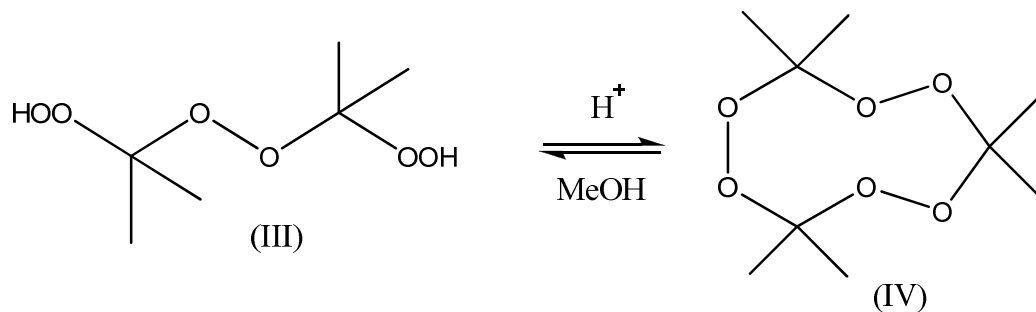


Figure 5: Formation of TATP

The approach taken by Milas is significantly different than that taken by Story, et al due to the addition of acid from the very start.⁹ In step one, acid and excess hydrogen peroxide are mixed with acetone to produce 2,2-dihydroperoxypropane in 95% yield. Next, acetone is added to create the 2-hydroperoxy-2'-hydroxypropyl-2,2'-diisopropylperoxide(II). Milas was able to isolate intermediate II in trace amounts by chromatography on a cellulose powder column. He dedicated a great deal of time to optimizing the synthesis and isolation of 2,2-dihydroperoxypropane, ultimately achieving the successful synthesis of this target.¹⁰ It should be noted that there are now numerous approaches known for the high-yielding synthesis of *geminal*-dihydroperoxides.²²

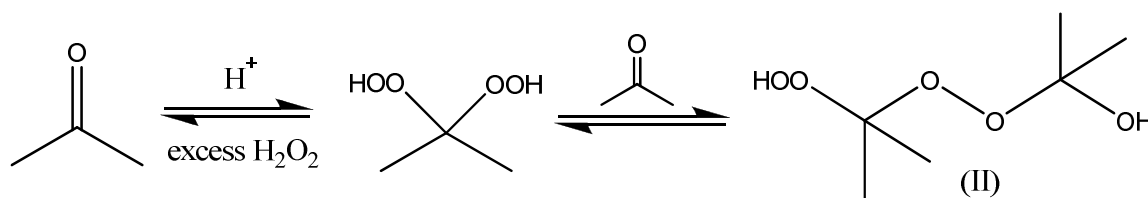


Figure 6: Formation of 2-Hydroperoxy-2'-hydroxypropyl-2,2'-diisopropylperoxide in one step

The Milas and Story approaches followed the same progression to reach intermediate III. Both approaches use acid and hydrogen peroxide to convert the hydroxyl group to a hydroperoxy group, although the method used by Milas took ten days to produce a 20% yield of the 2,2'-dihydroperoxy-2,2'-diisopropylperoxide product. (See Figure 4 above) However, Milas uses a different approach to get to TATP. He speculates that the addition of acetone creates 1,1,4,4,7,7-hexamethyl-1,4-diperoxy-1,7-hydroperoxy-7-hydroxyperoxide.

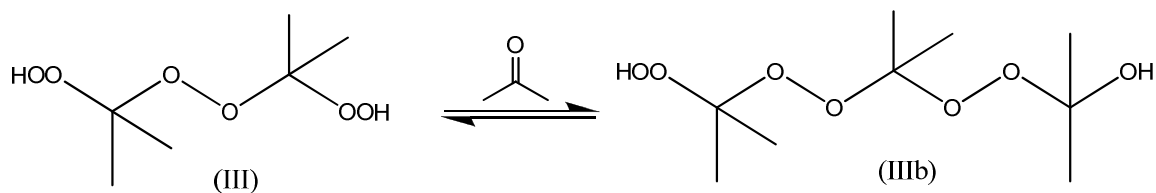


Figure 7: Proposed formation of 1,1,4,4,7,7-hexamethyl-1,4-diperoxy-1-hydroperoxy-7-hydroxyperoxide

The subsequent addition of acid results in a cyclocondensation with a loss of water to form a quantitative yield of TATP. See Attachment A for a full mechanistic scheme.

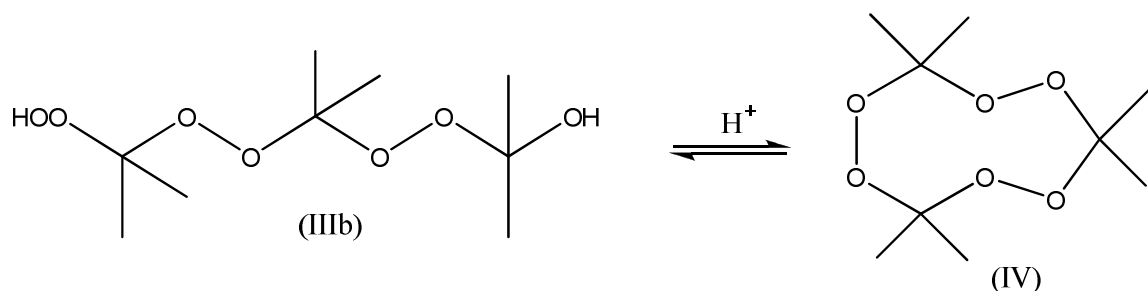


Figure 8: Formation of TATP from III

1.2.2 Syntheses of TATP and related acetone peroxides

There are a number of other easily accessible synthetic routes to choose from when preparing TATP. One procedure for the production of TATP was even posted on the website Wikibooks, an affiliate of Wikipedia, for a short time. The procedure is an adaptation of the Milas procedure, modified to account for the limitations of acquiring research grade ingredients outside of a laboratory setting. Table 1 summarizes six syntheses of TATP, highlighting the concentration of H_2O_2 employed, the catalyst system, the reaction times and temperature, and, when available, the isolated yield. Most procedures for TATP synthesis result in a mixture of TATP, DADP and other acetone

peroxides. Though similar in composition and structure, the peroxides can easily be differentiated by TLC and NMR.²³⁻²⁴

Table 1: Selected Examples of Reported Conditions for TATP Syntheses

Author	H ₂ O ₂ (%)	Catalyst used	Rxn Temp	Rxn Time	Precipitation Time	Yield
Wolffenstein ⁶	10	Phosphoric acid	RT	Several days		Quant.*
Wikipedia ²⁵	35	H ₂ SO ₄ or HCl	<10°C	15 min.	24 hrs	NR [□]
Milas et al ¹⁰	50	Conc. H ₂ SO ₄	0°C	3 hrs.	none	>90%
Kim et al ²⁶	30	Titania-incorporated mesoporous materials	25-50°C	2-7 days		2.8%
Kharasch & Sosnovsky ¹⁹	30	Glacial acetic acid/ 10% perchloric acid	~20°C	24 hrs.	24 hrs.	72%
Ledaal ²⁰	98	70% Perchloric acid	RT or <24°C	5 days		83%

*= No numerical yield was reported, however, it was stated that an almost theoretical yield was obtained.

□ = Not reported

1.2.3 Decomposition of TATP

In traditional explosives such as TNT and RDX, the composition of the molecule is chemically balanced in support of explosive combustion. For example, the combustion of two molecules of TNT produces three molecules of carbon dioxide, 1 molecule of carbon monoxide, five molecules of water, three molecules of nitrogen gas and ten molecules of solid carbon or soot.²⁷ However, TATP is reported to detonate via an entropic explosion, an explosion in which the reactants undergo a large change in volume without releasing a significant amount of heat.²⁸ Dubnikova et al used molecular modeling to study the explosive properties of TATP based upon analysis of transition states, potential reaction intermediates and predicted final products. Dubnikova et al concluded that the decomposition of TATP is not strongly favored by changes in enthalpy and therefore does not produce oxidation products as expected. Instead, decomposition is proposed to be driven by a tremendous increase in entropy, resulting from the formation and release of one ozone molecule and three acetone molecules for

each molecule of TATP. The calculations also predict that under other conditions, additional side products could be formed, such as singlet molecular oxygen, O₂, methyl acetate, ethane and carbon dioxide. Most of these products have been observed experimentally and reported by Oxley et al at the University of Rhode Island.²⁹ Although the Oxley analysis did not detect singlet molecular oxygen or O₂, the work done does support the theory that decomposition of TATP is essentially an entropic explosion.²⁹ This information is an important part of the overall characterization of TATP and is vital to the post-blast detection of the explosive.

1. 3 TATP Characterization & Detection

When TATP first re-emerged in the mid 1990's, not many people knew what it was, including the law enforcement officials who were handling it. As TATP re-gained popularity, it became more evident that we lacked a way to easily and safely differentiate it from every other white powder. To this end, many researchers began working on methods for detection. However, what was first required was good characterization of TATP and its decomposition products.

Some of the first characterizations of the explosive came from the forensic community. In 2002, the Forensic Explosives Laboratory (FEL), an organization that assists the UK police in criminal investigations involving explosives on the UK mainland, published an article on the characteristics of TATP, DADP and HMTD. The paper described the physical characteristics of the explosives as well as their sensitivity to initiation, and described applicable analytical techniques.²⁴ The same year, Oxley et al reported that the main decomposition product of TATP is acetone, with smaller amounts of CO₂, methyl acetate and acetic acid.²⁹ This information could possibly be used by law

enforcement agents to determine if TATP had been used during post-blast analysis. Another characteristic of TATP that could lead to its detection is vapor pressure. Depending on its vapor pressure, it may be possible to create a standoff method of detection either by doing a vapor space analysis of a would-be bomber or through the use of scent-sniffing dogs. Two groups have worked on determining the vapor pressure of TATP and have published two different answers. Using gas chromatography with electron capture detection (GC/ECD), the Oxley group calculated the vapor pressure to be 7 Pa.³⁰ The Ramirez group, using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) came up with a figure of 9.2 Pa for the vapor pressure at 25°C.³¹ Both numbers are much higher than that of TNT, which means that methods based upon vapor sampling may be able to detect TATP more successfully from a greater distance than TNT assuming that the sensitivity threshold for the analytical method is met.²⁹

There are four main reasons why the rapid detection of a peroxide-based explosive like TATP is a difficult challenge based upon conventional analytical techniques. First, TATP is thermally labile. Second, TATP lacks nitro, aryl, or other functional groups that are easily probed by mass spectrometry. Third, TATP has no significant ultraviolet absorption. Fourth, TATP does not exhibit fluorescence.³²⁻³⁴ Despite these limitations, advances have been made in recent years to enable rapid and sensitive detection of TATP in the pure form and in blast residues.

A non-destructive analytical method for the bulk detection of TATP was reported. The technique uses reverse phase high performance liquid chromatography (RP-HPLC) in conjunction with on-line Fourier transform infrared (FTIR) detection to analyze TATP

with no derivatization or decomposition of the peroxide.³³ Another technique for bulk detection of TATP is ion mobility spectrometry (IMS) coupled with a triple quadrupole mass spectrometer. This technique is useful because IMS is already being used to detect explosives in high security risk areas.³⁵ One drawback is that the limit of detection of IMS detection for TATP, 187 microgram per milliliter in toluene, is much greater than the 0.015 micrograms per milliliter detection limit for TNT³⁶. However, due to the nature of TATP as an explosive (i.e. its sensitivity and the rarity of finding it in large quantities) the requirement to use bulk detection techniques is low, making trace analysis the best fit.

In 2006, a simple spray technique was created for the rapid, specific and sensitive detection of TATP through desorption electrospray ionization (DESI) mass spectrometry of a TATP-alkali metal complex.³⁷ Later that year, a comparison of 7 different analytical techniques showed that positive ion chemical ionization (PICI) using ammonia as a reagent gas is the preferred analytical method for the detection of TATP. This method allows for low limits of detection, in the picogram range, and an abundant diagnostic adduct ion.³⁸ However, TATP was also detected by single photon ionization (SPI) time-of-flight (TOF) mass spectrometry³⁹ and, with the application of selected-ion flow tube (SIFT) mass spectrometry, was detected with no sample preparation and much greater sensitivity.³² TATP was analyzed by electrospray ionization mass spectrometry (ESI-MS) giving a 62.5 nanogram limit of detection.⁴⁰ However, both TATP and the reputed acetone peroxide tetramer can be detected in situ at significantly lower limits upon complexations with alkali metals or ammonium ions and through the use of DESI and desorption atmospheric pressure chemical ionization (DAPCI) techniques.³⁴

The advent of fluorescent detection techniques constituted a major advance in detection of TATP. The first fluorescent detection technique was developed by Schulte-Ladbeck et al. They created a field test in which TATP was first decomposed by ultraviolet irradiation to generate hydrogen peroxide, which was then detected by an assay employing oxidation of *p*-hydroxyphenylacetic acid (pHPAA) in the presence of horseradish peroxidase.⁴¹ The oxidation of pHPAA generates a strongly fluorescent dimer. The same group later showed that both TATP and HMTD could be detected from a mixture after separation by RP-HPLC⁴. In April 2008, Malashikhin and Finney of the University of Zurich reported a related technique as part of the first visual fluorescent assay for the detection of TATP. Irradiation of TATP with ultraviolet light resulted in release of hydrogen peroxide, which, in the presence of catalytic methyltrioxorhenium, oxidized a sulfoxide profluorophore⁴². Later that year, Germain and Knapp of the University of Massachusetts at Amherst reported the fluorescent detection of TATP using a zinc(salen) fluorophore. One significant difference between this method and those previously discussed is the use of acetic acid to release the peroxide. Once free, the peroxide was combined with zinc acetate to activate the prochelator through a deboronation reaction. This visual assay has the highest sensitivity of any TATP detection techniques thus far with a limit of detection of 2.2 parts per billion (ppb).⁴³

An exciting discovery in the area of identification of bulk samples of TATP was the invention of the Peroxide Explosives Tester or P.E.T manufactured by ACRO Security Technologies.⁴⁴ Professor Ehud Keinan, the founder of ACRO and inventor of the P.E.T., designed the unit to detect TATP by the enzyme-catalyzed oxidation of an organic substrate by hydrogen peroxide to produce colored pigments. The result is a

visual indicator of the presence of TATP using an instrument that can fit in your pocket. Another positive factor of this invention is the potential affordability; current prices on the internet are in the range of \$25/unit.

Table 2: Sensitivities of TATP analysis techniques.*

Technique	Sensitivity	Form Analyzed
ACRO P.E.T.	1-2 mg	solution (various solvents)
Sulfoxide Profluorophore fluorescence	444 ppm	solution (toluene/ethanol)
RP-HPLC + FTIR	222 ppm	solution (acetonitrile)
Ion Mobility Spectroscopy	187 ppm	solid & solution (toluene)
ESI-MS	12.5 ppm	solution (methanol)
PICI	0.50 ppm (500 ppb)	solution (acetonitrile)
RP-HPLC + fluorescence	0.44 ppm (444 ppb)	solution (acetonitrile)
Field test	0.18 ppm (178 ppb)	solution (acetonitrile)
DAPCI	0.10 ppm (100 ppb)	solution (methanol)
SIFT-MS	10.0 ppb	vapor
Zn(Salen) fluorescence	2.22 ppb	solution (methanol)

*Sensitivities were converted to ppm or ppb for comparison purposes.

1.4 Preparative Work

In preparation for our planned research into decomposition and detection of TATP, it was necessary to develop procedures for preparing pure samples of the substance. During the initial research, many paths were tested for the synthesis, extraction, isolation and recrystallization of TATP. First, the order that the reactants were added to the reaction was tested. The two predominantly used methods were the addition of the acid to a mixture of hydrogen peroxide and acetone and the addition of acetone to a mixture of the hydrogen peroxide and the acid.

Next, extraction and isolation were optimized. Originally, diethyl ether was used to extract the TATP and flash chromatography was used to separate TATP from DADP and the smaller peroxides. However, the silica used for the flash column interacted with the peroxides causing them to recyclize to DADP alone. Research showed that pentane

was a better extraction solvent for isolating TATP because neither DADP nor the smaller peroxides produced, such as dihydroperoxypropane, was soluble in it.

Next, recrystallization was attempted. Initially, diethyl ether was used to recrystallize TATP; however, the ether and TATP proved to be too volatile and would readily sublime if left in an open container. Next, a mixture of acetonitrile and water was attempted; though successful, the end product was not 100% pure. Finally, TATP was dissolved into warm pentane or the TATP in pentane was slowly heated in container with a vented cap and placed into the refrigerator at 4 °C causing the TATP to recrystallize and fall out of solution in about 10 minutes. By NMR, the recrystallization resulted in a purity of 98% or more.

Finally, in an effort to determine the strength of the catalyst required to push the reaction to completion, different reactants were used to catalyze the synthesis of TATP. The first catalyst attempted was iodine. Iodine was specifically chosen because it had been shown to effectively catalyze the conversion of ketones to *gem*-dihydroperoxides, a key intermediate in the synthesis of TATP²². A small amount of product was detected by TLC but isolating it from the iodine proved impossible. Sublimation of the iodine was attempted on the rotary evaporator, but resulted in the sublimation of the product instead. Next, sodium thiosulfate pentahydrate was used to eliminate the iodine; though the iodine was successfully removed, the product was also destroyed. We also investigated the use of methyl rhenium trioxide (MTO), which has also been employed as a catalyst for conversion of ketones to the corresponding *gem*-dihydroperoxides.⁴⁵ The TATP synthesis with 2 mole percent MTO as the catalyst resulted in a 42% yield of the product. Oxone was also used in an attempt to synthesize TATP due to the presence of potassium

peroxymonosulfate in the mixture. It has been hypothesized that the production of TATP is due to the reaction of Caro's acid, also known as peroxymonosulfuric acid, and acetone. If this is true, the potassium peroxymonosulfate should react with the acetone in the same way and produce TATP. The reaction of oxone with acetone did not produce TATP, but did result in an unidentified, significantly pure product. In the end, we returned to a procedure similar to that employed by Milas, in which acetone was added to a cold solution of hydrogen peroxide and sulfuric acid. Full details are provided in the experimental section below.

TATP is an organic peroxide that has seen a significant increase in exposure and use in recent years. The ketone peroxide has a high active oxygen content making it relatively shock sensitive, with explosive decomposition easily initiated. As a primary explosive TATP has a high explosive yield, possessing about 83 % of the power of TNT and can be prepared quickly and easily from inexpensive household chemicals in the absence of any specialized facilities, making it the explosive of choice for modern day terrorists. The attractiveness of TATP as a weapon to terrorists has made it a priority problem for law enforcement around the world. TATP and related peroxides do not include any of the functional groups commonly found in military or commercial explosives making it difficult to detect. In addition, there is currently no easy way to destroy bulk quantities of the explosive without detonating it in place. This poses a problem when/if the peroxide is found inside public places such as airports and train stations. For this reason, we investigated a novel approach to the detection and/or deactivation of TATP. Capitalizing on TATP's sensitivity, ultrasound was studied as a

means of inducing the decomposition of the explosive with the application of remotely discarding of the dangerous substance.

1.5 Experimental

1.5.1 Safety

Although no specific problems were experienced in the course of this work, standard safety precautions should be employed for all work with organic peroxides². TATP is a very unstable primary explosive; it is sensitive to shock, friction, heat and electrostatic charges. Extreme care should be taken when synthesizing and/or handling it. To mitigate the chances of accidental initiation, TATP should only be synthesized and handled in small quantities. Once synthesized, it should be stored in solution using containers with non-threaded caps to avoid detonation of sublimed crystals. Proper safety equipment should be used in the manufacture and handling of this explosives (i.e. safety goggles and gloves, blast shields and splinter-proof vessels).

1.5.2 Reagents and Chemicals

All reagents and solvents were used as supplied commercially, except THF and CH_2Cl_2 , which were distilled from $\text{Na}/\text{Ph}_2\text{CO}$ and CaH_2 , respectively.

1.5.3 Instrumentation

Unless otherwise indicated, ^1H spectra were recorded at 300 and 400 MHz and ^{13}C spectra were recorded at 75 and 100 MHz in CDCl_3 ; individual peaks are reported as (multiplicity, integration, coupling constant in Hz). Infrared spectra were recorded on an FTIR spectrophotometer as neat films unless otherwise stated, with selected absorbances reported in wavenumber (cm^{-1}). Progress of reactions involving peroxides were monitored by thin layer chromatography (TLC), using an N,N'-dimethyl-p-

phenylenediamine indicator (selective for peroxides and other oxidants)⁴⁶ or staining/charring with 1% ceric sulfate/2.5% ammonium molybdate in 10% aq. H₂SO₄, a general stain. TLC was performed on 0.25 mm hard-layer silica G plates.

1.5.4 Synthesis of 3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexaoxacyclononane.

Hydrogen peroxide (50%, 0.02 moles) was added to a 250 milliliter round bottom flask with a stir bar. The flask was chilled to 0°C with an ice bath; the temperature of the reaction flask was monitored with a thermometer. Concentrated sulfuric acid (0.05 moles) was added to the flask with stirring. The temperature of the reaction began to rise so the mixture was allowed to stir for approximately 5 minutes to lower the temperature. Acetone (0.02 moles) was slowly added to the reaction at a rate which ensured that the reaction temperature did not rise above 10°C. After complete addition of the acetone, the reaction was allowed to stir for one hour at 0°C. The stir bar and ice bath were then removed and the mixture was slowly warmed to room temperature; within minutes the precipitate began to form. The reaction was allowed to stand overnight to increase precipitation, yielding a white crystalline powder with an acrid smell.

The precipitate was vacuum filtered and washed with saturated aqueous sodium bicarbonate followed by deionized water to get rid of any remaining acid. To dry the crude product, phosphorus pentoxide and a drying pistol were used. To obtain pure TATP, the crude product was dissolved in warm pentane for recrystallization. This step can also be used to remove the water from the final product. The sample was placed in the refrigerator to speed up the recrystallization. TATP was obtained in 70% yield as a colorless crystal, mp 96°C (lit 90-97°C)^{4,8,20}; ¹H NMR (CDCl₃) δ 1.46 (s, 18H); ¹³C NMR (CDCl₃) δ 21.30, 107.48; TLC *R_f* 0.54 (10% ethyl acetate/hexanes, peroxide dip).

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2.0 Ultrasonication

Ultrasonication is the use of sound at frequencies above 20 kHz to produce waves. These sound waves can be transmitted through any substance that has elastic properties, defined as the ability to return to its original shape after the stress that deformed it has been removed. The vibrations from the ultrasonic device are transmitted to a molecule of the substance which then conveys that same vibration to another molecule before returning approximately to its original position¹. The effects that these vibrations have on a substance are dependent upon many factors, one of the most important being phase. This chapter will begin with discussions on the history and uses of ultrasonication in chemistry as well as the theory behind the effects of ultrasonication on a substance. Next, the results and analysis of the ultrasonication of TATP will be discussed. Finally, the chapter will conclude with the future of this research and its potential applications.

2.1 Background

Ultrasonication was first studied in the early 1900's as a specific branch of the field of acoustics. At the time, the main focus was on the phenomenon of cavitation, which was first reported in 1895 by Sir John Thornycroft and Sydney Barnaby². They were called on to investigate the poor performance of a new screw driven destroyer, the H.M.S. Daring. The destroyer was designed for 27 knots but would max out at 24 knots and though the engine had little vibration, there seemed to be quite a bit of vibration throughout the ship. It was found that the propeller blade was pitted and eroded resulting in insufficient thrust. Cavitation, caused by the blade of the propeller quickly cutting through the water produced enough negative pressure to create high pressure bubbles that, upon collapsing, eroded the propeller and over time rendered it useless³.

Ultrasonication has been employed for decades in a multitude of fields. In the early 1900s it was used commercially with an echo-sounding technique to estimate the depths objects under water. This advancement led to the invention of sound navigation and ranging (SONAR)⁴ and eventually radio detection and ranging (RADAR). As advancements continued ultrasonication found new uses in a broader range of fields. While industry and medicine have had a long history in the use of ultrasonics, chemical applications have emerged more recently.

2.2 Uses in Chemistry

Most of the applications of ultrasonication in chemistry can be placed into four main categories; 1) reactions with metal surfaces; 2) reactions with powders; 3) emulsification; and 4) catalysis of homogeneous reactions⁵. Though these applications represent the majority of the ways that ultrasonication is used in chemistry, the technique can be employed in a number of useful ways. See reference 6 for a review of the many ways that ultrasound can be utilized in chemistry.

Ultrasonication is now widely used to assist in initiation of Grignard, Reformatsky, and related reactions involving reduction of an organic halide at a metal surface. A typical example of this is the coupling of Grignard reagents with 1,3-dioxolanes, in which sonication has been shown to double or even triple the yields obtained by stirring alone⁷ (See Figure 10 and Table 3 below).

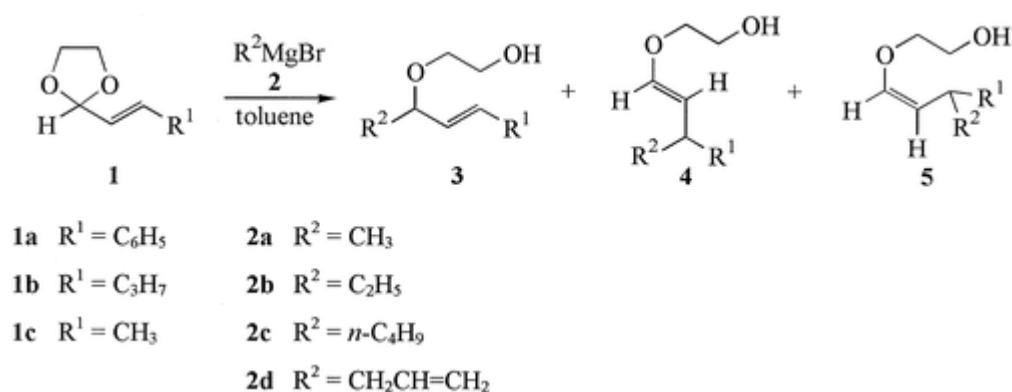


Figure 9: Reaction Scheme for Grignard and 1,3 Dioxolane⁷

Table 3: Influence of Ultrasound on Addition of Grignard Reagents to 1,3-Dioxolanes⁷

Entry	Acetal	R ² M	Stirring Yield (%)	Ultrasound Yield (%)
1	1a	2a	1	8
2	1a	2b	9	54
3	1a	2d	5	7
4	1b	2a	2	40
5	1b	2b	16	72
6	1b	2d	1	31
7	1c	2a	6	37
8	1c	2b	22	63
9	1c	2d	16	36

The authors attributed the increase in activity mainly to the cleaning of the metal surface⁸. However, a more recent example in a separate field suggests that the effects on reactivity may go well beyond simply cleaning the surface. For instance, ultrasound has been shown to improve the leaching rate of uranium from magnesium difluoride when compared to conventional stirring methods⁹. The authors' research concluded that the increase in reactivity could be attributed to two factors: 1) MgF₂ fragmentation, or the breaking apart of the MgF₂ agglomeration, leads to greater surface area exposure and therefore an increase in the surface diffusivity rate of the reactive species and 2)

convective motion caused by the cavitation enhanced the diffusion of the leach acid solvent through the micropores of the MgF_2 agglomerate. It has thus been proposed that the constant movement of molecules within a mixture results in the continuous removal of products and/or intermediates away from the face of the metal. The increased reactivity of the reaction can be attributed to this movement of molecules as well as the cleaning of the metal surface.

In reactions with powders, ultrasonication has often proven to be superior to conventional mixing techniques. When dissolving a powder or other submicron sized particles into a liquid, stirring can only saturate the liquid up to a certain degree before it reaches its maximum dissolution. Ultrasonication of partially soluble solids within a liquid appears to result in supersaturation thus increasing the reactive surface area between the powder and other reactants within the liquid and enhancing the reactivity of the reaction. This was demonstrated by Suslick and Doktycz on the Reformatsky reaction.¹⁰ Sonication of a suspension of zinc powder prior to mixing with the organic halide reactant resulted in a decrease in reaction time from 30 minutes to 6 minutes.

The greatest enhancements in reactivity have been observed for reactions in emulsions. The ability of ultrasonication to effectively mix two potentially reactive yet immiscible reagents or solvents can have a powerful effect due to the dispersing of the two phases into ultrafine emulsions, increasing the surface area for interaction of the immiscible liquids. For instance, in the synthesis of biodiesel, ultrasound is often used to accelerate the transesterification reaction¹¹. This reaction is accelerated by the production of a fine emulsion between the oil and alcohol created from the microturbulence caused by the cavitation bubbles. Now considered to be a biology laboratory staple, biological

cell disruptors are ideal for lysing membranes but can also be utilized for creating emulsions. The ultrasonic devices impart the same ultrasonic power as an ultrasonic cleaning bath except, cell disruptors concentrate their power into a horn, which can be placed above a reaction, or into a microprobe, which can be placed directly into the reaction solution.

Finally, results from homogeneous reactions provide some of the most convincing evidence that the positive effects of ultrasonication on the rate of heterogeneous reactions are not merely due to surface activation or enhancement of mixing. This is supported by the fact that sonoluminescence, the emission of light associated with cavitation, is observed during the sonication of pure water, which is known to generate hydroxyl radicals and hydrogen atoms. Though heavily debated, there is still no unambiguous explanation for sonoluminescence. Similarly, sonication of otherwise unreactive organic solvents and reactants is found to result in generation of sufficient amounts of organic radicals to allow performance of radical addition reactions.¹²

The vibrations created during ultrasonication are a potential means of initiating a controlled decomposition of shock sensitive TATP. To determine how ultrasonication should affect TATP we must first discuss how this technique affects different media.

2.3 Theory of Ultrasonication

As previously stated, the most important characteristic that determines how a substance reacts to ultrasonication is the phase of that substance. For example, when ultrasound is applied to a liquid or a gas, only longitudinal waves are produced, when it is applied to a solid, both longitudinal and transverse waves are produced.

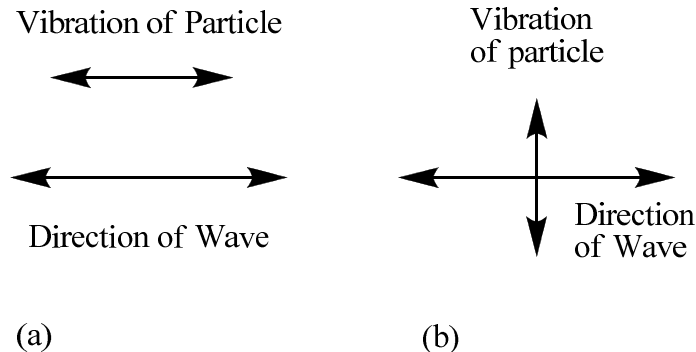


Figure 10: Wave & particle movement; a) longitudinal wave, b) transverse wave¹

The production of these waves has a significant effect on the molecules of the system to which they are being supplied.

2.3.1 Ultrasonication of Liquids

In liquids, ultrasonication causes acoustic cavitation, which is defined as the formation, growth and subsequent collapse of high temperature, high pressure bubbles in a liquid. These bubbles are caused by compression, the squeezing together of molecules, and rarefaction, the spreading out of molecules, in the liquid. During rarefaction the distance between the molecules of the liquid increases; if the distance between the molecules exceeds the critical molecular distance necessary to hold the liquid intact, the liquid will breakdown and voids or bubbles will begin to form¹³. These voids, because they were formed due to compression and rarefaction, have a variable pressure. As the sound wave oscillates through the liquid the pressure inside the bubble also oscillates from positive to negative pressure in relation to the hydrostatic pressure of the liquid of interest. During rarefaction, as the distance between the neighboring molecules of the liquid increases, the pressure in and around the bubble drops. This increase in distance

between molecules also allows the bubble to grow in size. In contrast, during compression, the distance between neighboring molecules decreases causing the pressure in and around the bubble to increase; the decrease in distance between molecules of the liquid also causes the bubble to decrease in size. If the pressure of the liquid around the bubble is high enough it can cause the bubble to collapse violently. Collapse of these bubbles is associated with extreme local temperatures. These temperatures have been estimated to be up to 19,000 K by Noltingk and Neppiras¹⁴, although the temperature has been measured experimentally up to 5200 K¹⁵. The pressures within collapsing bubbles are estimated to exceed 10,000 atmospheres¹⁶. These changes in the liquid cause the desired, and sometimes undesired, effects of ultrasound.

2.3.2 Ultrasonication of Solids

The ultrasonication of a solid is different from that of a liquid due to three important factors¹, 1) liquids are much more compressible than solids. When speaking of ultrasonication in liquids we talk about the acoustic pressure or the compressibility, however, in solids these terms are not used, instead we speak of stress and elastic constants; 2) solids are inherently rigid and can therefore support a static shear stress whereas liquids cannot; and 3) sound waves induce longitudinal waves in liquids but both longitudinal and transverse waves in solids, accounting for the tremendous differences in how each media reacts.

In a solid, the dynamics of cavitation are drastically different. In liquids, the bubble retains a spherical shape during collapse due to its uniform surrounding. When a solid surface is present, bubbles collapse asymmetrically creating high-speed jets of liquid that drive into the surface of that solid at speeds close to 250 miles per hour⁵.

These jets are considered to be the cause of extensive corrosion of components near the bubble.

2.4 Ultrasonication of TATP

2.4.1 Intro

In the following experiments we sought to show that TATP could be decomposed or even detonated through a controlled ultrasonication process. Either outcome could be used by law enforcement officials as the basis for a standoff procedure for the destruction of bulk quantities of TATP. The shockwave and pressure and temperature extremes caused by ultrasonication of a medium could exploit TATP's sensitivity to shock, friction, heat and electrostatic charge and induce decomposition of the molecule in a controlled (i.e. distant) environment.

2.4.2 Experimental

Sonication was performed using Fisher Scientific FS30 and FS30D Ultrasonic cleaning baths at a frequency of 40-60 Hz each and 130/240 watts, respectively. A Misonix XL 2000 cell disruptor at a frequency of 23 kHz and 100 watts was also used.

For experiments using the ultrasonic cleaning bath, the following procedures were used. Fifty milligram samples of TATP were measured out and added to a vial marked with the experiment name and number. A control sample of TATP was taken before any experiments were performed and analyzed by TLC and/or NMR. For experiments with solid TATP, the vial was capped loosely to allow for expansion and release of gases and placed in a holder positioned above the water in the sonication bath. For solution experiments with TATP, approximately 1-2 milliliters of the solvent of choice was added and the vial was capped and secured as described above. Once all vials were in place,

they were lowered to the same level in the sonication bath. The temperature of the bath was noted prior to beginning the experiment. For experiments carried out in the Fisher Scientific FS30D the bath temperature was set to 25 °C; for those carried out in the FS30, the temperature was monitored by a thermometer and manipulated using ice chips or hot water to maintain a temperature of 25 °C ± 5 °C. For experiments over 10 minutes in length, a clock was used to annotate the time of sonication. For experiments under 10 minutes, a stop watch was used. Once sonication began, any observed visual changes were annotated in the lab notebook. Samples were periodically removed for analysis by TLC to determine if new peroxide species had emerged during sonication. Selected samples were also concentrated and re-dissolved in CDCl₃ for analysis by NMR.

For experiments using the microprobe, the following procedures were used. For indirect sonication, fifty milligrams of TATP was weighed out and added to a test tube. A control sample of TATP was taken and analyzed by TLC and/or NMR. For experiments on solid TATP, the test tube was placed in a holder with the bottom of the test tube positioned ~1 inch away from the tip of the sonicator. Experiments with TATP in solution were augmented with approximately 1-2 milliliters of the solvent of choice. The temperature of the bath was annotated as noted above. The sonicator was set to the maximum setting allowable for the microprobe, and the experiment was run for the specified time. The experiments were analyzed as previously described.

For direct sonication, the procedures were slightly different. Fifty milligrams of TATP was measured and dissolved in 5-10 mL of a solvent. The solution was placed into a jacketed flask, which was cooled with cycling water and the tip of the microprobe

was put into the solution. The experiment was carried out using the same procedures as the indirect sonications.

2.4.3 Results & Conclusions

The initial sonication experiments were performed on fifty milligram samples of crude TATP, either dry or in solution, for one to four hours in the Fischer Scientific FS30. Here the term “dry” refers to the fact that the samples are not dissolved in a solvent for the experiment. However, dry samples of TATP actually contain a small amount of water from the synthesis reaction. The initial sonication samples showed a small amount of degradation by TLC; the TATP spot, which was identified as a large pink spot (N,N'-dimethyl p-phenylenediamine dip, see Experimental section) with an R_f of ~0.54, was less intense (i.e. lighter colored) than the baseline TLC. There were also new spots at R_f 0.2, 0.13, and at the baseline of the TLC plate indicating the presence of less polar (i.e. smaller) peroxides. The samples in solution showed larger acetone peaks on the NMR spectra than their dry counterparts. This was obviously due to the effectiveness of ultrasound on the liquid media versus the solid. However, the temperature of the sonication bath had risen considerably, from 19 °C to 39 °C. Due to TATP's heat sensitivity, the results could have been caused by the bulk heating of the samples. For fidelity, the experiment was replicated using only heat, provided by a heated water bath. The experiment was setup behind a blast shield and the reaction was monitored closely to minimize the potential for initiation. The results were the same as those achieved by sonication. Therefore, to eliminate the possibility of getting only heat-induced results, the temperature of each subsequent experiment was controlled. Though

this would eliminate bulk heating of the liquid media, it should not significantly effect the “hot spot” generation that is indicative of sonication.

The follow-on set of experiments was performed using the Fischer Scientific FS30D. This ultrasonic cleaning bath allowed for temperature monitoring and control through heating, though it could not cool the reaction vessel. Cooling was achieved using ice chips, as previously stated. In the follow-on experiments, pure TATP was sonicated in different solvents from five to thirty minutes. The time trial was used to determine if any specific amount of time was required for sonication to activate or initiate the TATP. The experiments were carried out either neat (“pure” solid, as described above), or on solutions of TATP in diethyl ether, dichloromethane or deuterated chloroform. All of the experiments, with the exception of one, resulted in no reaction. A successful reaction was determined by multiple factors. If there were additional spots or peaks by TLC or NMR analysis and a decrease or a complete lack of the TATP spot or peak, then some reaction was said to have occurred. If none of these factors were present and the spectra looked exactly the same as the control or pre-test spectra then there was no reaction. For example, in one of the above experiments, there was no TATP in the post-test NMR spectra. Usually, this would mean that the TATP had decomposed, however, there were no other peaks in the spectra either, save the analyte. It was concluded that due to TATP’s high vapor pressure, the substance had sublimed during sonication, leaving no trace behind.

The next set of reactions was performed using a Misonix cell disruptor. The switch to the cell disruptor was made because, with longer reaction times, the cell disruptor could be used in conjunction with a jacketed flask making cooling of the

reaction easier to accomplish. Another area of concern was in the measurement of the power being input into each reaction by the ultrasonic device. The cell disruptor displayed the power output of the device in real time. In addition, the move to the cell disruptor also allowed for direct sonication of the TATP in a liquid media, versus the indirect sonication of the bath. Several indirect reactions were also accomplished with the cell disruptor for continuity. These experiments had the same results as the previous ones carried out in the sonication bath, no reaction.

The direct sonication of TATP was performed in an array of solvents in jacketed glassware. Other peroxides, including DADP, were not observed for reactions in pentane. This may be due to the fact that the next most stable form of the acetone peroxide (i.e. DADP) is insoluble in pentane. When reacted in ethyl acetate, hexane, deuterated chloroform and toluene, TATP decomposed slightly, signified by small amounts of acetone and DADP peaks observed in the ^1H NMR spectrum. In none of the experiments did TATP decompose completely and neither solvent polarity nor reaction time seemed to have an effect on the results of the reaction.

TATP was also sonicated in anhydrous hexane. A TLC was taken before sonication began and periodically over the course of sonication. The TLC showed different spots throughout the sonication, though the final only showed TATP and DADP. This led us to believe that while TATP was to some degree activated by sonication, the initial products were too unstable to persist. For this reason, a reactant was added to the next set of experiments in an attempt to capture/trap the more reactive peroxides derived from the opening of TATP.

To trap any open chain peroxides derived from the activation of TATP, unsaturated organic compounds, such as benzene and heptene, were added to the reaction. The expectation was that activation of TATP by sonication might result in heterolytic or homolytic activation of the weak O-O bond creating partial negative and partial positive oxygens or an oxygen radical. The presence of unsaturated compounds was anticipated to potentially capture any reactive intermediates. Six different unsaturated compounds were tested; methylene cyclohexane, 1-trimethylsiloxy-cyclohexene, heptene, benzaldehyde, cyclohexanone and cycloheptanone. Most of the experiments resulted in no reaction with the exception of one. In that case, TATP was sonicated in deuterated water with benzaldehyde as the trapping agent. The resulting NMR spectrum was drastically different from the control. Unfortunately, the products could not be isolated or identified. Though this shows that chemistry was happening in the reaction, it does not prove that TATP was activated. The products of the reaction could have been the result of benzaldehyde undergoing oxidation by air or else chemistry with itself during sonication.

Finally, it is important to discuss some of the obstacles facing this research project. One major obstacle related to the variability of power output from the ultrasonicators, making it difficult to replicate experiments exactly. Second, the ultrasonicators employed in these studies emitted at a fixed frequency, making it impossible to investigate the influence of different frequencies. Through the use of a sonicator designed for this type of application, it may be possible to impart more power at different frequencies to the decomposition or activation of TATP.

Finally, the issue of our method of analysis and detection must be addressed. At the outset of these studies, we had planned on using in-situ IR monitoring to follow the decomposition of TATP. This methodology can be directly performed on reaction solutions, thereby avoiding the losses of volatile materials associated with preparation of samples for NMR or MS analysis.¹⁷ Furthermore, the functional groups present in TATP, DADP, and anticipated decomposition products (ketones, esters, hydrogen peroxide) are easily detected and assigned by characteristic IR absorptions. Unfortunately, the only IR instrument available to us proved inoperable, and never became functional during the course of these investigations.

Although we did not obtain consistent and replicable results from the ultrasonication of TATP, the results suggest that there is chemistry occurring within the system. Further experiments with a more powerful sonicator, better experimental planning and, in particular, an improved protocol for in situ analysis of products, might establish ultrasonication as a reliable and safe way of activating and/or decomposing TATP, making its detection and destruction safer for law enforcement officials around the world.

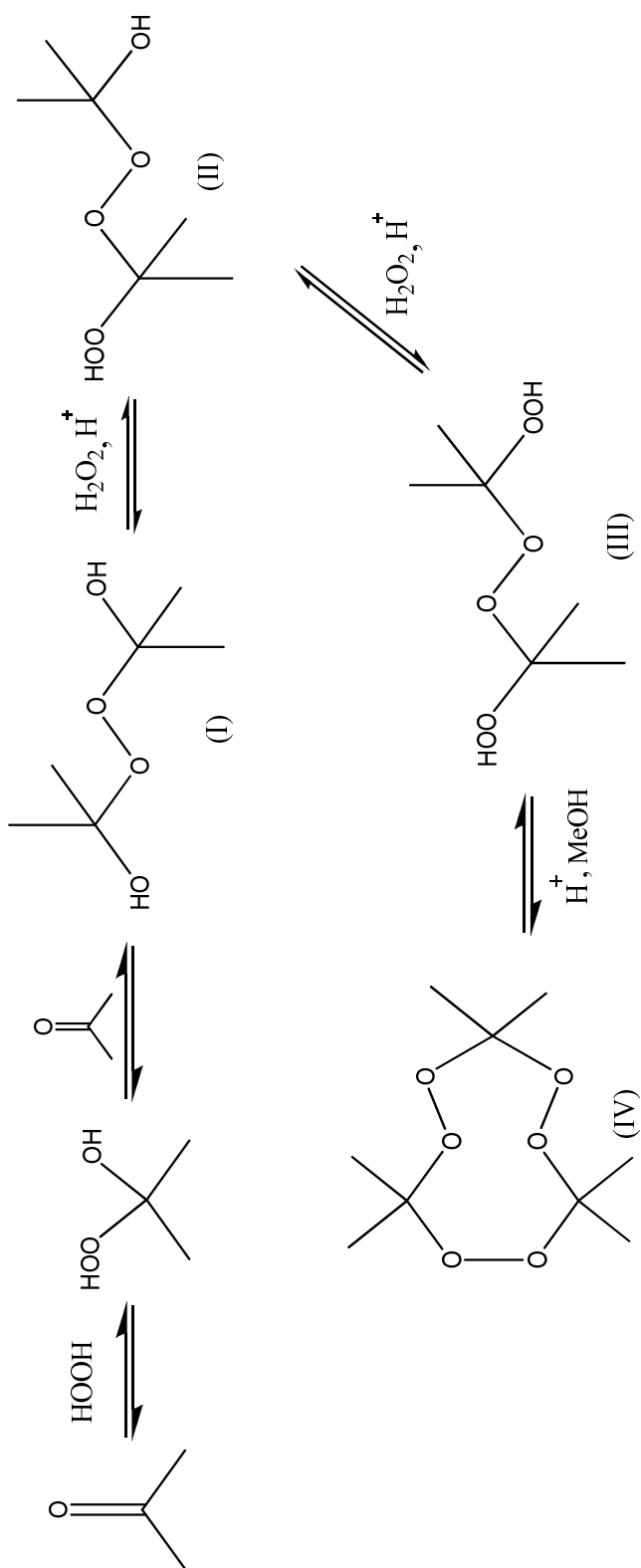
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Attachment A

Story TATP Mechanism



Milas TATP Mechanism

