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**FACTORS INFLUENCING THE SAFETY OF UNCONVENTIONAL
EXPLOSIVES**

BY

F. LUCUS STEINKAMP

**A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF**

DOCTOR OF PHILOSOPHY

IN

CHEMISTRY

UNIVERSITY OF RHODE ISLAND

2013

DOCTOR OF PHILOSOPHY DISSERTATION

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Abstract

Factors Influencing Safety of Unconventional Explosives

This dissertation details three studies regarding safety aspects for the formation, decomposition and use of unconventional explosives. The first study is a mechanistic study for the formation and decomposition of triacetone triperoxide (TATP). Using GC-MS, LC-MS, and NMR, the mechanism for the formation of TATP was elucidated detailing how experimental conditions affect the product composition. The presence of water had a significant impact on the distribution of the products TATP and diacetone diperoxide (DADP), a common contaminant in the synthesis. Water also had an impact on the decomposition of TATP resulting in a slower and more complete decomposition. The second study pertains to copper acetylide, a primary explosive sensitive towards initiation by impact, friction or spark. Copper acetylide is regarded as a safety risk in the petrochemical industry due to the presence of copper catalysts in refinery gas streams contaminated with acetylene. Analysis of the products formed after catalyst samples were exposed to acetylene gas suggested that acetylene readily reacts with many copper catalysts, likely via a copper acetylide intermediate, to form an amorphous phase of carbon. It was found that proprietary catalyst compositions inhibit the reaction significantly, reducing the potential risk of acetylide formation and subsequent accidental explosion. The third study is aimed at mitigating potential failure of direct borohydride fuel cells. The incompatibility of sodium borohydride and hydrogen peroxide poses a serious safety risk for electrochemical cells using these substances. The hydrolysis kinetics of sodium borohydride in dilute hydrogen peroxide solutions was studied to obtain

fundamental information regarding the reaction. Hydrolysis by water is slow and yields hydrogen gas while hydrolysis by hydrogen peroxide is fast and yields a potentially combustible mixture of hydrogen and oxygen gases.

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Preface

This dissertation has been prepared in the manuscript format in accordance with the guidelines of the Graduate School of The University of Rhode Island. The research is divided into four manuscripts. The first manuscript, Factors Influencing TATP & DADP Formation: Part II, has been accepted for publication in *Propellants, Explosives, and Pyrotechnics*. The second manuscript, Factors Influencing TATP & DADP Formation: Part III, has been submitted to *Propellants, Explosives, and Pyrotechnics*. The third manuscript, Hazards of Exposing Copper Compounds to Acetylene Feedstocks, has been prepared and will be submitted to the Journal of Chemical Health and Safety. The fourth manuscript, Hydrolysis of Sodium Borohydride by Hydrogen Peroxide, has been prepared and will be submitted to the Journal of Chemical Health and Safety.

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Manuscript 1

Factors Influencing Triacetone Triperoxide (TATP) and

Diacetone Diperoxide (DADP) Formation: Part II

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Diacetone Diperoxide (DADP) Formation: Part 2**

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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 to complete decomposition of TATP by acid. A mechanism is proposed for the production of TATP and DADP.

1.1. 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 $^1\text{H}/^{13}\text{C}$ nuclear magnetic resonance spectroscopy (NMR). Intermediates were monitored during formation and destruction experiments to elucidate mechanisms.

1.2 Experimental Section

1.2.1 Reagents and Chemicals

HPLC-grade solvents, deuterated acetone (99.8 wt% d), and acids trifluoroacetic (99 wt%), nitric (70wt%), hydrochloric (37 wt%) and sulfuric (98wt%) were obtained from Fisher Scientific; deuterated acetonitrile, from Cambridge Isotopes Lab. Syntheses of TATP and DADP were previously reported [5]. For synthesis of deuterium-labeled TATP d^6 acetone was used. Precipitates were filtered, rinsed with water, dried under aspiration 30 minutes and re-crystallized in methanol. Final products were analyzed by GC/MS, GC/uECD, ^1H NMR and ^{13}C NMR. Anhydrous hydrogen peroxide was prepared by dissolving 20 g of L-serine in 20 mL 65 wt% hydrogen peroxide.⁶ To confirm its concentration, the hydrogen peroxide was dissolved in acetonitrile (ACN) and titrated with 0.25N potassium permanganate.

1.2.2 GC/MS Method

An Agilent 6890 gas chromatograph with 5973 mass selective detector (GC/MS) was used with inlet in splitless mode at 110°C, with purge flow 20 mL/min at 0.5 min,

total helium flow of 24.1 mL/min and a Varian VF-200MS column (15m, 0.25 mm inner diameter, 0.25 μ m film) under constant helium flow (1.5 mL/min). Oven temperature was held at 40°C for 2 minutes, ramped 10°C/min to 70°C, then 20°C/min to 220°C; post-run oven was held 3 min at 310°C. Transfer line, MS detector source, and quadrupole were held at 150°C, 150°C, and 106°C, respectively. Chemical ionization used anhydrous ammonia.

1.2.2.1 TATP Formation (GC/MS): All reagents were chilled to 0°C. Hydrogen peroxide (HP) (67 wt%, 0.47 g, 9.3 mmol) in 10 mL acetonitrile was stirred in a round bottom flask while sulfuric acid (0.95 g, 96.5 wt%, 9.3 mmol) and then acetone (0.54 g, 9.3 mmol) were added dropwise. Periodically, 100 μ L of the solution was removed, placed in 1 mL CH_2Cl_2 , and rinsed with 3 wt% sodium bicarbonate. Organic layer was dried over MgSO_4 and analyzed by GC/MS.

1.2.2.2 Effect of water (GC/MS): Acetone and HP were mixed and chilled to 0°C. Water was mixed with sulfuric or hydrochloric acid, chilled to 0°C, and added dropwise to the acetone/HP mixture keeping the temperature below 5°C. The ratio of HP:acetone:acid was maintained at 1:1:1 (8.6 mmol). Once all acid was added the mixture was removed from the ice water bath and allowed to stir at room temperature 24 hours; resulting products were analyzed by GC/MS.

1.2.2.3 TATP Destruction (GC/MS): TATP (100 mg) was placed in a 40 mL vial; and 5 mL solvent, added. In a second 40 mL vial 200 μ L 96.5 wt% sulfuric acid was added to a solvent/ water mix of total volume 5 mL. Both vials were equilibrated at 45°C. Once equilibrated, the two solutions were mixed. At intervals 100 μ L aliquots were removed, quenched as above

(2.2.1) and analyzed by GC/MS. TATP and DADP were quantified by external calibration.

1.2.2.4 Acetone Exchange Reactions (GC/MS): TATP was stirred at room temperature with 2.6 mmol sulfuric acid in aqueous ethanol spiked with d⁶ 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 ACN, methanol or chloroform/TFA as solvent were conducted.

1.2.3 LC/MS Method

Certain experiments identified intermediates by liquid chromatography/mass spectrometry at high mass resolution (LC/MS). The Thermo Scientific Exactive Orbitrap MS 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 μ A; the sheath gas and auxiliary gas operated at 25 and 10 arbitrary units, respectively. The LC was ramped from 70/30 methanol/ammonium acetate (4mM) in water to 15/85 methanol/ammonium acetate (4 mM) in 5.5 minutes followed by a 30 second hold. The eluent was returned to 70/30 methanol/ ammonium acetate and held for 4 minutes. Resolution was set to high (50,000 at 2 Hz), and the maximum injection time was 250 ms.

1.2.3.1 TATP Formation (LC/MS): Acetone and HP (67 wt%) mixtures were prepared as molar ratios of 1:1, 2:1 and 1:2 and held at room temperature (r.t.) without

stirring. For LC/MS analysis 100 μ L of each mixture was diluted to 1 mL with methanol.

1.2.3.2 d^6 -Acetone Insertion into Proteo-TATP (LC/MS): To a room temperature, stirred solution of TATP (222mg, 1.0 mmols) and d^6 -acetone (75 μ L, 1.0 mmols) in 10 mL ACN, methanol or chloroform was added trifluoroacetic acid (TFA, 150 μ L, 2.0 mmols). Every 24 hours, 0.5mL of the mixture was removed and diluted to 1.5mL total volume for LC/MS analysis.

1.2.4 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 ^1H -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 ^1H (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.

1.2.4.2 Formation of TATP/DADP (NMR): In a 10 mL vial, HP (1 mL, 65 wt%, 24.6 mmols) was mixed with acetone (1.9 mL, 25.8 mmols); 100 μ L of the mixture was transferred into an NMR tube with 1.2 mL CD_3CN . Trifluoroacetic acid (TFA) (20-80

μL , 0.26-1.04 mmols) and trace of tetramethylsilane (TMS for calibration and quantification) were added.

1.2.4.3 Decomposition of TATP or DADP (NMR): TATP (45 mg, 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), transferred to 5mm NMR tube, and acid added [TFA (20-100 μL , 0.26-1.3 mmols), sulfuric (10-20 μL , 0.18-0.36 mmols) or hydrochloric acid (10 μL , 0.12 mmols)]. DADP (29mg, 0.2 mmols) dissolved in CDCl_3 (1mL) was decomposed with TFA (60-100 μL , 0.78-1.3mmols) or sulfuric acid (10 μL , 0.18 mmols).

1.2.4.4 Acetone Exchange Without Acid (NMR): In 5 mm NMR tubes with 100 μL CH_2Cl_2 TATP (111 mg, 0.5 mM) and 1 mL d^6 -acetone or d^{18} -TATP (120 mg, 0.5 mM), 0.9 mL acetone, and 100 μL d^6 acetone (for lock) were sealed and stored at room temperature a week.

1.2.4.5 Acetone Exchange Reactions (NMR): To d^{18} -TATP (48mg, 0.2mmols) in 1.2 mL CD_3CN or 1.0 mL CDCl_3 was added 50 μL (0.68 mmols) or 40 μL (0.55 mmols) acetone, respectively. The solution was transferred to an NMR tube and TFA (20-40 μL , 0.26-0.52 mmols) was added.

1.2.4.6 1,3-Dichloroacetone insertion into Proteo-TATP and d^{18} -TATP (NMR): A tenth millimole TATP (22 mg) or d^{18} -TATP (25 mg) was dissolved in 1.2 mL CD_3CN ; 1,3-dichloroacetone, 1,1-dichloroacetone (42 mg, 0.3 mmols) or monochloroacetone (27 μL , 0.3 mmols) was added, and the solution placed in a 5mm NMR tube. TFA (40 μL , 0.54 mmols) was added.

1.3 Results and Discussion

1.3.1 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 precipitation from 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 1.1 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) TATP concentration reached a maximum, remained constant for several days, and then gradually decreased as DADP concentration continually increased. DADP is the final product if TATP cannot precipitate from 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, had an effect. Figure 1.2 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 early in the reaction.

Figure 1.1 GC/MS data 1:1:1 (9.3 mmol) of 65%HP to acetone to 96.5% sulfuric acid at 0°C

Figure 1.2 GC/MS data shows effect of varying the mole ratio of acid and the concentration of acid and hydrogen peroxide. Increasing the water content slows the rate of formation of TATP.

1.3.2 Formation of TATP with no acid

GC/MS analysis of the products when 70 wt% hydrogen peroxide (HP) and acetone were mixed highlighted the importance of the ratios. When HP was in excess 5:1 over acetone more TATP was produced than DADP. When the ratio of HP to acetone was adjusted 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. The reaction between HP (70 wt%) and acetone without acid was monitored for up to 14 days. A number of peaks appeared in ^1H NMR and ^{13}C spectra as well as in GC/MS chromatogram/spectra. Assignments of intermediates by NMR and GC/MS are given in Table 1.1. 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 ^1H NMR and ^{13}C NMR for 14 days. The

relative reaction progress in terms of proton resonances (as large, medium, small or tiny peaks) is given in the right columns of Table 1.1. On day zero there were two prominent methyl resonances in the ^1H NMR (Table 1): one at 2.1 ppm, assigned to the methyl protons of acetone and the other at 1.38 ppm attributed to 2-hydroxy-2-hydroperoxypropane (I) (Figure 1.3 shows structures 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 ^1H NMR which was assigned to a dimeric species where two molecules of acetone were linked by a peroxide functionality. By that time the protonated acetone species had decreased substantially with 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 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 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 1.1).

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 1.1.

Table 1.1: GC/MS & NMR resonance assignments & relative abundance by days of reaction

	1:1 HP:acetone no acid, in acetonitrile	CI mass spectrum (		^1H NMR	^{13}C NMR	^{13}C NMR	Relative NMR abundance on day										
		mass	amount	(CH ₃) ppm	(CH ₃) ppm	(CO) ppm	0	1	3	5	7	10	12	14			
I	2,2-hydroxy hydroperoxy propane	92.1	s	1.38	24.2	102.4	L	L	M	M	S	S	S	S			
II	2,2-dihydroperoxy propane	108.1	m	1.38	20.2	109.4	M	L	L	L	L	L	L	L			
III	2,2'-dihydroxy-2,2'-diisopropyl peroxide	150.2	m	1.44	24.66	102.5	T	S	S	S	S	S	S	S			
IV	2,2'-hydroxy hydroperoxy-2,2'-diisopropyl peroxide	166.2	--		uncertain												
V	2,2'-dihydroperoxy-2,2'-diisopropyl peroxide	182.2	l	1.44	20.5	109	T	M	M	M	L	L	L	L			
	TATP (3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexoxonane)	222.2	vary	1.42	20.97	107.8	T	S	S	S	S	S	S	S			
	DADP (3,3,6,6-tetramethyl-1,2,4,5-tetroxonane)	148.2	vary	1.35, 1.79	20.8, 21.1	108.7				T	T	T	S	S			
	acetone			2.1	31	209	L	L	L	L	L	L	L	L			
	dihydroxy trimer	224.3	s														
	hydroxy hydroperoxy trimer	240.3	--														
	dihydroperoxy trimer	256.3	m														

* CI with NH₃, M+1, M+18 were observed & for compound I M+35.

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

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 (Fig. 1.3) [10]. Species with terminal peroxide functionalities are

favored, and increasing amount of HP enhances their formation. Only TATP and DADP precipitated under reaction conditions where acid was present and when no co-solvent, employed. 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.

Cyclic acetone peroxides

Figure 1.3 Products of HP/acetone reaction as observed by LC/MS

1.3.3 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 1H 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 1.2). However, when no acid was added, 1H 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.

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 1H 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 (1H , ^{13}C , GC/MS) even in the presence of acid (Table 1.3). Nevertheless, the observation of dichloro-substituted TATP indicates ring opening and re-closing does occur.

Table 1.2: Acid catalyzed insertion of labeled acetone into TATP

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

Experiment	Solvent	mL Solvent	Acid	μ L Acid	mmols Acid	mg TATP	mmol TATP	Ratio Acid:TATP	μ L Acetone	mmols acetone	Ratio acetone : TATP	Analysis	TATP	DADP
h^6-Acetone + d^{18}-TATP 288K														
h^0 -acetone + d^{18} -TATP	CD ₃ CN	1.2	TFA	30,40	0.40,0.54	48	0.20	2.0, 2.7	50	0.68	3.40	¹ H-NMR	insertion	insertion
h^0 -acetone + d^{18} -TATP	CDCl ₃	1.0	TFA	20,30	0.27,0.40	48	0.20	1.3,2.0	40	0.54	2.72	¹ H-NMR	insertion	insertion
h^0 -acetone + d^{18} -TATP	d^6 & h^6 acetone	1.0	none	0	0	120	0.50	--	900	12.2	24.5	¹ H-NMR LC/MS	no insertion 7 days	no insertion 7 days
d^6-Acetone + h^{18}-TATP Reaction for 7 days 298K														
d^0 -acetone + h^{18} -TATP	d^6 acetone	1.0	none	0	0	111	0.50	--	1000	13.6	27.2	¹ H-NMR LC/MS	no insertion 7 days	no insertion 7 days
d^6 -Acetone + h^{18} -TATP	acetone+ water or EtOH	10	sulfuric	140	2.6	222	1.0	2.6	1200	16.4	16.4	GC/MS	d^6 TATP, TATP after 24 hr	d^{12} DADP, d^6 DADP & DADP+other in 48h
d^6 -Acetone + h^{18} -TATP	CH ₃ OH, ACN, or CHCl ₃	10	TFA	150	2.01	222	0.92	2.2	75	1.02	1.1	LC/MS	d^6 , d^{12} , d^{18} TATP observed	insertion, d^{12} DADP major, d^6 DADP but no parent ion
ChloroAcetone + d^{18} & h^{18}-TATP 288K (dichloroacetone is a solid)														
1,3 dichloro acetone + d^{18} -TATP	CD ₃ CN	1.2	TFA	40	0.54	22	0.10	5.4	42 mg	0.33	3.3	¹ H-NMR & GC/MS	1 dichloro in TATP	no insertion
1,3 dichloro acetone + h^{18} -TATP	CD ₃ CN	1.2	TFA	40	0.54	22	0.10	5.4	42 mg	0.33	3.3	¹ H-NMR & GC/MS	1 dichloro in TATP	no insertion
1,1 dichloro acetone + h^{18} -TATP	CD ₃ CN	1.2	TFA	40	0.54	22	0.10	5.4	42 mg	0.33	3.3	GC/MS	no insertion	no insertion
monochloro acetone + h^{18} TATP	CD ₃ CN	1.2	TFA	40	0.54	22	0.10	5.4	27	0.33	3.3	GC/MS	no insertion	no insertion
1,3 dichloro acetone + h^{18} -TATP	CD ₃ CN	1.2	none	0	0	22	0.10	0	42 mg	0.33	3.3	GC/MS	no insertion	no insertion

1.3.4 Rate of TATP Formation

¹H NMR was used to monitor the one-to-one reaction of acetone and HP (25 mmol each) at 15°C using 20, 40 or 80 μ L 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-dihydroperoxypropane (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 ^1H NMR resonance of TATP (1.42 ppm) when treated with various volumes of TFA (Figure 1.5). 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. 1.6), although TFA was still capable of decomposing TATP.

Figure 1.4 Formation of TATP followed by ^1H NMR using 40 μL TFA

Figure 1.5 Formation of TATP followed by ^1H NMR 20, 40, & 80 μL TFA

1.3.5 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 1.3: Acetone, HP, acid, 1:1:1 (8.6 mmol each) & varied H₂O

Acetone (0.5 g), HP, Acid (1:1:1) (8.6 mmol each)				
water (mL)	yield (mg)	% yield	% TATP	% DADP
50% HP (0.586 g), 96.5% H ₂ SO ₄ (0.876g)				
0.25	308	48.3	0	100
0.5	246	38.6	7.6	92
0.75	348	54.6	81	19
1	378	59.3	100	0
30% HP (0.976 g), 96.5% H ₂ SO ₄ (0.876g)				
	218	34	11	89
0.25	140	22	72	28
0.5	265	42	72	28
0.75	161	25	89	11
30% HP (0.976 g), 37% HCl (0.85g)				
	92.1	14	81	0
0.25	98.7	15	83	0
0.5	92.2	14	87	0
0.75	99.3	16	94	0

Figure 1.6 Rate of TATP formation with 8.6 mmol each HP-acetone-acid vs water

1.3.6 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 1.4). The final precipitates, as well as in-situ products, were monitored by extracting aliquots of 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 1.4) [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°C, while alcohols favored TATP (cf. exp.1 with 1*, Table 1.4). 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°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 1.4: GC/MS analysis of cyclic peroxide products vs HP/acetone reaction conditions

exp	Order of Reactant Addition			Conditions		crude yield	in situ products	% Final Product analysis		
	HP (66.8%)	acetone	sulfuric acid (96.5%)	solvent	temp			TATP	DADP	GC
(repeat)	2.7g, 54mmol	3.0g, 51mmol	10.4g, 102mmol	ACN (mL)	°C	gram				
1 (3)	1	3	2	30	0	2.6	TATP/DADP	--	98	uECD
2 (2)	3	1	2	30	0	3.1	DADP	--	100	uECD
3 (1)	2	1	3	30	0	3.1	TATP/dimer/DADP	--	87	MS
2'	3	1	2	30	-20	3.0	TATP/DADP	7	77	MS
1'	1	3	2	30	-25	3.3	TATP/dimer/DADP	67	22	MS
	1.5g, 26mmol	1.5g, 26mmol	5.24g, 51mmol							
3'	2	1	3	15	-40	1.7	TATP/dimer/DADP	93	1	MS
1*	1	3	2	15 EtOH	0	1.0	n/a	98	--	uECD
1*	1	3	2	15 MeOH	0	0.8	n/a	100	--	MS
1'	1	3	2	15	-40	1.8	TATP/DADP	90	1	MS
1"	1	3	2 TFA (99%, 5.8g)	15 ACN	0		dimer->TATP, DADP		no ppt	

1.3.7 Rate of TATP Decomposition

The decomposition of TATP by acid in CD₃CN or CDCl₃ was monitored by ¹H NMR. In ACN and CDCl₃ decomposition of TATP was pseudo-first order and formed DADP and acetone (Table 1.5). 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 1.5. 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 1.4 & 1.6). As TATP decomposed to DADP and acetone, other intermediates could be observed by ¹H NMR in d³-ACN. In ACN, 2,2'-dihydroperoxy-2,2'-diisopropylperoxide (V) and 2,2-dihydroperoxypropane (II) were observed as intermediates, whereas in CDCl₃ only 2,2'-dihydroperoxy-2,2'-diisopropylperoxide (V) was observed. NMR and MS data suggests these intermediates are identical to those observed in formation experiments (Table 1.1).

Table 1.5: First order rate constants obtained from ^1H 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 $\text{d}^3\text{-CH}_3\text{CN}$

TATP Formation & Destruction Monitored by ^1H NMR

Acid	uL	mmol acid	Rate Constant (s^{-1})
Decomposition of TATP (45mg, 0.2 mmol) in Chloroform			
TFA	30	0.392	1.50E-05
TFA	40	0.522	1.83E-05
TFA	60	0.784	6.67E-05
TFA	80	1.045	2.48E-04
SA	10	0.188	2.17E-05
SA	15	0.281	3.00E-05
SA	20	0.375	6.17E-05
Decomposition of TATP (45 mg, 0.2mmol) in Acetonitrile			
TFA	60	0.784	1.17E-05
TFA	100	1.306	3.50E-05
Decomposition of DADP (29 mg) in Chloroform			
SA	10	0.188	3.67E-05
Formation of TATP (45mg, 0.2mmol) in Acetonitrile			
TFA	20	0.261	1.75E-04
TFA	40	0.522	4.83E-04
TFA	80	1.045	4.83E-04

Table 1.6 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 1.6 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.

Table 1.6: GC/MS monitoring of TATP (100 mg, 0.45 mmol) + H₂SO₄ (96.5 wt%, 200 μ L, 3.6 mmol)

GC/MS monitoring of TATP Decomposition (298K)
TATP (100 mg, 0.45 mmol) + H₂SO₄ (96.5wt%, 200 μ L, 3.6 mmol)

Solvent (10 mL)	k (sec ⁻¹)	Result
Acetonitrile	2.41E-03	DADP
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
90:10 methanol:water	2.13E-04	no DADP
80:20 methanol:water	2.96E-04	no DADP
Ethanol	6.43E-04	no DADP
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
90:10 n-propanol:water	1.72E-05	no DADP
isopropanol	8.86E-05	no DADP
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
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

1.3.8 Mechanism

A proposed mechanism for the production of TATP and DADP is given in Figure 1.7. In a reaction between HP and acetone without acid catalyst, 2-hydroxy-2-hydroperoxypropane (I) was observed in high quantities soon after mixing. When acid was added 2,2-dihydroperoxy-propane (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 1.4).

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 or alcohol retards TATP loss and prevents the formation of DADP. The retarding effect of water and alcohol can be attributed to the intermediate species competing with the solvent for protonation. The lack of DADP formation 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 1.7 Mechanism for synthesis of TATP and DADP

1.4 Conclusions

We have reported that the synthesis of TATP is achieved in best yield by use of a 1 to 1 molar ratio of HP to acetone with modest amounts of acid (10-50 mole %). However, acid catalyzes TATP synthesis and decomposition, especially at high acid levels. Herein we examine the intermediates of the acetone/HP reaction and the rates of formation and destruction of TATP and postulate a mechanistic pathway. The oxidation of acetone by HP occurs whether or not acid is added; it is dramatically slower without acid, taking weeks and months to precipitate TATP and DADP [15]q. Other linear and even cyclic peroxides have been observed in the reaction solution, but only TATP and DADP precipitate out due to their low solubility in aqueous media. If an organic solvent is present, TATP does not precipitate out of solution and, in the

presence of acid, converts to DADP. Whether or not acid is present as soon as HP and acetone are mixed 2-hydroxy-2-hydroperoxypropane (I) forms. This then proceeds to form 2-hydroxy-2'-hydroperoxy-2,2'-diisopropylperoxide (IV) (the precursor to DADP) or 2,2'-dihydroperoxy-2,2'-diisopropylperoxide (V) (the precursor to TATP) depending on whether water content in the reaction mix is low or high, respectively. Water, which comes into the reaction via the acid and the HP, slows the formation of TATP and DADP, DADP most dramatically. Indeed, the same effect is observed when alcohol, which like water is susceptible to protonation, is added to the reaction mixture.

Under nearly anhydrous conditions sulfuric acid and trifluoroacetic acid decompose TATP in a pseudo first-order fashion to DADP. Under mildly acidic conditions the TATP ring opens to form 2,2'-dihydroperoxy-2,2'-diisopropylperoxide (V) and acetone; this may re-cyclize with a new acetone molecule or further decompose to DADP and other smaller molecules. 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 continues to open and reclose allowing all acetone molecules to be replaced with their deuterated counterparts. Both these possibilities seem reasonable; which dominates may depend

upon the solvent. Regarding formation, the insertion of acetone seems to indicate that (V) reacts with acetone 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.

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Manuscript 2

Factors Influencing Triacetone Triperoxide (TATP) and

Diacetone Diperoxide (DADP) Formation: Part III

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**Factors Influencing Triacetone Triperoxide (TATP) and
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Abstract

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

Keywords: Triacetone Triperoxide (TATP), Diacetone Diperoxide (DADP), Hexamethylene Triperoxide Diamine (HMTD), Gentle Destruction, Kinetics, Calorimetry, Large-scale Decomposition, Decomposition Products

2.1. Introduction

The hazardous nature of peroxides in general is well established. Those with multiple peroxide functionalities, such as triacetone triperoxide (TATP), diacetone diperoxide (DADP), or hexamethylene triperoxide diamine (HMTD), can be explosive. (Fig. 2.1)

Fig. 2.1: Chemical structures of TATP, DADP and HMTD

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

The oldest, most popular and safest approach to disposal of illegal explosives is blow-in-place. Direct handling and transporting of potentially sensitive materials by law enforcement and other qualified personnel is avoided. Since peroxide explosives

are frequently found in high-population density areas, blow-in-place protocols are not always practical. There are documented examples where law enforcement has taken extreme measures to destroy illicit explosives involving complete destruction of the premises. For example, in November 2010 a rented house in Escondido, CA was destroyed because, to quote law enforcement officers, the house contained “the largest amount of certain homemade explosives ever found in a single U.S. location. Nearly every room was packed with piles of explosive material....six mason jars with highly unstable hexamethylene triperoxide diamine, or HMTD....” Controlled burn of the house was deemed the only safe way to handle the disposal.¹

There are few publications that have addressed safe, effective, field-usable methods for destroying TATP; two have suggested copper and tin salts to effect destruction at elevated temperature; ^{2,3} one used mineral acids and elevated temperature.⁴ These articles offered guidance in the search for a room-temperature answer for gentle chemical destruction of peroxides. Ideal protocols would involve a homogeneous liquid chemical solution to spray over solid peroxide stashes or a method involving immersion of peroxide saturated materials into a solution that would quiescently destroy the explosive in hours without further handling. Our first approach was to seek a general solution applicable to peroxide explosives with no prior characterization. Concentrated sulfuric acid was found to effectively destroy milligram amounts of TATP; however, when scaled-up to even 1 gram, the excessive heat release caused violent rapid release of energy, perhaps detonation.⁵

TATP is formed by reaction of acetone and hydrogen peroxide. Under suitable conditions the two reagents can slowly form TATP at room temperature.⁶⁻⁸ However;

the usual methods for synthesis of TATP involve controlled addition of acid. Excess acid and/or elevated temperature can favor the formation of DADP. If the heat of the reaction is substantial, it can initiate the peroxide mixture, causing detonation. Herein, we explore the region where acid can be used to affect quiescent decomposition of TATP. This work mainly focused on the destruction of 0.5 g or 3g quantities of solid TATP, but it was helpful to obtain kinetics for the destruction of TATP in solution. Field tests were performed on 50, 100 and 460g quantities of TATP.

2.2.0 Experimental Section

2.2.1 Synthesis of TATP and DADP

TATP and DADP were synthesized in our laboratory.⁷⁻⁹ TATP was prepared by stirring hydrogen peroxide (7 g, 50 wt% in water) and acetone (5.8 grams) below a temperature of -5°C with slow addition of 0.5 mL of HCl (18% m/m). The mixture was kept at -14°C overnight (14-18 hours). Water was added to the mixture; and the precipitate filtered out and rinsed with copious amounts of water. Crude yields were typically 5 g (67.6%), melting point 88-92°C; recrystallization from hot methanol yielded a white, finely divided crystalline product, melting point 94-95°C.

DADP was prepared by adding concentrated sulfuric acid (10.7 g, 96%, 105 mmol) with stirring to a cold (< 3°C) acetonitrile solution of hydrogen peroxide (3.00 g, 70%, 62 mmol). Acetone (2.9 g, 50 mmol) and acetonitrile (10 mL) were combined and chilled (~ 0°C). The acetone mixture was added drop-wise to the hydrogen peroxide mixture while the temperature was maintained between -4 and 4°C, and the mixture was allowed to stir for 90 minutes, during which time a white precipitate formed. The precipitate was collected by vacuum filtration and rinsed with copious

amounts of cold water. The crude solid (2.9 g, 76% yield) had a melting point of 131-132°C and was recrystallized from ethyl acetate.

2.2.2 Destruction of TATP

For the TATP destruction experiments, 500 mg (2.25 mmol) of the recrystallized TATP was placed in clear 40 mL glass vials and moistened with 0.5, 1, 2, or 4 mL ethanol, isopropanol, acetone, ethyl acetate, diesel, iso-octane or toluene. This was followed by addition of 0.5, 1, 2, 3, 4, 5, 9 mL of acids in varying concentrations. More than 600 individual experiments were performed. All mixtures were allowed to react at room temperature uncovered for 2-24 h before extraction with 10 mL dichloromethane (TATP solubility at room temperature >1g/4mL) and rinsing with 3 mL distilled water followed by 3 mL of 1% Na₂CO₃. The organic layer was dried over anhydrous magnesium sulfate and analyzed via gas chromatography with mass selective detector (GC/MS). Each analytical run began with a series of five or more authentic TATP samples ranging in concentration from 10-10,000 µg/mL. These samples were used to monitor instrument responses and plot calibration curves.

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

2.2.3 Kinetics for Destruction of TATP

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

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

To quantify TATP, an Agilent 6890 gas chromatograph with 5973i mass selective detector (GC/MS) was used. The inlet temperature was 110°C and total flow was 24.1 mL/min (helium carrier gas). The inlet was operated in splitless mode, with a purge flow of 20 mL/min at 0.5 minutes. The column was a Varian VF-200MS

(15m x 0.25mm x 250 μ m), operated in constant flow mode with a flow rate of 1.5 mL/min. The oven program was initial temperature of 40°C for 2 minutes 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 250°C and the mass selective detector source and quadrupole temperatures were 230°C and 150°C, respectively. Electron impact ionization at 70 eV was used.

2.2.4 Large-Scale Decomposition

For all large-scale experiments addition of reagents was done remotely. A pumping apparatus was erected and an electronic means of actuating the pumps via remote control was assembled. TATP (460g) was placed in a 4 L beaker with thermocouples and tubes from the output of the pumps already in place. A secondary means of adding acid was included in case of pump failure. This was accomplished by securing a Nalgene bottle with a spigot above the beaker containing the TATP. Tygon tubing attached to the spigot was placed in the beaker. The valve could be operated remotely by mechanical means ensuring that if some acid were added and the pump failed that more acid could be added without approaching the acidified TATP. Two thermocouples were used in this experiment. One was attached to the outside of the beaker and one submerged in the TATP. Alcohol solution (950 mL 50wt% isopropanol/water) was pumped onto the TATP first at approximately 100 mL/min using an aquarium pump. The TATP did not appear wet. The acid was then metered (120 mL/min) in the mixture using a peristaltic pump with acid resistant tubing; when the temperature rose to 70°C the pump was stopped. A total addition of 425 mL of acid was added. Once the experiment was completed the products of the reaction were

neutralized with sodium bicarbonate and put into a 4 L glass waste container. A sample of the waste was extracted in DCM followed by GC/MS analysis.

2.2.5 Heat Release

Heat released during the reaction of acid with dissolved TATP was measured using a Thermal Hazards Technologies micro-calorimeter. To calibrate the instrument two amber GC vials containing 1 mL reagent alcohol were placed in the sample and reference positions of the instrument. In calibration mode, the number of pulses was set to 3; the pulse size to 300 mJ; the pulse interval to 300 seconds; and the lead time to 30 seconds; samples were stirred at 200 rpm. To determine the heat of mixing between sulfuric acid and reagent alcohol, the instrument was set to collection mode with an experimental duration of 1000 seconds. A modified acid injection method was designed to accommodate the corrosive nature of strong acids. A glass capillary syringe needle was attached to a 1 mL plastic syringe. The syringe was primed to remove excess air and reduce dead volume, and the desired mass of acid was pulled into the syringe. Once a stable baseline was achieved, data collection began followed by manual injection of acid into alcohol. To determine heat released during the reaction between acid and TATP, the steps described above were followed using 1 mL of a 40 mg/mL TATP/alcohol solution in the sample position and an experimental duration of 50,000 seconds.

2.2.6 Decomposition Product Identification

The type and concentration of acid used to destroy TATP determined reaction progress and products formed. Experiments, in duplicate, were conducted to examine the effect of acid type. TATP (500 mg) and 1 mL of 50% water/alcohol (either

ethanol or isopropanol) were combined. To this mixture was added 2 mL of one of the following: sulfuric acid (65%), hydrochloric acid (36%), nitric acid (70%), phosphoric acid (85%), methanesulfonic acid (99%), boron trifluoride (48% in diethyl ether), trifluoroacetic acid (99%), or perchloric acid (99%). WARNING: The addition of nitric acid resulted in violent fuming. Mixtures reacted for 3 hours before extraction as described above. Products were identified by comparison of mass spectra to authentic samples of TATP, DADP, and various chlorinated acetones or by spectral matching to the NIST database. Relative amounts of each material in solution are expressed as percentage of the total chromatographic signal.

2.3.0 Results & Discussion

2.3.1 Relative rates of TATP Decomposition with Acid

It was proposed that the application of mineral acid, an inexpensive and widely available liquid, applied as a spray or mist, could be a field approach to destruction of TATP. Addition of concentrated sulfuric acid (3 mL of 80% or 90%) to solid TATP (3 g) resulted in detonation. In an attempt to slow the reaction, solvents were added to the TATP (3 mL of diesel fuel, various alcohols). Addition of 98% sulfuric to the TATP moistened with a solvent resulted in violent decomposition, but not detonation. To avoid violent reactions, experiments were designed to screen different solvent and acid combinations. TATP destruction did not occur with bases, but many acids, even BF_3 , destroyed TATP to some extent. [Not every acid was compatible with the organic solvent used. The addition of methylsulfonic acid (MSA), BF_3 , or HClO_4 resulted in instant and violent boiling of the solutions, and the solutions quickly turned from white to brownish-black. A survey of acids was accomplished, both with solvent

wetted TATP (Table 2.1) and neat, solid TATP (Table 2.2). The results in Table 2.1 are expressed as percent TATP remaining after a specified time interval. The solid TATP was first moistened with the solvent followed by addition of the acid. Note that in Table 2.1 decomposition of TATP is more complete in the same time interval, when using 36 wt% HCl than when using 65wt% H₂SO₄, though the molar concentrations of these acids were roughly the same. This may be explained by the higher pK_a value for HCl. In Table 2.2, aqueous acid was added directly to the TATP and the amount remaining vs time was determined by quenching the reaction at specified time intervals. The first-order rate constants from this data also indicated that HCl decomposed TATP more quickly than sulfuric acid at highest concentration (i.e. 12M). Table 2.3 shows first-order rate constants for the decomposition of TATP dissolved in the solvent system indicated. Decomposition is much faster in solution than in solid so that lower concentrations of acid can decompose TATP relatively quickly (Table 2.3); again the effectiveness of HCl is noticeable.

Table 2.1: Percent TATP remaining (0.5 g initial mass) after wetting with solvent and then adding acid

Ratio solvent:acid	Solvent	Acid (pK _a)	% remaining	Ratio solvent:acid	Solvent	Acid (pK _a)	% remaining
1:2	EtOH/i-PrOH (3 hours)	Methanesulfonic (-13)	0	1:0.5	Toluene (24 hours)	Methanesulfonic (-13)	43
1:2		HClO ₄ (-8)	0	1:0.5		HClO ₄ (-8)	violent
1:2		36% HCl (-6.3)	0/9	0.5:2		36% HCl (-6.3)	36
1:2		65% H ₂ SO ₄ (-3)	30/37	0.5:1		65% H ₂ SO ₄ (-3)	73
1:2		70% HNO ₃ (-1.6)	0	1:0.5		70% HNO ₃ (-1.6)	0
1:2		Trifluoroacetic (0.23)	0/1	1:2		Trifluoroacetic (0.23)	
1:2		BF ₃	0	1:2		BF ₃	
1:2		H ₃ PO ₄ (2.2)	75/83	1:2		H ₃ PO ₄ (2.2)	
2:2, 2:3		Acetic (4.8)	100	2:2, 2:3		Acetic (4.8)	

Table 2.2: First-order decomposition rate constant of solid TATP (5 mg) at 22°C with 1 mL aqueous acid

H ₂ SO ₄	wt%	k(sec ⁻¹)	HCl	wt%	k(sec ⁻¹)	HNO ₃	wt%	k(sec ⁻¹)	HClO ₄	wt%	k(sec ⁻¹)
16M	89	7.1E-03									
14M	82	1.9E-03				13M	60	1.8E-02			
12M	74	8.8E-04	12M	36	1.4E-03						
10M	64	1.9E-04	10M	32	2.6E-04	10M	49	2.4E-03	9.3M	61	7.9E-03
8.1M	54	9.8E-05	8.8M	28	1.8E-04	8.1M	41	1.5E-04	8.4M	58	1.7E-03
4.7M	34	2.7E-05	5.4M	18	1.3E-05						

Table 2.3: First-order decomposition rate constants for dissolved TATP with aqueous acid rate(mg/s) = k*solubility

Temperature 22C						Temperature 45C					
TATP (mg)	Acid (3.7 mmol)	Solvent (10 mL)	k (s ⁻¹)	Solubility (mg/mL)	Rate (mmol/sec)	TATP (mg)	Acid (3.7 mmol)	Solvent (10 mL)	k (s ⁻¹)	Solubility (mg/mL)	Rate (mmol/sec)
100	97%*	Acetonitrile (ACN)	1.4E-01	125	1.8E+01	100	97%	Ethanol (EtOH)	6.4E-04	143	9.2E-02
100	97%	90:10 ACN:H ₂ O	1.8E-04	105	1.9E-02	100	97%	90:10 EtOH:H ₂ O	8.6E-05	123	1.1E-02
100	97%	80:20 ACN:H ₂ O	4.7E-05	49	2.3E-03	100	97%	80:20 EtOH:H ₂ O	1.5E-04	76.9	1.1E-02
100	97%	70:30 ACN:H ₂ O	1.8E-05	44	8.0E-04	100	97%	70:30 EtOH:H ₂ O	2.0E-04	51.4	1.0E-02
7.5	97%	50:50 ACN:H ₂ O	7.4E-05	11.1	8.2E-04	7.5	97%	50:50 EtOH:H ₂ O	3.0E-04	13.2	4.0E-03
7.5	36%	Acetonitrile	2.0E-04	125	2.5E-02	100	97%	n-propanol (n-PrOH)	3.0E-04	188	5.6E-02
7.5	36%	50:50 ACN:H ₂ O	9.9E-05	11.1	1.1E-03	100	97%	90:10 n-PrOH:H ₂ O	1.7E-05	141	2.4E-03
7.5	18%	Acetonitrile	4.8E-04	125	6.0E-02	100	97%	Isopropanol (i-PrOH)	8.9E-05	217	1.9E-02
7.5	18%	50:50 ACN:H ₂ O	1.1E-04	11.1	1.2E-03	100	97%	90:10 i-PrOH:H ₂ O	2.9E-05	155	4.5E-03
7.5	97%	Methanol (MeOH)	5.2E-04	35.7	1.9E-02	100	97%	80:20 i-PrOH:H ₂ O	2.3E-05	109	2.5E-03
7.5	97%	50:50 MeOH:H ₂ O	5.6E-05	1.45	8.0E-05	100	97%	70:30 i-PrOH:H ₂ O	7.0E-05	69	4.8E-03
7.5	65%	Methanol	4.7E-05	35.7	1.7E-03	7.5	97%	50:50 i-PrOH:H ₂ O	2.5E-04	24.0	6.0E-03
7.5	65%	50:50 MeOH:H ₂ O	5.3E-05	1.45	7.7E-05	100	97%	Methanol	2.0E-03	80	1.6E-01
7.5	35%	Methanol	6.7E-05	35.7	2.4E-03	100	97%	90:10 MeOH:H ₂ O	2.1E-04	57.6	1.2E-02
7.5	35%	50:50 MeOH:H ₂ O	3.7E-05	1.45	5.3E-05	100	97%	80:20 MeOH:H ₂ O	3.0E-04	33.3	9.9E-03
7.5	36%	Methanol	1.7E-04	35.7	6.0E-03	7.5	97%	60:40 MeOH:H ₂ O	8.8E-04	12.7	1.1E-02
7.5	36%	50:50 MeOH:H ₂ O	5.8E-05	1.45	8.4E-05	7.5	97%	50:50 MeOH:H ₂ O	9.7E-04	5.99	5.8E-03
7.5	18%	Methanol	2.4E-04	35.7	8.6E-03	100	97%	t-butanol (t-BuOH)	acid reacts preferentially with t-butanol		
7.5	18%	50:50 MeOH:H ₂ O	6.3E-05	1.45	9.1E-05	100	97%	90:10 t-BuOH:H ₂ O			

*20 uL 96.5wt% H₂SO₄ [18.2M]

97% = 96.5wt% H₂SO₄ [18.2M]

65% = 65wt% H₂SO₄ [10.2M]

35% = 35wt% H₂SO₄ [4.5M]

36% = 36 wt% HCl [12.2M]

18% = 18wt% HCl [5.4M]

We previously reported that in synthesis water content affected the ratio of TATP/DADP; high water favoring TATP.⁸ Water also affects the rate of decomposition as well as the decomposition products. Water, entering the reaction with the acid, and in some cases with the solvent, slows the rate of TATP decomposition (Table 2.3). Solubility is part of the effect. TATP is soluble in the alcohols and acetonitrile but practically insoluble in water, yet the acid can more freely dissociate in water. The highest observed decomposition rate constant was for TATP in acetonitrile with no water, and in that solvent TATP converted to DADP. This conversion was not observed in alcohol solutions of TATP, nor when 10% or more water was added to the acetonitrile solutions of TATP. Furthermore, use of an alcohol solvent or addition of water slowed the decomposition of TATP. Similar observations were noted when using alcohols as co-solvents in TATP formation reactions.⁸ Rates of TATP decomposition were dependent on the type of alcohol. TATP decomposition was faster in primary alcohols (MeOH > EtOH > n-PrOH) than in isopropanol, a secondary alcohol. The acid reacts preferentially with t-butanol rather than TATP forming 2,2,4,6,6-pentamethyl-3-heptene, a condensation product of t-butanol.

The rate constants for TATP decomposition in alcohol are at a maximum in pure alcohol but pass through a minimum as the amount of water increases. The formation of alcohol/water complexes were shown to have a significant impact upon protonation of organic acids and bases and is attributed to preferential solubility by water or the organic solvent depending on the nature of the substance.¹⁰⁻¹² Table 2.4 shows the solubility of TATP in the various solvents. If rate (mg/sec) were calculated

from the product of the rate constant and solubility (assuming solvent-wetted solid TATP maintains a film of saturated solution), the decreased solubility negates (i.e. Table 2.3, far right columns) the effect of increasing rate constants with increasing water content.

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

Fig. 2.2: Ternary diagram of destruction of 500 mg TATP wetted with alcohol (ethanol or i-propanol), water and acid [left H_2SO_4 (17-24 hr); right HCl (3-7 hr) ($\square$ =0-25% remaining, Δ =25-50% remaining, $\square$ =50-100% remaining)]

Figure 2.2 summarizes attempts to decompose 500 mg TATP using the method outlined in section 2.2.2. The ternary diagrams express the percentage by weight of water, alcohol and acid present in the experiments. Note that the percentage does not represent the concentration of solvent nor acid added but is the percentage after all components in the composition are accounted for totaling 100%. Compositions which successfully destroyed TATP are outlined by an oval in the ternary diagrams. Successful destruction was defined as 0-25% of TATP remaining following reaction (3-7 hours for experiments with hydrochloric acid and 17 to 24 hours for experiments with sulfuric acid). The trends revealed in these diagrams of wetted, solid TATP, is in agreement with observations made on TATP in solution (Table 2.3). HCl destroyed TATP significantly faster and at lower acid concentrations than did sulfuric acid. Increased amounts of water, and reduced amounts of acid slowed decomposition to an extent that decomposition was incomplete (i.e. more than 50% TATP remaining). When acetone, ethylene glycol, and ethyl acetate were used as the wetting agents, the acid decomposition of TATP proceeded but somewhat slower than it did with alcohol wetting agents. Interestingly, with 50wt% ethylene glycol/water wetting agent, 65% sulfuric acid did not destroy TATP in 24 hr while 36% HCl did. Although TATP was soluble in iso-octane, toluene and diesel (Table 2.4), using these as wetting agents rendered acid treatment rather ineffective (65% sulfuric destroying 20-25% and 36% HCl destroying 40% of the TATP). This is likely due to the immiscibility of the aqueous acids with these solvents.

Table 2.4: Milliliters solvent required to dissolve 100 mg TATP at room temperature

	acetone	diesel	EtAc	i-octane	toluene	EtOH(100%)	EtOH(50%)	i-PrOH	i-PrOH(50%)	water
average	1.0	3.0	1.2	2.1	0.8	3.0	62.2	3.8	40.2	
sd	0.5	1.0	0.2	0.5	0.2	0.8	7.4	1.2	3.5	14-16
rsd(%)	44	33	14	23	20	26	12	33	9	ppm ⁶

2.3.2 Decomposition Products

Minor amounts of peroxo-acetone species have been previously identified in the acid destruction of TATP.⁸ Depending on the reaction conditions DADP could be a significant decomposition product. Table 2.3 reports that the highest decomposition rate constant for TATP was observed in dry acetonitrile and that in that solvent TATP converted to DADP. This conversion was not observed in alcohol solutions of TATP, nor when 10% or more water was added to the acetonitrile solutions of TATP. An important difference was also observed when TATP was moistened with alcohol rather than completely dissolved; some DADP formed with most acids used, but acid was applied in molar excess, which favors conversion of TATP to DADP.^{8,13,14} When sulfuric and hydrochloric acids were at roughly the same molarity (65% and 36%, respectively); the decomposition of TATP occurred at about the same rate (Table 2.2). However, the sulfuric acid produced significant amounts of DADP from 500 mg TATP, whereas HCl did not (Table 2.5). This production of DADP was also noted when 35% (4.7M) sulfuric acid was used to treat TATP at 50°C, conditions meant to simulate the use of battery acid and the normal self-heating effect of the decomposition. To minimize DADP formation HCl was chosen for the field destruction of TATP. Decomposition of TATP using HCl produced a variety of chlorinated acetones as well as chloroacetic acid ester (Figure 2.2). The decomposition affected by 70% nitric acid formed primarily DADP as well as nitro- and nitroso-organics.¹⁵

Table 2.5: Conversion of TATP (2.25mmol, 500 mg) to DADP alcohol in 3h at 25°C

acid	pKa	conc M	mmol	TATP	DADP	R-OOH's peroxy	Other Products
conc HCl (36%)	-6	12	24	0-20%	2-5%	0.7-2%	chlorinated acetones (73-97%)
conc HNO ₃ (70%)	-1.64	16	32	0.1-0.2%	81-92%	0.1-0.5%	R-ONO, R-ONO ₂ (8-17%)
conc TFA (98%)	0.23	13	26	0.1-1%	99-100%	0.1-0.2%	none identified
H ₂ SO ₄ (65%)	-3.6	10	24	47-48%	48-50%	2-5%	none identified
H ₃ PO ₄	2.15	15	29	83-87%	13-17%	0.2-2%	none identified

2.3.3 HMTD

Because it is likely that the user of the acid destruction technique might not have distinguished between the peroxides TATP and HMTD, the same technique was used on HMTD and found to be a safe and effective method of destruction. [HMTD (1 g) was wetted with 2 mL 50wt% ethanol/water solution followed by remote injection of 2 mL 36wt% hydrochloric acid, and gentle decomposition occurred in 4 hours.] Table 2.6 illustrates how the use of acids and organic solvents affect the rate of decomposition of HMTD compared to TATP.

Concentrated sulfuric acid causes both TATP and HMTD to detonate. Adding concentrated sulfuric acid to TATP wetted with alcohol solutions resulted in a violent reaction but this was not observed with HMTD. This is likely due to the insolubility of HMTD in most solvents, such as alcohols. The data suggests that hydrochloric acid is the acid of choice when attempting to decompose both peroxides. TATP and HMTD are effectively decomposed in similar amounts of time when using hydrochloric acid. Slightly dilute sulfuric acid was also effective at decomposing HMTD but not as effective at decomposing TATP. The data in Table 2.6 suggests that 50wt% ethanol/water solution with 36wt% hydrochloric acid was most effective.

Table 2.6: Comparison of HMTD and TATP decomposition under similar conditions

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

In an attempt understand violent reactions, even detonations, that concentrated sulfuric acid causes with TATP and HMTD, high-speed video was used to examine the reaction of a single drop of acid on each peroxide. A 5 cm line of TATP (200 mg) was placed onto a microscope slide. A drop of concentrated sulfuric acid was pipetted onto one end. Once initiation was observed, the TATP disappeared in linear progression in 17 ms. No immediate flame was produced. A 12 ms delay was observed before a blue flame formed in the air above the microscope slide. The flame transitioned from blue to yellow as a fireball grew. A similar experiment was conducted with HMTD. The first observation was a burst of smoke or fine particulate. In the same fashion as TATP the pile disappeared in linear progression, but before the entire pile of HMTD was gone a yellow flame was already forming above the HMTD. From initiation to the moment that the pile had disappeared 15 ms had elapsed. To determine the reactive species, the peroxides were treated with 80% sulfuric acid in a sealed GC vial. Subsequent GC/MS analysis of the TATP decomposition gases showed acetone, TATP and DADP in the headspace. We believe minute hot particles are responsible for igniting this gaseous mixture. Similar analysis of the HMTD headspace showed one broad hump. When HMTD was moistened with ethanol and treated with HCl, carbon dioxide, esters of formic acid, and, possibly, tetramethyl hydrazine were found in the headspace vapors.

2.3.4 Decomposition Mechanism

All the strong acids decomposed TATP, but rates (Tables 2.1, 2.2) and final products (Table 2.5) differed. If a protic solvent, e.g. water or alcohol, is used the carbocation formed when the TATP ring opens is stabilized and the intermediate will react more slowly and decompose into smaller molecules. If no water was present, the carbocation is not stabilized and the intermediate quickly cyclizes to DADP. In both cases acetone was formed. Figure 2.3 illustrates these alternate routes.

Fig. 2.3: TATP decomposition by acid with and without water present

The chloroacetones and chlorinated esters observed during the decomposition of TATP in hydrochloric acid suggest an acid catalyzed haloform reaction (Figure 2.4). Multiple chloro substitutions are generally observed under basic conditions with

the presence of hypochlorite¹⁶ but the presence of organic peroxy groups can oxidize chloride to chlorine or hypochlorite facilitating this type of reaction under acidic conditions.

Fig. 2.4: By-product formation

2.3.5 Calorimetry

During calorimetry experiments when 65 wt% H₂SO₄ was added to 1 mL (40 mg/mL) alcohol solutions of TATP, no reaction was observed until the solution was raised to 50°C. At 50°C temperature the reaction started within minutes. The experiment was repeated using 80 wt% sulfuric acid. Within minutes heat release was visible and after about 11 hours it appeared to be complete. Duplicate experiments were run using sulfuric, hydrochloric and nitric acids taking care to deliver similar quantities of water while delivering the same number of moles of acid because previous work had shown that water affects the formation and destruction of TATP.⁸ Under the same conditions hydrochloric acid resulted in a faster reaction rate but with less heat released overall than tests using nitric or sulfuric acid. Figure 2.5 shows the calorimetry traces and the heat release observed for each of the duplicate experiments.

Fig. 2.5: Calorimetry trace acid added to ethanol (1 mL) solution of 40 mg TATP

2.3.6 Scaleup

When the 500 mg tests were scaled to 3 g TATP wetted with 3 mL alcohol, the acid (3mL) was added remotely. With concentrated HCl (36%), the decomposition went quiescently; when it was 90% sulfuric acid, the reaction was violent (see Figure 2.6). Outdoor field tests were conducted on 100g and 460 g quantities of TATP. Quantities of acid and solvent are detailed in Table 2.7. Hydrochloric acid was chosen due to its ability to decompose TATP quickly without the formation of DADP and its reduced heat of reaction with TATP. Aqueous ethanol and isopropanol (50/50 with water) were tested on the 100 g scale with similar results (Table 2.7). Aqueous isopropanol was chosen for the 460g experiment over the lower molecular weight alcohols due to its higher boiling point (82.5°C); butanol was not considered due to its reactivity with acid. Data points for these experiments are also labeled on the ternary diagrams in Figure 2.1. For the 100g experiments the solvent and acid were added rapidly via mechanical means. Scaling up further to 460g the alcohol and acid were pumped onto the TATP via a remote control pumping setup described in section 2.2.4. The alcohol was added first with no significant change in temperature. The addition of acid

followed, and the reaction and temperature were continually monitored by video and by thermocouples both inside the beaker and at the outer surface. During the addition of 425 mL of acid, the temperature rose rapidly to about 75°C; therefore, acid addition was stopped. The temperature dropped to about 45°C and then gradually rose again. As the temperature increased some gentle boiling became visible, and the solid TATP began to visibly disappear. At a peak temperature of 75°C the solution was vigorously boiling, and all solid TATP was gone. The boiling slowly subsided and the temperature returned to ambient. The total elapsed time for the experiment was approximately 25 minutes from time of start of alcohol addition until the TATP was no longer visible by visual inspection. The acidic solution was neutralized, and products identified by GC/MS as reported above.

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

Fig. 2.6: TATP (3g) violently reacting with acid

Table 2.7: TATP destruction field tests

Mass TATP	Solvent	Solvent (mL)	Acid	Acid (mL)	Time to Destruction
100g	EtOH 50%	200	HCl 36%	400	20 min
100g	IPA 50%	200	HCl 36%	400	20 min
100g	IPA 50%	100	HCl 36%	400	<3 hours
460g	IPA 50%	900	HCl 36%	425	25 min

2.4.0 Conclusions

TATP can be destroyed quiescently under certain conditions. The ternary diagrams (Fig. 2.2) suggest that the optimum ratio of water, solvent and acid may vary depending on the acid. TATP decomposes faster with hydrochloric acid than with sulfuric acid of about comparable molarity but sulfuric acid can lead to the formation of DADP on larger scales. The same decomposition mechanism is postulated (Fig. 2.3), but different conjugate bases result in different decomposition products and different amounts of heat released.

Treating TATP with concentrated mineral acids may cause its detonation. Decreasing the concentration of the acid may results in decomposition that is far too slow. Initially, solvent was added to produce a thin layer of solvated TATP. This

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

TATP and HMTD are effectively decomposed in similar amounts of time when using hydrochloric acid. We prefer concentrated hydrochloric acid for the gentle destruction of TATP because it reacts slightly faster than a comparable concentration of sulfuric acid; its heat release is lower; and it does not tend to create DADP.

Hydrochloric acid and aqueous alcohol wetting agent have gently destroyed TATP on the 460 gram scale.

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

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Manuscript 3

Hazards of Exposing Copper Compounds to Acetylene Feedstocks

by

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3.1 Introduction

Mercury removal from heavy naptha feedstocks can be accomplished in a number of ways. Using a non-regenerable metal sulfide adsorbent has several benefits but one potential catastrophic drawback. Copper sulfide effectively scavenges mercury; but since acetylene is a possible contaminant under these circumstances, the potential formation of explosive copper acetylide is a cause for concern.

Copper acetylide is a general term used somewhat ambiguously for compounds containing copper and acetylene moieties. If the alkyne is acetylene (C_2H_2), both hydrogen atoms can be substituted with a cuprous ion (Cu^+), yielding a molecule with the formula Cu_2C_2 . If acetylene reacts with the cupric ion (Cu^{2+}), CuC_2 may be formed. To eliminate ambiguity Cu_2C_2 will be referred to as cuprous acetylide and CuC_2 will be referred to as cupric acetylide for the purposes of this research.

Fig. 3.1. Proposed structure of cuprous (a) and cupric (b) acetylides

Cuprous acetylide, a primary explosive, has the subject of research regarding carbon structures composed of linear chains of sp hybridized carbons.¹ It is a bright red powder that undergoes Glaser oxidative coupling reactions to form copper polyynides.¹ Identification of cuprous acetylide using infrared spectroscopy (IR) shows three distinct peaks circa 1200 cm⁻¹, 1400 cm⁻¹ and 1600 cm⁻¹.¹ Differential Scanning Calorimetric (DSC) trace shows broad exothermic peaks ~192°C. Cupric acetylide, a primary explosive, has sometimes been cited as the cause of accidental explosions.² Although it has been assigned a CAS number, only qualitative data is available. Cupric acetylide, or copper carbide, is brown to black in color, sometimes forming lustrous plates and is extremely sensitive towards initiation. Its structure is envisioned as the copper ion coordinated to the pi system of acetylene. The lack of physical data makes this assignment speculative, and most reports are only qualitative.³

A fundamental understanding of “copper acetylides” is necessary for evaluation of the hazards of using copper materials for mercury removal. Herein we determine whether copper adsorbents on an alumina substrate--copper oxide, copper carbonate, and copper sulfide— form hazardous acetylides when exposed to acetylene. Various analytical techniques were employed in an attempt to make that determination.

3.2 Experimental Section

3.2.1 Acetylene exposure: A 3-neck, 500 mL round-bottom flask was placed in a heating mantle connected to a variable alternating current controller. A thermocouple was pushed through a rubber septum and inserted into the middle neck of the flask. Stopcock flow controllers were placed in the two remaining necks. A bubbler filled with mineral oil was attached to the outlet so that a visual confirmation of flow could be monitored. An acetylene tank containing acetylene dissolved in acetone was regulated into a vacuum trap filled with water when moisture was desired. When moisture was not used the flow of acetylene was allowed to flow directly into the flask. The vacuum trap filled with water was wrapped with a heating sleeve controlled by a second variable AC controller.

Standard procedure involved placing 10.00g of the ground adsorbent into the apparatus, sealing everything and insulating it with glass wool and aluminum foil. The flask was put under vacuum and the backfilled with a flow of acetylene. When moisture was desired, the water temperature was maintained at 37°C to prevent any possible condensation while operating at 40°C. Once the flow of acetylene began, the temperature controller for the flask was turned on and monitored until the flask achieved the desired temperature. Once the temperature stabilized, the flow of acetylene was maintained for 1 week. The entire apparatus was kept behind a blast shield for safety. After 1 week, the acetylene flow was stopped, the temperature controllers were turned off and the flask was lifted from the heating mantle. Once again the contents were put under vacuum to remove residual acetylene and backfilled with dry nitrogen.

3.2.2 Phenylacetylene experiments: A 5:1 molar ratio of phenylacetylene to copper material mixture was stirred at room temperature for 16 hours followed by extraction into methylene chloride and analysis by GC/MS.

3.2.3 Elemental Analysis/Isotopic Ratio Mass Spectrometry: A Thermo Flash 2000 organic elemental analyzer coupled to a Thermo Delta V Advantage isotopic ratio mass spectrometer was used to determine the carbon content of samples before and after exposure to acetylene. Urea was used as an external standard for carbon quantification.

3.2.4 Thermal analysis: A TA Instruments Q100 differential scanning calorimeter was used to collect DSC data. Approximately 2.00 mg of material was placed into a hermetically sealed aluminum DSC pan. The sample and empty reference sample were heated at a rate of 20°C/minute from 30°C to 450°C. Flowing nitrogen (50 mL/min) purged the DSC cell during the experiments.

A TA Instruments Q5000 thermogravimetric analyzer was used for the TGA analysis. In a high temperature platinum pan the sample was heated under an inert nitrogen atmosphere (25 mL/min) from room temperature to 900°C at a rate of 20°C/min.

3.2.5 Infrared Spectroscopy: A Thermo Nicolet 6700 fourier transform infrared spectrometer was used to collect 64 scans at a resolution of 4 cm⁻¹ from 375-4000 cm⁻¹. Approximately 2 wt% of sample was mixed for 2 minutes with KBr in a wobble bug followed by pressing under 15000 psi for approximately 10 minutes into a pellet.

3.2.6 Raman Spectroscopy: A Bruker Senterra Raman microscope was used to collect Raman data. The laser source was 785 nm set at 100 mW. With a resolution

of 9-15 cm^{-1} spectra were collected from 148-3818 cm^{-1} using an integration time of 3 seconds and 2 coadditions.

3.2.7 Gas Chromatography/Mass Spectrometry: An Agilent GC6980 gas chromatograph coupled to an Agilent 5973 mass selective detector was used for analysis of the phenylacetylene experiments. The inlet was operated at 225°C in split mode with a 2:1 split. Helium was used as the carrier gas in constant flow mode using a Varian VF200MS column. The oven program started at 50°C followed by a 20°C/min ramp to 300°C.

3.2.8 X-Ray Photoelectron Spectroscopy: A Physical Electronics 5500 Multi-Technique Surface Analyzer was used to collect ESCA (electron spectroscopy for chemical analysis) surveys as well as multiplex analysis of specific elements. An aluminum source was used with a resolution of 0.125 eV and a spot size of 600 microns. Peaks were calibrated to a C1S peak of 284.5 eV.

3.3 Results

3.3.1 Elemental Analysis: Three adsorbents were exposed to acetylene: copper oxide (GB238); copper carbonate (GB220); and copper sulfide (GB562S from two different batches; batch B was derived from copper carbonate). Both moist and dry acetylene were used. Table 3.1 shows the elemental analyses of these samples. All samples contained more carbon after exposure than the initial samples; the increase in carbon content depended on the copper compound used. Copper carbonate showed the highest carbon content post-exposure, followed by copper oxide, and then copper sulfide batch B. The response of copper carbonate to acetylene exposure was unique in that it changed color from teal green to brown upon exposure to dry or moist acetylene

for 1 week at 40°C and a flame test of this brown materials resulted in ignition. In contrast, the acetylene-exposed copper oxide and copper sulfide did not change color nor ignite in a flame.

Table 3.1: Elemental analysis of copper compounds pre and post exposure

	Elemental Analysis						TGA		
	As received		Exposed to C ₂ H ₂ /H ₂ O for 1 week at 40C		Exposed to dry C ₂ H ₂ for 1 week at 40C		As received	Exposed to C ₂ H ₂ /H ₂ O for 1 week at 40C	Exposed to dry C ₂ H ₂ for 1 week at 40C
	%C by mass	std dev	%C by mass	std dev	%C by mass	std dev	% mass loss	% mass loss	% mass loss
copper oxide (GB238)	trace		7.92	0.15	8.49	0.19	12.1	19	12.9
copper carbonate (GB220)	4.05	0.19	18.96	0.21	17.21	0.68	28.5	17.4	20.1
copper sulfide B (GB562S from carbonate)	trace		1.59	0.17	1.62	0.03	21.8	20.6	22.7
copper sulfide A (GB562S)	trace		1.22	0.07	2.22	0.08			

3.3.2 DSC & TGA: Thermal analysis experiments were useful in monitoring changes in the adsorbents upon acetylene exposure but offered little evidence as to the nature of the observed changes. The differential scanning calorimetry (DSC) results are summarized in Table 3.2 (summary of DSC thermographs, Figs. 3.2-3.13). All the copper compounds showed only endotherms prior to exposure to acetylene. A common endotherm around 100°C may be attributed to the evaporation of trace moisture. Upon exposure to acetylene (moist or dry) the oxide and carbonate samples formed a material, which also exhibited an exotherm (Figs. 3.2-3.7); copper sulfide did not (Figs. 3.8-3.13).

Table 3.2: DSC (20°C/min) of copper materials as received & post exposure to acetylene with/without moisture 1 week at 40°C

Materials	Exposure	Endotherm (°C)	Exotherm(°C)
CuO	none	110	
	C ₂ H ₂ /H ₂ O	120	212
	C ₂ H ₂	130	210
CuCO ₃	none	108/260	
	C ₂ H ₂ /H ₂ O		115/280
	C ₂ H ₂	110	233
CuS (batch A)	none	100	
	C ₂ H ₂ /H ₂ O	100	
	C ₂ H ₂	100	
CuS (batch B)	none	100/278	
	C ₂ H ₂ /H ₂ O	90	
	C ₂ H ₂	283	

DSC GB238 (copper oxide)

Fig.3.2 GB238 as received

Fig. 3.3 GB238 exposed to a flow of acetylene bubbled through water; 40°C for 1 week.

Fig.3.4 GB238 exposed to a flow of dry acetylene; 40°C for 1 week.

DSC GB220 (copper carbonate)

Fig. 3.5 DSC GB220 as received

Fig. 3.6 DSC GB220 exposed to a flow of acetylene bubbled through water; 40°C for 1 week.

Fig. 3.7 DSC GB220 exposed to a flow of dry acetylene; 40°C for 1 week.

DSC GB562S (Batch B; copper sulfide from copper carbonate starting material)

Fig. 3.8 DSC GB562S batch B as received

Fig. 3.9 DSC GB562S batch B exposed to a flow of acetylene bubbled through water; 40°C for 1 week.

Fig. 3.10 DSC GB562S batch B exposed to a flow of dry acetylene; 40°C for 1 week.

DSC GB562S (Batch A; copper sulfide)

Fig. 3.11 DSC GB562S batch A as received

Fig. 3.12 DSC GB562S batch A exposed to a flow of acetylene bubbled through water; 40°C for 1 week.

Fig. 3.13 DSC GB562S batch A exposed to a flow of dry acetylene; 40°C for 1 week.

Thermogravimetric analysis (TGA) of copper sulfide was relatively unchanged before and after exposure to acetylene seeming to support the idea that this material did not react with acetylene (Figs. 3.20-3.22). In contrast, the TGA traces of the copper carbonate or oxide samples changed dramatically with exposure to acetylene (Table 3.1) (Figs. 3.14-3.19). The TGA traces of the copper carbonate before exposure to acetylene showed a mass loss of 29% (peak at 282°C) which is a little low for complete loss of carbonate (36%). (Fig. 3.16).⁴ Copper carbonate exposed to either moist or dry acetylene showed a TGA loss of 17-20% (peak 205°C) (Figs. 3.18 & 3.19) consistent with a carbon content of 17-19% determined by elemental analysis

(Table 3.1). Likewise copper oxide exposed to moist acetylene exhibited a weight loss of 19% (Fig. 3.15), an increase of 7% by weight, consistent with elemental analysis. The low weight loss from the copper oxide exposed to dry acetylene was unique (Fig. 3.16); its Raman and IR spectra were unique, as well.

TGA GB238 (copper oxide)

Fig. 3.14 TGA GB238 as received

Fig. 3.15 TGA GB238 exposed to a flow of acetylene bubbled through water; 40°C for 1 week.

Fig. 3.16 TGA GB238 exposed to a flow of dry acetylene; 40°C for 1 week.

TGA GB220 (copper carbonate)

Fig. 3.17 TGA GB220 as received

Fig. 3.18 TGA GB220 exposed to a flow of acetylene bubbled through water; 40°C for 1 week.

Fig. 3.19 TGA GB220 exposed to a flow of dry acetylene; 40°C for 1 week.

TGA GB562S (batch B; copper sulfide from copper carbonate starting material)

Fig. 3.20 TGA GB562S batch B as received

Fig. 3.21 TGA GB562S batch B exposed to a flow of acetylene bubbled through water; 40°C for 1 week.

Fig. 3.22 TGA GB562S batch B exposed to a flow of dry acetylene; 40°C for 1 week.

3.3.3 Raman & Infrared Spectroscopies: The copper oxide and copper carbonate exposed to acetylene showed a new peak in the Raman spectra around 1370 cm^{-1} (Figs. 3.23-3.28). There was little to distinguish these except the intensity of the peak near 1370 cm^{-1} and the appearance of multiple peaks in this region for the copper oxide sample exposed to dry acetylene (Fig. 3.25). Reported literature values suggest the 1370 cm^{-1} peak is due to the presence of a highly disordered phase of carbon.⁵⁻⁷ Acetylide or carbyne carbons which are sp hybridized should be have a peak around 2100 cm^{-1} similar to that seen in the Raman spectra of phenylacetylene (figure 3.35);⁸⁻¹⁰ however, no such peak was observed in any of the exposed samples. The acetylene-exposed copper oxide and carbonate samples also exhibited a small peak around 1860 cm^{-1} (Figs. 3.24, 3.27 & 3.28). This may be assigned to cumulenenic carbon associated with a highly oxidized form of copper at the terminal ends of the carbon chain.⁸ Cupric oxide had sharp peaks at 285 and 600 cm^{-1} which broaden out to reduced intensity as the cupric oxide was reduced to the cuprous oxide.^{11,12} Peaks in these regions were observed in the as-received copper oxide and copper carbonate samples (Fig. 3.23) and were barely visible in the spectrum after exposure to acetylene.

On the basis of the DSC and TGA results, we have suggested that the copper sulfide does not react with acetylene. The Raman spectra of batch A support this hypothesis (Figs. 3.29-3.31). In the post-acetylene sample of copper sulfide, batch B, there was a small peak near 1370 cm^{-1} (Figs. 3.33 & 3.34) which suggested that some copper carbonate contamination remained in the copper sulfide and reacted with the acetylene. This is supported by the presence of an endotherm at 275°C in the DSC of copper sulfide batch B (Fig. 3.8).

Raman GB238 (copper oxide)

Fig. 3.23 Raman GB238 as received

Fig. 3.24 Raman GB238 exposed to a flow of acetylene bubbled through water; 40°C for 1 week.

Fig. 3.25 Raman GB238 exposed to a flow of dry acetylene; 40°C for 1 week.

Raman GB220 (copper carbonate)

Fig. 3.26 Raman GB220 as received

Fig. 3.27 Raman GB220 exposed to a flow of acetylene bubbled through water; 40°C for 1 week.

Fig. 3.28 Raman GB220 exposed to a flow of dry acetylene; 40°C for 1 week

Raman GB562S (Batch B; copper sulfide from copper carbonate starting material)

Fig. 3.29 Raman GB562S batch B as received

Fig. 3.30 Raman GB562S batch B exposed to a flow of acetylene bubbled through water; 40°C for 1 week

Fig. 3.31 Raman GB562S batch B exposed to a flow of dry acetylene; 40°C for 1 week.

Raman GB562S (Batch A; copper sulfide)

Fig. 3.32 Raman GB562S (from original starting material) as received

Fig. 3.33 Raman GB562S (from original starting material) exposed to a flow of moist acetylene; 40°C for 1 week.

Fig. 3.34 Raman GB562S (from original starting material) exposed to a flow of dry acetylene; 40°C for 1 week.

Raman phenylacetylene

Fig. 3.35: Raman phenylacetylene

Infrared (IR) spectroscopy indicates that all samples, except for the copper oxide exposed to dry acetylene, remained relatively unchanged after exposure to moist and dry acetylene (Figs. 3.36-3.47). As in Raman, the IR spectrum of the copper oxide exposed to dry acetylene produced a unique spectrum with multiple peaks in the 1700 to 1100 cm^{-1} region (Fig. 3.38). In no case did the acetylene exposed samples exhibited peaks in the 2200 to 2100 cm^{-1} region expected for carbon-carbon triple bonds.¹³

IR GB238 (copper oxide)

Fig. 3.36 IR GB238 as received

Fig. 3.37 IR GB238 exposed to a flow of acetylene bubbled through water; 40°C for 1 week.

Fig. 3.38 IR GB238 exposed to a flow of dry acetylene; 40°C for 1 week.

IR GB220 (copper carbonate)

Fig. 3.39 IR GB220 as received

Fig. 3.40 IR GB220 exposed to a flow of acetylene bubbled through water; 40°C for 1 week.

Fig. 3.41 IR GB220 exposed to a flow of dry acetylene; 40°C for 1 week.

IR GB562S (Batch B; copper sulfide from copper carbonate starting material)

Fig. 3.42 IR GB562S batch B as received

**Fig. 3.43 IR GB562S batch B exposed to a flow of acetylene bubbled through water;
40°C for 1 week**

Fig. 3.44 IR GB562S batch B exposed to a flow of dry acetylene; 40°C for 1 week.

IR GB562S (Batch A; copper sulfide)

Fig. 3.45 IR GB562S batch A as received

Fig. 3.46 IR GB562S batch A exposed to a flow of dry acetylene; 40°C for 1 week.

Fig. 3.47 IR GB562S batch A exposed to a flow of acetylene bubbled through water; 40°C for 1 week

3.3.4 X-ray Photoelectron Spectroscopy (XPS): After an initial survey of 0 to 1000 eV binding energies, the Cu 2p (970-920 eV) and the C1s regions (280-300eV) were examined in detail. Copper peaks were observed at 935 and 955 eV with CuO satellite peaks at 943 and 963 eV in the as-received copper oxide and carbonate and in the acetylene exposed samples (Figs. 3.48-3.60). Readily observed in the acetylene-exposed copper carbonate sample is a decrease in the intensity of the CuO satellites

with a concomitant increase the Cu peaks, i.e. reduction is observed by XPS as well as Raman. (Fig. 3.59). This change is not as dramatic in the copper oxide sample although the reduced intensity of the satellite peaks suggests that reduction may have occurred (Fig. 3.53). Decomposition of the carbonate in the exposed copper carbonate samples is also observed by XPS (Fig. 3.60). In the as received copper carbonate sample a peak is observed near 290 eV that is absent in the exposed samples.

In the carbon region, the C1s peaks of the acetylene-exposed samples were asymmetric, centered at 284.5 eV (Figs. 3.51 & 3.56). Cataldo claimed sp hybridized carbon made up the majority of the C1s peak, but our Raman results of the exposed adsorbent samples would indicate that sp³ and sp² hybridized carbon comprised the majority of the peak. The tail of the peak toward the higher binding energies is likely due to the formation of oxides of carbon such as carbonyl and alcohol functionalities.^{14,15} Evidence of dicopper acetylide (Cu₂C₂) and dicopper diacetylide (Cu₂C₄) has been claimed from the observation of peaks at higher binding energies (285.3 and 288.2 eV, respectively).¹⁶ However, unlike that work which scrupulously removed oxygen, we cannot claim the tailing to higher energies supports the presence of acetylides. In agreement with the other analytical methods, the XPS spectrum of the copper sulfide was not changed by exposure to acetylene. (Figs. 3.61-3.65).

XPS GB238 (copper oxide)

Fig. 3.48 XPS GB238 as received, ECSA survey

Fig. 3.49 XPS GB238 as received, Cu region

Fig. 3.50 XPS GB238 exposed to a flow of acetylene bubbled through water; 40°C for 1 week, ECSA survey.

Fig. 3.51 XPS GB238 exposed to a flow of acetylene bubbled through water; 40°C for 1 week, Cu region.

Fig. 3.52 XPS GB238 exposed to a flow of acetylene bubbled through water; 40°C for 1 week, carbon region.

Fig. 3.53: XPS overlay of Cu2p regions of copper oxide samples as received and post exposure

XPS GB220 (copper carbonate)

Fig. 3.54 XPS GB220 as received, ESCA survey

Fig. 3.55 XPS GB220 as received, Cu region

Fig. 3.56 XPS GB220 exposed to a flow of acetylene bubbled through water; 40°C for 1 week, ESCA survey.

Fig. 3.57 XPS GB220 exposed to a flow of acetylene bubbled through water; 40°C for 1 week, Cu region

Fig. 3.58 XPS GB220 exposed to a flow of acetylene bubbled through water; 40°C for 1 week, carbon region

Fig. 3.59: XPS overlay of Cu2p regions of the copper carbonate samples as received and post exposure

Fig. 3.60: XPS overlay of C1s regions of the copper carbonate samples as received and post exposure

XPS GB562S (Batch B; copper sulfide from copper carbonate)

Fig. 3.61 XPS GB562S batch B as received, ECSA survey

Fig. 3.62 XPS GB562S batch B as received, Cu region

Fig. 3.63 XPS GB562S batch B exposed to a flow of acetylene bubbled through water;
40°C for 1 week, ESCA survey

Fig. 3.64 XPS GB562S batch B exposed to a flow of acetylene bubbled through
water; 40°C for 1 week, Cu region

Fig. 3.65 XPS GB562S batch B exposed to a flow of acetylene bubbled through water;
40°C for 1 week, carbon region

3.4.0 Discussion

The typical method for synthesizing cuprous acetylide is to dissolve a cuprous salt such as cuprous iodide in aqueous ammonia in the presence of a reducing agent such as hydroxylamine.¹⁹ Upon bubbling acetylene into the solution a bright red precipitate forms. This precipitate is sensitive to oxygen and begins to undergo Glaser oxidative polymerization forming copper polyynides.² By this route a standard cuprous acetylide was prepared as a standard and model for determining the most effective technique for identifying copper acetylide if it was formed in our experiments. Figures 3.66 and 3.67 show an IR and Raman spectrum of the freshly prepared red powder prepared by the above route. No peak is observed in the 2100cm^{-1} region of either spectrum.

Fig. 3.66 IR prepared cuprous acetylide

Fig. 3.67 Raman prepared cuprous acetylide

Cataldo et al concluded that attempts to make a material composed of purely sp-hybridized carbon (polyynes) resulted in the formation of linear acetylide chains that cross-link with one another resulting in a mixture of carbon with sp² and sp³ hybridization.¹⁹ This mixture of carbon also resembles activated charcoal and hardwood charcoal although the Raman spectra of charcoal has more graphitic carbon present (i.e. peak around 1600 cm⁻¹)(Figs. 3.68-3.70).

Fig. 3.68: Raman activated charcoal

Fig. 3.69: Raman hardwood charcoal

Fig. 3.70: Raman graphite

The IR and Raman spectra shown in Figures 3.66 and 3.67 are very similar in appearance to those of the products formed when either the copper oxide or carbonate adsorbents were exposed to a stream of acetylene. Furthermore, their Raman spectra are strikingly similar to various forms of carbon charcoal and graphite (Figs. 3.68-3.70). The absence of a peak near 2100 cm^{-1} in any of these samples, including the red powder produced by the “standard” preparation method, suggests an acetylide was not formed or, if formed, and rapidly underwent further reaction. There is precedence for substituted acetylene molecules coupling in the presence of copper in various oxidation states without solvent.¹⁷⁻²⁰

To probe the reactivity of the copper compounds with other acetylene bearing molecules, each was stirred with phenylacetylene for ~16 hours, followed by GC/MS analysis (Fig. 3.71). Identification of 1,4-diphenylbutadiyne indicates the ability of the copper compounds to couple acetylene moieties without any further assistance from solvents or added base. With copper sulfide much less diphenylbutadiyne was observed than when copper oxide or copper carbonate were used. This result is in keeping with the lack of reaction between the sulfide material and acetylene.

Fig. 3.71 Mass spectrum of phenylacetylene stirred with GB238 (copper oxide) material for 16 hours followed by extraction in methylene chloride

3.5 Conclusions

Under the experimental conditions used, acetylene exposure of copper oxide or copper carbonate formed energetic materials, but these resulting materials do not appear to be cuprous acetylide (Fig. 3.1a). Indeed previous reports of cuprous acetylide synthesis do not isolate it.^{3,19} If formed, cuprous acetylide likely underwent further polymerization and crosslinking resulting in a very disordered form of carbon, as observed by Raman spectroscopy. The absence of copper acetylide as a product in the exposed samples reduces the risks associated with exposing these compounds to acetylene. Nevertheless, with copper oxide and carbonate there is evidence that the end products are energetic as evidenced by the exotherm in their DSC traces and the energetic behavior of the post-exposure copper carbonate sample when exposed to flame. This is likely due to the exothermic reaction between copper oxide and carbon at elevated temperatures.²⁰ Thus, exposure of copper oxide or carbonate to acetylene

under conditions, such as were used in this study, may be hazardous; but the conditions of this study were designed to be extreme. Using copper sulfide adsorbents in the presence of trace amounts of acetylene should result in minimal risk as it pertains to copper acetylide.

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Manuscript 4

Hydrolysis of Sodium Borohydride by Hydrogen Peroxide

by

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Abstract

Fuel cells offer the promise of a clean energy by converting chemical energy into electrical energy. One such example is a direct borohydride fuel cell. Although many of the challenges associated with these fuel cells have been addressed with success a serious concern still remains: These fuel cells utilize sodium borohydride and hydrogen peroxide, two highly incompatible materials. If the fuel cell were to be physically compromised during storage or use the borohydride and hydrogen peroxide could mix and result in catastrophic failure. The goal of this work is to begin to address this safety issue by understanding the reaction between the two materials on a fundamental level.

4.1 Introduction

Fuel cells are attractive because they provide an efficient, safe and renewable alternative to traditional petroleum fuels. A number of technologies, such as polymer electrolyte fuel cells (PEFCs) and direct methanol fuel cells (DMFCs) are promising, but their commercialization has been restricted due to various problems such as electrode poisoning.¹ Direct borohydride fuel cells (DBFCs) have been developed and studied in order to overcome some of these obstacles, but they suffer from the potential of catastrophic failure of the fuel cell due to chemical incompatibilities

between hydrogen peroxide and sodium borohydride. To examine the potentially hazardous reactivity between hydrogen peroxide and sodium borohydride, we studied the kinetics and heat release of the reaction by gas evolution and reaction calorimetry.

4.2.0 Experimental

4.2.1 Reagents and Chemicals

Sodium hydroxide pellets of 99% purity were obtained from Sigma Aldrich. Sodium borohydride (98% purity) was obtained from Alfa Aesar. Hydrogen peroxide (30 wt% and 50 wt%) were obtained from Univar. Concentrated solutions of hydrogen peroxide were obtained by distillation. Concentrations were confirmed by refractive index measurements.

4.2.2 Micro reaction calorimetry

Isothermal calorimetry experiments were conducted using a Thermal Hazards Technology (THT) micro-reaction calorimeter. The instrument was calibrated at 25°C by supplying 300 mJ pulses after an initial period of 30 seconds. Data was collected for a total of 500 seconds, and the experiment was repeated 3 times. For the isothermal experiments, data was collected at a rate of 1 data point/second in titration mode, using 1mL solvent as reference. One mL of the borohydride solution was equilibrated in the sample cell. Hydrogen peroxide (HP) was measured into a 100 μ L THT syringe, its tip was placed into the equilibrated borohydride solution, the syringe secured, to the instrument, and the entire setup allowed to equilibrate. The experimental duration, duration of baseline data collection, dosage, dosage rate, and other necessary parameters were set, before the experiment, initiated.

4.2.3 Gas Evolution

A gas burette was made by inverting a 50 mL burette and securing a 1/4" ID piece of Tygon tubing to the tip. The other end of the length of tubing was secured to a ground glass fitting; the fitting was sealed to a 50 mL 3-neck round bottom flask using Dow Corning silicone vacuum grease. A stopcock and a rubber septum were secured to the other necks on the flask. A length of flexible rubber tubing was used to link the burette to a 200 mL graduated cylinder. The burette and graduated cylinder were filled with water. Leveling the meniscus in the burette with the meniscus in the graduated cylinder ensured the pressure in the burette was equal to atmospheric pressure. The 50 mL round bottom flask was placed in a water bath on top of a hot plate fitted with a temperature control probe and thermometer.

For liquid additions a 5 mL BD syringe was used to penetrate the rubber septum for hydrogen peroxide injections into borohydride solutions. For solid addition, a metal spatula was placed through the rubber septum and an aluminum DSC pan was glued to the tip. The solid sample was placed into the DSC pan and secured so that the system could be sealed prior to adding the solid sample. Turning the metal spatula emptied the solid contents into the solution. Gas evolved was measured; and time intervals, recorded.

4.2.4 Product Identification

Gaseous products were analyzed using an Agilent 7890 gas chromatograph coupled to a thermal conductivity detector (TCD). Argon was used as a carrier gas and kept at a constant flow of 5 mL/min. A 5 μ L injection split 5:1 was injected into a 50°C inlet. A Varian Molsieve 5A column was used, and the oven was kept

isothermal for 3 minutes. Gases were identified by retention times compared to injections of known gas samples.

4.3 Results & Discussion

Spot tests were conducted to probe the reactivity between hydrogen peroxide and sodium borohydride as a solid and in solution. Low concentrations of reactants (<1 wt% sodium borohydride and < 30 wt% hydrogen peroxide) were deemed safe so that larger scale studies could be conducted. Observations are recorded in Table 4.1.

Table 4.1: Spot tests for combinations of sodium borohydride and hydrogen peroxide

4-6 mg solid NaBH ₄ in each well		4-6 mg solid NaBH ₄ in 0.5 mL 3 wt% NaOH		2 drops 1 wt% NaBH ₄ in 3 wt% NaOH	
67% HP	instant pop	67% HP	gradual bubbling	67% HP	gradual bubbling observed
53% HP	instant pop	53% HP	gradual bubbling	53% HP	nothing observed
44% HP	violent bubbling and pop	44% HP	no immediate response	44% HP	nothing observed
30% HP	violent bubbling	30% HP	no immediate response	30% HP	nothing observed

4-6 mg solid NaBH ₄ in 0.5 mL water		25% by weight NaBH ₄ in 3% NaOH 1 drop followed by 1 drop 67% HP extremely loud report	2 drops 10 wt% NaBH ₄ in 3 wt% NaOH	
67% HP	instant bubbling		67% HP	instant violent bubbling
53% HP	instant bubbling		53% HP	vigorous bubbling
44% HP	instant bubbling		44% HP	vigorous bubbling
30% HP	instant bubbling		30% HP	delayed but vigorous bubbling

This qualitative data suggests the degree to which concentration affects the reactivity of HP with sodium borohydride solutions. Calorimetric results are summarized in Table 4.2.

Table 4.2: Heat of reaction of sodium borohydride (0.4 mg) solution with HP

Additive		ave heat output mJ	kJ/mol X	std dev	X
30% HP	3% NaOH	6600	27	0.32	HP
70% HP	3% NaOH	17200	26	1.4	HP
30% HP	NaBH ₄ in iPrOH		950	48	NaBH ₄
70% HP	NaBH ₄ in iPrOH		890	100	NaBH ₄
30% HP	NaBH ₄ in 3% NaOH aq soln		940	215	NaBH ₄
70% HP	NaBH ₄ in 3% NaOH aq soln		1600	56	NaBH ₄

When hydrogen peroxide was injected into a 3wt% sodium hydroxide solution an exothermic reaction occurred due to the base catalyzed decomposition of hydrogen peroxide.² When sodium borohydride was dissolved in the aqueous 3wt% sodium

hydroxide the addition of HP resulted in an even more highly exothermic reaction. To remove the potential additive effects to the overall heat release (HP decomposition in NaOH and HP reaction with borohydride), sodium hydroxide was not used; rather sodium borohydride was dissolved in isopropanol. With 30wt% and 70 wt% hydrogen peroxide, the heat released per mole of sodium borohydride in isopropanol was similar to that obtained by adding 30wt% hydrogen peroxide to an aqueous 3wt% sodium hydroxide solution containing sodium borohydride. However, when 70wt% HP was added to a sodium borohydride solution in aqueous 3wt% sodium hydroxide the heat released was much greater than when 30wt% HP was used. This is most likely due to the decomposition of hydrogen peroxide by strong base being dependent upon the ratio of hydrogen peroxide to hydroxide ion.³ In comparison to hydrolysis of borohydride by water, hydrolysis by hydrogen peroxide is considerably more exothermic, 250 kJ/mole⁴ versus more than 900 kJ/mole (Table 4.2).

To analyze the progress of the reaction, we attempted both ¹H and ¹¹B NMR experiments; but the rate of the reaction and the formation of gas bubbles made this very difficult. NMR was useful in identifying the end product as boric acid. Monitoring the reaction by gas evolution was successful. The difficulty with that approach was the fact more than one reaction was taking place. Sodium borohydride reacts with water (eq. 4.1); but, the presence of base greatly retards this reaction.⁵ Unfortunately, while alkaline conditions stabilize borohydride in water, they catalyze the decomposition of hydrogen peroxide (eq. 4.2).³

Eq. 4.1 Water hydrolyzes sodium borohydride.

Eq. 4.2 Base catalyzed decomposition of hydrogen peroxide

For this reason each possible reaction was analyzed individually as well as together by gas evolution: decomposition of hydrogen peroxide in NaOH solution, hydrolysis of sodium borohydride by hydrogen peroxide in NaOH solution, and hydrolysis of sodium borohydride in aqueous hydrogen peroxide with no added base. Hydrolysis of sodium borohydride by water is reasonably slow at room temperature. Hydrolysis of borohydride by hydrogen peroxide was much faster than by water (Tables 4.3 and 4.4). It is interesting to note that hydrolysis of borohydride in water resulted in 4 molar equivalents of hydrogen gas;⁵ whereas hydrolysis by hydrogen peroxide only resulted in 1 molar equivalent of hydrogen gas (Table 4.3). This was confirmed using gas chromatography coupled to a thermal conductivity detector (GC-TCD) (Fig. 4.1).

Fig. 4.1: GC-TCD analysis of gases observed from mixing sodium borohydride with hydrogen peroxide at room temperature in water (solid line) and in 3wt% NaOH (dashed line)

Table 4.3: First-order rate constants and Arrhenius activation parameters for hydrolysis of NaBH_4 by 3 wt% hydrogen peroxide without added NaOH

HP (0.019 mol)	NaBH_4 (mol)	solvent (20 mL)	temp °C	mmol gas evolved	average gas evolved (mL)	1/T	$\ln(k)$	E_a (kJ/mole)	A (sec ⁻¹)
0	0.00185	water	25						
3% HP(20 mL)	0.0008	water	0	0.8	19.4	0.00366	-6.27	36.58	1.96E+04
3% HP(20 mL)	0.0009	water	20	0.9	20.8	0.00341	-5.02		
3% HP(20 mL)	0.0008	water	20			0.00341	-5.24		
3% HP(20 mL)	0.0008	water	25			0.00336	-4.88		
3% HP(20 mL)	0.0010	water	25			0.00336	-4.99		
3% HP(20 mL)	0.0008	water	25			0.00336	-4.93		
3% HP(20 mL)	0.0007	water	25	0.8	19.1	0.00336	-4.61		
3% HP(20 mL)	0.0008	water	25			0.00336	-5.13		
3% HP(20 mL)	0.0008	water	25			0.00336	-4.68		
3% HP(20 mL)	0.0008	water	25			0.00336	-4.79		
3% HP(20 mL)	0.0008	water	25			0.00336	-5.04		
3% HP(20 mL)	0.0008	water	30			0.00330	-4.63		
3% HP(20 mL)	0.0008	water	30	0.8	19.5	0.00330	-4.42		
3% HP(20 mL)	0.0008	water	30			0.00330	-4.32		
3% HP(20 mL)	0.0008	water	35			0.00325	-5.28		
3% HP(20 mL)	0.0008	water	35	0.8	19.7	0.00325	-4.69		
3% HP(20 mL)	0.0008	water	35			0.00325	-4.45		
3% HP(20 mL)	0.0008	water	35			0.00325	-4.21		

Table 4.4: First-order rate constants and Arrhenius activation parameters for hydrolysis of NaBH₄ in 3 wt% NaOH by hydrogen peroxide

HP (0.019 mol)	NaBH ₄ (mol)	solvent (20 mL)	temp °C	mmol gas evolved	1st order k (s ⁻¹)	E _a (kJ/mole)	A (sec ⁻¹)
30% HP (2 mL)	0.0017	3% aq NaOH	18	1.6	2.83E-04	52.5	8.36E+05
30% HP (2 mL)	0.0017	3% aq NaOH	17		2.66E-04		
30% HP (2 mL)	0.0017	3% aq NaOH	17		3.31E-04		
30% HP (2 mL)	0.0018	3% aq NaOH	20	2.7	5.33E-04		
30% HP (2 mL)	0.0017	3% aq NaOH	31		5.76E-04		
30% HP (2 mL)	0.0017	3% aq NaOH	31		6.06E-04		
30% HP (2 mL)	0.0017	3% aq NaOH	30		5.91E-04		
30% HP (2 mL)	0.0017	3% aq NaOH	40	2.7	1.43E-03		
30% HP (2 mL)	0.0017	3% aq NaOH	40		2.21E-03		

The use of strong base to stabilize sodium borohydride hydrolysis in water also effectively stabilized the sodium borohydride against hydrolysis by hydrogen peroxide (cf Table 4.3 to Table 4.4). However, the retarding of borohydride hydrolysis was not sufficient to prevent the reaction from being potentially catastrophic, and the decomposition of the HP, promoted by the base, resulted in oxygen formation (eq. 4.2). At room temperature 1 molar equivalent of gas was evolved from the reactions shown in Table 4.4, but at elevated temperatures, e.g. 40°C (Table 4.4), more gas was evolved. Analysis of the gaseous products showed that instead of just hydrogen gas evolution there was also oxygen gas evolution, due to hydrogen peroxide decomposition in the presence of strong base (Fig. 4.1).

The difference in the amount of gas evolved when comparing hydrolysis by water or hydrogen peroxide may be rationalized by the hydroboration/oxidation reaction, which utilizes strong base and hydrogen peroxide⁷ (eq. 4.3, Fig. 4.2). Following this type of mechanism the hydride could react with the acidic proton of the hydrogen peroxide evolving hydrogen gas followed by the nucleophilic anion of

hydrogen peroxide attacking the electrophilic boron resulting in the formation of hydroxide ion.

Eq. 4.3: Overall reaction of hydrogen peroxide with sodium borohydride in 3wt% NaOH

Fig. 4.2: Reaction scheme for hydrolysis of sodium borohydride by hydrogen peroxide in strong base.

4.4 Mitigating Strategies

The reaction between sodium borohydride and HP is extremely violent, especially when both are at high concentrations. It is difficult to chemically alter the formulation in a manner that would lessen the severity of the reaction but not prevent it from being harnessed, as intended. When a drop of 70wt% HP was dripped onto a NaOH solution of 25wt% sodium borohydride sitting in a spot plate, there was a flash

and loud report. High-speed video showed more details. The two solutions mixed readily; they were completely miscible. Boiling commenced and became increasingly more vigorous as the reaction progressed and threw solution into the air where it ignited into a fireball. Reducing the ability of the solutions to diffuse into one another may offer a possible way to tame their unintended interaction. Manipulating the solution viscosities so that diffusion between the solutions would be slowed could potentially mitigate some of the hazard. In a “quick-look” experiment, sodium alginate was added to 70% HP. When the amount of alginate was ~1wt%, the viscosity of the HP solution increased to the consistency of maple syrup. When a drop of this viscous solution was added to a drop of 25wt% sodium borohydride basic solution, the reaction was still vigorous, but noticeably slower, to the point that it could be observed without the aid of a high-speed camera. The reactants remained in the spot plate and were not thrown into the air nor ignited. Additional alginate, up to 2wt% in HP further increased the viscosity and slowed the reaction with borohydride. The reaction was sufficiently slow that a red glow could be observed at the boundary layer between the HP and borohydride. The glowing red boundary layer progressed across the drops as diffusion between them occurred. These observations suggest that efforts to increase viscosity may mitigate catastrophic mixing if engineering cannot absolutely guarantee no leakage between cells.

4.5 Conclusions

Sodium borohydride hydrolysis by water is slow compared to hydrolysis by hydrogen peroxide. The reaction is also more exothermic when hydrogen peroxide is used. Although strong base can stabilize borohydride hydrolysis in both cases, it

cannot prevent the potential catastrophic failure of a DBFC if it were to be physically compromised and the components, mixed. In a DBFC the concentration of the chemicals is high, and qualitative tests have shown they react in a hypergolic fashion. Limiting diffusion between the solutions may be the solution to mitigating the violence of this reaction. How addition of contaminants, like sodium alginate, would effect the performance of these cells is unknown, but perhaps thickening agents could be selected that would not have any adverse effects on the cell performance.

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Appendix A: Data for Manuscript 1

Identification of intermediates and relative rates of formation

The following GC-MS data was collected using anhydrous ammonia positive chemical ionization mass spectrometry. All peaks were analyzed in select ion monitoring mode unless otherwise specified.

Table A1: GC-MS monitoring of a 1:1 mole ratio acetone:67wt% HP mixture at room temperature with no stirring (* indicates that the response on the MSD was at maximum threshold value)

time(minutes)	m/z 240 Area	TATP (mg/mL)	m/z 166 Area	DADP (mg/mL)	Cyclic tetramer m/z 314 area	2-hydroxy-2- hydroperoxypropane m/z = 127, (+35) area	2,2- dihydroperoxypropane m/z 126 area	2,2-dihydroxy-2,2- diisopropylperoxide m/z 168 area	2,2-dihydroperoxy-2,2- diisopropylperoxide m/z 200 area	dihydroxy trimer m/z 242 area	dihydroperoxy trimer m/z 274 area
30	1.3E+05	0.030	2.1E+03	0.092			1.6E+05	9.6E+04	3.3E+06		
520	2.3E+06	0.34	1.8E+04	0.35			7.7E+05	7.3E+05	1.7E+08		
1360	6.7E+06	0.93	2.6E+04	0.51			2.4E+04	1.1E+06	3.9E+08		
7080	4.0E+07	3.5	4.9E+05	1.60	1.5E+06	9.6E+04	1.0E+05	1.1E+08	1.4E+09*	5.8E+05	1.3E+06
10020	7.6E+07	7.9	8.7E+05	2.54		1.1E+05		6.2E+07	1.8E+09*	9.0E+05	8.5E+06
11400	8.5E+07	5.8	8.6E+05	3.17	2.5E+06	9.3E+04		9.4E+07	2.3E+09*	1.6E+06	1.3E+08
15720	1.2E+08	8.7	1.0E+06	3.35	3.8E+06	1.1E+05		1.2E+08	2.5E+09*	2.3E+06	1.8E+07
17220	6.5E+07	8.9	6.4E+05	4.3	1.6E+06	6.2E+04	2.8E+04	4.1E+07	1.4E+09	7.1E+05	6.9E+06
20010	8.2E+07	10.7	5.6E+05	3.97	2.2E+06	5.1E+04	1.9E+06	3.3E+07		1.1E+06	1.3E+07
25890	1.2E+08	13.9	7.1E+05	5.05	2.5E+06	4.8E+04	3.8E+06	3.6E+07	1.9E+09*	2.2E+06	2.4E+07
30525	1.1E+08	22.5	4.4E+05	6.04	2.8E+06			3.5E+07	1.2E+09	1.5E+06	1.2E+07
36045	1.4E+08	27.8	6.5E+05	8.40	2.3E+06	1.4E+05		3.0E+07	1.1E+09*	1.2E+06	1.1E+07
41805	1.7E+08	35.5	7.4E+05	9.26	5.2E+06	7.6E+04		1.7E+07	1.2E+09	4.5E+05	9.6E+06
92160			1.9E+04		4.4E+03			1.4E+05	6.6E+04

Fig. A1: GC-MS: Concentration TATP and DADP vs time for 1:1 mole ratio 67wt% HP:acetone at room temperature with no stirring

Table A2: GC-MS monitoring of a 1:10 mole ratio acetone:67wt% HP mixture at room temperature with no stirring

time (minutes)	m/z 240 Area	TATP (mg/mL)	m/z 166 Area	DADP (mg/mL)	Cyclic tetramer m/z 314 area	2-hydroxy-2- hydroperoxypropene m/z = 127, (-35) area	2,2- dihydroperoxypropene m/z 126 area	2,2'-dihydroxy-2,2'- dipropylperoxide m/z 168 area	2,2'-dihydroperoxy-2,2'- dipropylperoxide m/z 200 area	dihydroxy trimer m/z 242 area	dihydroperoxy trimer m/z 274 area
30	5.4E+03	0.0022	5.4E+03	0.17			9.6E+04	3.0E+05	6.9E+06		
520	4.2E+05	0.081	7.8E+03	0.21			3.5E+04	3.4E+05	7.0E+06		
1360	4.7E+05	0.14	9.9E+03	0.26			5.5E+04	3.9E+05	6.3E+06		
7080	7.2E+05	0.09	3.6E+04	0.30	4.1E+03	2.9E+04					
10020	1.1E+06	0.17	6.1E+04	0.50		2.0E+04		8.6E+05	2.0E+06		
11400	1.5E+06	0.25	1.0E+05	0.75	3.8E+03	3.0E+04		2.4E+06	7.2E+06		
15720	1.6E+06	0.22	1.1E+05	0.63	7.6E+03	2.6E+04		3.7E+06	1.5E+07		
17220	1.2E+06	0.24	8.1E+04	0.66	7.4E+03	2.2E+04		2.8E+06	1.3E+07		
20010	1.8E+06	0.30	1.2E+05	0.58	8.8E+03	2.5E+04	1.0E+05	7.1E+06	4.3E+07		4.5E+03
25890	2.8E+06	0.54	1.8E+05	0.90	9.1E+03	2.9E+04	2.4E+05	7.5E+06	7.0E+07	2.6E+03	2.7E+04
30525	3.6E+06	0.31	2.5E+05	0.98	1.8E+04			1.1E+07	5.9E+07		
36045	1.5E+06	0.13	8.5E+04	0.46	6.4E+03			8.7E+05	1.7E+07		
41805	4.0E+06	0.34	2.2E+05	0.87	1.9E+04		3.9E+05	3.5E+06	9.8E+07		9.2E+03
92160	1.8E+06	0.19	4.2E+05	0.69	1.3E+04		7.2E+04	1.1E+07	4.7E+07		
	2.8E+07		1.2E+08		9.3E+05		1.2E+09	1.9E+07	2.0E+09

Fig. A2: GC-MS: Concentration TATP and DADP vs time for 1:10 mole ratio acetone:67wt% HP at 0°C with no stirring

Table A3: GC-MS monitoring of a 10:1 mole ratio acetone:67wt% HP mixture at room temperature with no stirring

time(minutes)	m/z 240 Area	TATP (mg/mL)	m/z 166 Area	DADP (mg/mL)	Cyclic tetramer m/z 314 area	2-hydroxy-2- hydroperoxypropane m/z = 127, (+35) area	2,2- dihydroperoxypropane m/z 126 area	2,2'-dihydroxy-2,2'- diisopropylperoxide m/z 168 area	2,2'-dihydroperoxy-2,2'- diisopropylperoxide m/z 200 area	dihydroxy trimer m/z 242 area	dihydroperoxy trimer m/z 274 area
30	1.9E+03	0.001									
520	nd										
1360											
1360											
7080	1.1E+08	949	1.6E+06	0.34				8.4E+06	2.6E+09		
10020	4.4E+03	0.06				3.3E+04					
11400	5.0E+03	0.15				1.9E+04					
15720				0.00		1.8E+04					
17220	4.9E+03	0.16				1.8E+04					
20010	6.8E+03	0.18				1.9E+04		1.2E+04	2.5E+03		
25890	2.4E+04	0.40				2.3E+04		3.8E+04	2.7E+04		
30525	4.6E+04	0.14	4.9E+03	0.05		3.4E+04		1.2E+05	9.4E+04		
36045	7.5E+03	0.05						3.3E+04	4.1E+04		
41805	1.7E+05	0.14	1.5E+04	0.10			1.6E+04	4.3E+05	2.9E+06		
92160	5.3E+05	0.17	2.0E+04	0.10	7.4E+03		1.2E+04	5.5E+06	1.1E+07		
	1.3E+07	0.04	1.2E+07		6.1E+05		3.3E+08	1.3E+07	1.4E+09		

Table A4: GC-MS monitoring of a 1:1 mole ratio acetone:67wt% HP mixture at 0°C, stirring (* indicates that the response on the MSD was at maximum threshold value)
2.00 g acetone added to 1.86g 67wt% HP in 10 mL acetonitrile at 0°C while stirring

time(minutes)	m/z 240 Area	TATP (mg/mL)	m/z 166 Area	DADP (mg/mL)	Cyclic tetramer m/z 314 area	2-hydroxy-2- hydroperoxypropane m/z = 127, (+35) area	2,2- dihydroperoxypropane m/z 126 area	2,2'-dihydroxy-2,2'- disopropylperoxide m/z 168 area	2,2'-dihydroperoxy-2,2'- disopropylperoxide m/z 200 area	dihydroxy trimer m/z 242 area	dihydroperoxy trimer m/z 274 area
30	1.7E+06	0.14	1.0E+05	0.36	1.4E+04	1.3E+05	1.7E+05	1.8E+07	4.4E+07	1.6E+03	6.3E+04
120	1.9E+06	0.14	1.2E+05	0.39	6.5E+03	1.6E+05	3.9E+04	3.8E+06	4.4E+06		
300	4.7E+06	0.24	1.7E+05	0.45	5.8E+04	1.4E+05	5.4E+05	1.5E+07	6.9E+07	4.8E+03	6.2E+05
2730	3.6E+07	1.2	7.5E+05	1.25	4.8E+05	1.3E+05	1.4E+07	1.1E+08	2.9E+09*	2.9E+05	7.0E+06
8610	1.1E+07	5.0	2.9E+06	3.72	1.8E+06	9.4E+04	3.0E+06	4.1E+07	1.9E+09*	5.2E+05	6.5E+06
13245	9.2E+07	4.8	1.5E+06	3.91	3.7E+06			1.6E+08	2.6E+09*	2.4E+06	2.1E+07
18765	6.9E+07	7.1	1.1E+06	6.37	1.6E+06		3.1E+05	9.4E+07	1.6E+09	9.8E+05	7.5E+06
24525	7.4E+07	7.8	1.1E+06	6.16	2.3E+06		2.4E+06	2.0E+07	1.5E+09*	2.2E+05	3.2E+06
30525	8.7E+07	9.2	1.2E+06	7.00	3.9E+06		2.3E+06	3.2E+07	1.7E+09*	8.7E+05	1.8E+07
30525	5.7E+07	9.3	8.0E+05	7.77					1.5E+09*		
	1.2E+08	12.09	2.1E+06	9.66	2.9E+06		2.6E+06	2.8E+07	1.5E+09*	7.2E+05	9.3E+06
74880	9.5E+07	9.16	2.9E+05	2.72	6.2E+05		3.2E+05	1.3E+08	1.3E+09	1.9E+06	6.4E+05
96000	2.5E+09	7.52	2.2E+08		8.1E+07		2.3E+08	6.2E+08	1.6E+10

Fig. A3: GC-MS: Concentration TATP and DADP vs time for 1:1 mole ratio acetone:67wt% HP at 0°C stirring

Note: The ratio of TATP to DADP is higher at higher temperatures when no acid is added. This supports that TATP is the kinetic product and DADP is the thermodynamic product (Figs. A1 & A3).

Table A5: GC-MS monitoring of a 1:1 mole ratio acetone:30wt% HP mixture at 0°C, stirring

1.01 g acetone added to 1.95g 30wt% HP in 10 mL acetonitrile at 0°C while stirring

time(minutes)	m/z 240 Area	TATP (mg/mL)	m/z 166 Area	DADP (mg/mL)	Cyclic tetramer m/z 314 area	2-hydroxy-2- hydroperoxypropene m/z = 127, (-35) area	2,2- dihydroperoxypropene m/z 126 area	2,2'-dihydroxy-2,2'- diisopropyl peroxide m/z 168 area	2,2'-dihydroperoxy-2,2'- diisopropyl peroxide m/z 200 area	dihydroxy trimer m/z 242 area	dihydroperoxy trimer m/z 274 area
30	5.5E+03	0.14									
90	2.5E+04	0.28									
1020	8.7E+03	0.09									
4278	7.5E+06	0.26	4.1E+05	0.70	3.4E+04		7.6E+05	5.2E+06	4.5E+07	2.7E+03	1.5E+04
46080	5.0E+07	1.30	2.1E+05	0.55	1.1E+05		9.4E+05	2.3E+08	1.2E+09	3.7E+05	2.4E+05
	5.4E+08		1.1E+08		2.0E+07		1.4E+08	1.6E+08	8.2E+09		

Table A6: GC-MS monitoring of a 1:1 mole ratio acetone:12wt% HP mixture at 0°C, stirring

1.01 g acetone added to 4.88g 30wt% HP in 10 mL acetonitrile at 0°C while stirring

time(minutes)	m/z 240 Area	TATP (mg/mL)	m/z 166 Area	DADP (mg/mL)	Cyclic tetramer m/z 314 area	2-hydroxy-2- hydroperoxypropene m/z = 127, (-35) area	2,2- dihydroperoxypropene m/z 126 area	2,2'-dihydroxy-2,2'- diisopropyl peroxide m/z 168 area	2,2'-dihydroperoxy-2,2'- diisopropyl peroxide m/z 200 area	dihydroxy trimer m/z 242 area	dihydroperoxy trimer m/z 274 area
2820	9.2E+04	0.08	1.7E+04	0.06				6.0E+04	2.0E+04		
44640	1.6E+06	0.24	2.7E+04	0.15	1.1E+04		1.3E+05	1.5E+07	5.5E+07	2.2E+03	
	7.2E+07		3.2E+07		3.9E+06		5.9E+08	2.0E+07	2.9E+09		

Note: The concentrations of TATP & DADP when using 30% and 12% HP are too low for accurate quantification. These still resulted in formation of solid TATP but when compared to the experiment with 67% HP the amount of solid was minimal.

Table A7: GC-MS monitoring of a 14:14:1 mole ratio acetone:67wt% HP:3M H₂SO₄ mixture at 0°C, stirring

0.53 g acetone added to 0.46g 67wt%HP in 10 mL acetonitrile followed by addition of 0.26g 3M sulfuric acid

time(minutes)	TATP Ret time (min)	m/z 240 Area	TATP (mg/mL)	DADP Ret time (min)	m/z 166 Area	DADP (mg/mL)	2,2'-dihydroperoxypropane Ret time (min)	2,2'-dihydroperoxypropane m/z 126 area	2,2'-dihydroperoxy-2,2'-disopropylperoxide m/z 168 area	2,2'-dihydroperoxy-2,2'-disopropylperoxide Ret time (min)	2,2'-dihydroperoxy-2,2'-disopropylperoxide m/z 200 area
2.5	4.94	3.1E+04	0.016						1.2E+05	7.92	8.1E+05
10	4.95	5.5E+04	0.026								
20	4.95	1.6E+05	0.060	3.2	7.7E+03	0.15			1.7E+05	7.944	5.9E+06
30	4.95	2.9E+05	0.10	3.2	1.0E+04	0.16			2.1E+05	7.955	9.7E+06
55	4.94	5.9E+05	0.16	3.2	9.4E+03	0.16			3.5E+05	7.952	7.8E+06
75	4.94	9.1E+05	0.23	3.2	1.6E+04	0.20	6.664	5.4E+06	3.2E+05	7.972	1.6E+07
153	4.94	1.4E+06	0.33	3.2	1.4E+04	0.19	6.655	4.0E+06	2.7E+05	7.98	1.7E+07
238	4.93	4.0E+06	0.75	3.2	2.1E+04	0.23	6.645	7.3E+06	5.0E+05	8.005	2.9E+07
322	4.94	6.1E+06	1.0	3.2	2.4E+04	0.25	6.59	5.1E+06	3.9E+05	8.014	2.9E+07
402	4.93	7.4E+06	1.2	3.2	2.3E+04	0.24	6.624	5.8E+06	4.0E+05	8.009	2.6E+07
440	4.93	8.1E+06	1.3	3.2	2.1E+04	0.23	6.621	6.3E+06	5.8E+05	8.01	2.4E+07
536	4.93	9.2E+06	1.4	3.2	2.3E+04	0.24			3.9E+05	8.008	2.5E+07
638	4.94	1.3E+07	1.9	3.2	4.0E+04	0.34	6.602	5.3E+06	4.8E+05	8.011	2.7E+07
758	4.94	1.5E+07	2.1	3.2	3.2E+04	0.29	6.599	7.9E+06	4.9E+05	8.009	2.5E+07
1292	4.94	2.4E+07	3.0	3.2	2.6E+04	0.25	6.707	6.3E+06	3.4E+05	8.009	2.3E+07
2550	4.89										
3870	4.9										
8130	4.02	2.7E+07	7.00								
12330	4.9	1.1E+08	8.40	3.0	1.0E+04	0.34					
13770	4.87	4.4E+07	7.90	3.1	4.1E+03	0.42			8.0E+04	7.776	9.6E+05
18090	4.87	5.7E+07	9.17	3.0	7.9E+03				9.8E+04	7.792	1.6E+06

Fig. A4: GC-MS: Concentration TATP and DADP vs time for 14:14:1 mole ratio acetone:67wt%HP:3M H₂SO₄ at 0°C with no stirring

Table A8: GC-MS monitoring of a 3.5:3.5:1 mole ratio acetone:67wt% HP:97wt% H₂SO₄ mixture at 0°C, stirring

0.54 g acetone added to 0.47g 67wt%HP in 10 mL acetonitrile followed by addition of 0.27g 97wt% sulfuric acid

time(minutes)	TATP Ret time (min)	m/z 240 Area	TATP (mg/mL)	DADP Ret time (min)	m/z 166 Area	DADP (mg/mL)	dihydroperoxypropane m/z 156 area	2,2'-dihydroxy-2,2'-disopropylperoxide m/z 168 area	2,2'-dihydroperoxy-2,2'-disopropylperoxide Ret time (min)	2,2'-dihydroperoxy-2,2'-disopropylperoxide m/z 200 area	dihydroperoxy trimer Ret time (min)	dihydroperoxy trimer m/z 274 area
5.4	4.02	1.8E+06	1.2				4.72	1.3E+05	4.892	2.6E+06	8.641	1.4E+04
10.4	4.02	2.2E+07	6.2	3.15	3.3E+03	0.3	4.72	6.8E+04	4.902	8.6E+06	8.641	1.0E+05
23.9	4.02	4.2E+07	9.4	3.16	4.2E+03	0.3	4.72	6.3E+04	4.893	3.1E+06	8.639	8.1E+04
88.8	4.05	2.0E+08	25.8	3.16	1.6E+04	0.6	4.72	3.2E+04	4.894	4.1E+06	8.646	3.7E+04
204.2	4.05	2.1E+08	26.5	3.15	2.5E+04	0.8	4.72	2.3E+04	4.892	2.1E+06	8.644	7.5E+03
894	4.86	3.1E+07	27.4	3.09	4.4E+03	2.2	7.03	5.0E+03	7.794	1.0E+04		
4824	4.86	3.8E+07	37.3	3.04	1.5E+04	5.0						
6114	4.86	3.0E+07	29.6	3.01	1.7E+04	5.9	6.01	6.1E+03	7.786	3.0E+03		
10554	4.86	3.2E+07	30.4	3.06	2.9E+04	6.8	7.09	6.2E+03	7.853	1.6E+03		
11994	4.86	3.4E+07	29.7	3.05	4.0E+04	10.7	7.01	6.6E+03	7.777	1.8E+04		
14814	4.85	2.9E+07	23.4	3.07	5.7E+04	11.4	7.03	7.5E+03	7.778	2.2E+04		
16494	4.85	1.5E+07	15.3	3.05	3.9E+05	23.9	7.01	4.1E+03	7.781	2.3E+04

Fig. A5: GC-MS: Concentration TATP and DADP vs time for 3.5:3.5:1 mole ratio acetone:67wt%HP:97wt% H₂SO₄ at 0°C, stirring

Table A9: GC-MS monitoring of a 2:2:1 mole ratio acetone:67wt% HP:97wt% H₂SO₄ mixture at 0°C, stirring

0.55 g acetone added to 0.49g 65wt%HP in 10 mL acetonitrile followed by addition of 0.46g 97wt% sulfuric acid

time(minutes)	TATP Ret time (min)	m/z 240 Area	TATP (mg/mL)	DADP Ret time (min)	m/z 166 Area	DADP (mg/mL)	Cyclic tetramer Ret time (min)	Cyclic tetramer m/z 314 area	2,2'-dihydroxy-2,2'-disopropylperoxide Ret time (min)	2,2'-dihydroxy-2,2'-disopropylperoxide m/z 168 area	2,2'-dihydroxy-2,2'-disopropylperoxide Ret time (min)	2,2'-dihydroxy-2,2'-disopropylperoxide m/z 200 area
1.0	4.6	2.1E+07	7.9	3.11	1.1E+05	2.0	8.74	1.8E+04	6.13	6.8E+03	6.35	3.8E+05
3.0	4.6	2.6E+07	9.4	3.11	1.6E+05	2.4	8.74	6.6E+03			6.34	1.6E+04
5.3	4.61	3.3E+07	11.5	3.12	2.2E+05	2.9	8.74	1.5E+04	6.12	3.3E+03	6.35	3.6E+04
8.0	4.61	3.9E+07	13.6	3.12	1.9E+05	2.7	8.74	1.0E+04	6.16	1.6E+03	6.35	6.7E+03
13.0	4.62	5.5E+07	18.6	3.12	1.3E+05	2.2	8.73	3.6E+04	6.13	6.9E+03	6.35	2.2E+05
20.0	4.63	6.6E+07	21.9	3.12	1.4E+05	2.3	8.73	2.2E+04	6.15	3.9E+03	6.35	3.3E+04
38	4.64	9.7E+07	31.0	3.06	1.4E+05	2.3	8.73	3.2E+04	6.14	5.9E+03	6.34	1.2E+05
61.0	4.65	1.1E+08	33.3	3.11	1.1E+05	2.0	8.75	3.8E+03			6.36	2.1E+03
120	4.65	1.2E+08	38.2	3.05	1.1E+05	2.0	8.76	1.8E+03				
196.0	4.65	1.0E+08	32.6	3.12	9.6E+04	1.9						
1594	4.66	1.3E+08	38.8	3.12	2.2E+05	3.0						
5711	4.66	1.2E+08	36.1	3.12	4.1E+05	4.7

Fig. A6: GC-MS: Concentration TATP and DADP vs time for 2:2:1 mole ratio acetone:67wt%HP:97wt% H₂SO₄ at 0°C, stirring

Table A10: GC-MS monitoring of a 1:1:1 mole ratio acetone:67wt% HP:97wt% H_2SO_4 mixture at 0°C, stirring

0.50 g acetone added to 0.45g 65wt%HP in 10 mL acetonitrile followed by addition of 0.87g 97wt% sulfuric acid

time(minutes)	TATP Ret time (min)	m/z 240 Area	TATP (mg/mL)	DADP Ret time (min)	m/z 166 Area	DADP (mg/mL)
1.0	4.64	8.4E+07	31.8	3.105	1.7E+05	2.5
3.0	4.65	1.1E+08	40.8	3.094	2.3E+05	3.1
5.0	4.65	1.1E+08	38.8	3.094	2.2E+05	3.0
8.0	4.65	1.2E+08	44.0	3.093	2.1E+05	2.9
12.0	4.65	1.1E+08	40.7	3.093	2.0E+05	2.8
18.0	4.66	1.2E+08	44.0	3.093	2.6E+05	3.5
25	4.65	1.1E+08	41.1	3.094	2.3E+05	3.1
35.0	4.61	4.3E+07	17.1	3.096	2.0E+04	0.8
50	4.66	1.3E+08	47.5	3.095	3.7E+05	4.6
75.0	4.66	1.4E+08	48.3	3.094	3.5E+05	4.4
112	4.66	1.2E+08	44.9	3.088	4.0E+05	4.9
180	4.65	1.1E+08	39.5	3.093	4.5E+05	5.5
244	4.65	1.1E+08	39.1	3.091	6.0E+05	7.2
1140	4.62	5.4E+07	23.2	3.103	5.8E+05	8.0
2310	4.60	3.6E+07	15.8	3.102	6.7E+05	8.9
3780	4.60	3.5E+07	15.5	3.103	6.3E+05	8.5

Fig. A7: GC-MS: Concentration TATP and DADP vs time for 2:2:1 mole ratio acetone:67wt%HP:97wt% H_2SO_4 at 0°C, stirring

Table A11: GC-MS monitoring of a 1:1:1 mole ratio acetone:67wt% HP:97wt% H_2SO_4 with 0.5 mL added water at 0°C, stirring

0.56 g acetone added to 0.50g 65wt%HP in 10 mL acetonitrile followed by addition of 0.5 mL water and 0.87g 97wt% sulfuric acid

time(minutes)	TATP Ret time (min)	m/z 240 Area	TATP (mg/mL)	DADP Ret time (min)	m/z 166 Area	DADP (mg/mL)	2,2'-dihydroxy-2,2'-disopropylperoxide Ret time (min)	2,2'-dihydroxy-2,2'-disopropylperoxide m/z 168 area	2,2'-dihydroxy-2,2'-disopropylperoxide Ret time (min)	2,2'-dihydroxy-2,2'-disopropylperoxide m/z 200 area
1.0	4.58	7.7E+06	3.9	3.11	1.4E+04	0.70	5.93	3.7E+03	6.33	1.8E+04
3.0	4.58	1.0E+07	4.9	3.10	2.3E+04	0.80	5.91	1.6E+04	6.33	8.9E+04
5	4.58	1.5E+07	6.8	3.11	1.2E+04	0.69	5.92	9.0E+03	6.33	6.2E+04
12	4.59	2.8E+07	11.6	3.09	1.1E+04	0.67	5.92	2.4E+03	6.35	5.5E+03
18	4.60	3.7E+07	14.8	3.10	1.4E+04	0.71	6.22	3.5E+03	6.34	6.8E+03
25	4.61	4.2E+07	16.9	3.10	1.8E+04	0.75	5.93	1.0E+04	6.33	2.9E+04
35	4.62	5.4E+07	21.3	3.12	1.6E+04	0.73	5.91	1.3E+04	6.33	3.5E+04
51	4.62	6.3E+07	24.3	3.09	1.6E+04	0.73	5.92	5.0E+03	6.38	9.4E+02
78	4.63	7.1E+07	27.3	3.10	1.9E+04	0.77	5.93	8.7E+03	6.34	7.3E+03
119	4.64	8.2E+07	30.9	3.10	2.3E+04	0.81	5.94	3.0E+03	6.35	6.9E+02
173	4.64	9.6E+07	35.5	3.09	3.6E+04	0.95	5.91	7.3E+03	6.34	4.2E+03
810	4.63	7.2E+07	27.5	3.10	6.7E+04	1.30				
2655	4.63	6.8E+07	26.1	3.10	1.9E+05	2.70				
4110	4.63	7.1E+07	27.2	3.10	3.3E+05	4.20

Fig. A8: GC-MS: Concentration TATP and DADP vs time for 1:1:1 mole ratio acetone:67wt%HP:97wt% H_2SO_4 with 0.5 mL added water at 0°C, stirring

Table A12: GC-MS monitoring of a 2:2:1 mole ratio acetone:anhydrous HP:97wt% H_2SO_4 at 0°C , stirring

0.13 g acetone added to 0.25 mL 0.28 g/mL HP(in acetonitrile) in 2.5 mL acetonitrile followed by addition 143mg 97wt% sulfuric acid

time(minutes)	TATP Ret time (min)	m/z 240 Area	TATP (mg/mL)	DADP Ret time (min)	m/z 166 Area	DADP (mg/mL)
5	4.68	2.4E+09	52.0	3.09	8.8E+07	8.3
10	4.68	2.3E+09	51.1	3.10	7.4E+07	7.3
15	4.67	2E+09	46.3	3.10	1.1E+08	9.5
20	4.67	2.1E+09	47.0	3.10	9.2E+07	8.6
30	4.68	2.3E+09	49.8	3.10	1.1E+08	9.9
45	4.69	2.5E+09	52.7	3.10	1.6E+08	12.8
60	4.66	1.9E+09	45.2	3.10	1.3E+08	11.1
90	4.66	1.9E+09	44.3	3.10	1.7E+08	13.3
120	4.66	1.7E+09	41.8	3.10	2E+08	14.4
240	4.67	2E+09	46.3	3.10	4.5E+08	24.7

Fig. A9: GC-MS: Concentration TATP and DADP vs time for 2:2:1 mole ratio acetone:anhydrous HP:97wt% H_2SO_4 at 0°C , stirring

Relative rates of formation

Table A13: Experimental details; relative rate of formation with different acids, 1:1:1 mole ratio acetone:anhydrous HP:acid at 0°C, stirring

0.25 g acetone added to 0.24g 65wt% HP in 5 mL acetonitrile followed by addition acid

acetone (g)	65% HP (g)	acid	Amount of acid (g)	moles acid	water from reagents (g)	added water (g)	total water (g)
0.26	0.23	97% H ₂ SO ₄	0.44	0.0043	0.10	0.00	0.10
0.25	0.24	97% H ₂ SO ₄	0.45	0.0044	0.10	0.25	0.35
0.25	0.23	37% HCl	0.42	0.0043	0.35	0.00	0.35
0.25	0.24	70% HNO ₃	0.39	0.0043	0.20	0.15	0.35
0.25	0.24	citric acid	0.83	0.0043	0.08	1.00	1.08
0.26	0.24	TFA	0.50	0.0044	0.08	0.26	0.35
0.27	0.23	none				0.00	

Table A14: Results for relative rate of formation with different acids, 1:1:1 mole ratio acetone:anhydrous HP:acid at 0°C, stirring

Data for Figure 1.6

[SA=sulfuric acid, HCl=hydrochloric acid, HNO₃= nitric acid, CA=citric acid, TFA=trifluoroacetic acid, control=no acid]

sample ID	time(minutes)	TATP (mg/mL)	DADP (mg/mL)	sample ID	time(minutes)	TATP (mg/mL)	DADP (mg/mL)
conSA_1	120	41.23	10.69	conSA_3	1440	5.86	11.67
dilSA_1	120	2.06	0.96	dilSA_3	1440	27.26	2.72
HCl_1	120	11.79	0.68	HCl_3	1440	22.86	1.60
HNO3_1	120	2.15	0.51	HNO3_3	1440	3.33	0.09
CA_1	120	0		CA_3	1440	0.00	0.00
TFA_1	120	1.94	0.35	TFA_3	1440	1.32	0.10
control_1	120	0		control_3	1440	0.00	0.00
conSA_2	228	34.98	17.21	conSA_4	5760	0	
dilSA_2	231	28.31	1.40	dilSA_4	5760	23.44	8.91
HCl_2	229	19.67	0.83	HCl_4	5760	17.20	4.35
HNO3_2	230	2.57	0.59	HNO3_4	5760	15.84	1.06
CA_2	232	0		CA_4	5760	0	0
TFA_2	233	1.95	0.35	TFA_4	5760	3.30	0.29
control_2	234	0		control_4	5760	0	0

Table A15: Effect of water on 1:1:1 mole ratio acetone:HP:acid

Acetone and HP mixed, water and acid mixed, everything chilled in an ice bath and then diluted acid added to HP/acetone mix while in ice bath keeping cold, then RT 24 hours

	acetone (g)	50% HP (g)	Added water (mL)	97wt% H ₂ SO ₄ (g)	total water (g)	yield (mg)	% yield	mg TATP	mg DADP	% TATP	% DADP	m.p. (°C)
A	0.5	0.59	0.25	0.88	0.57	308	48	-0.20	7.18	0	100	100-102
B	0.5	0.59	0.50	0.88	0.82	246	39	0.54	6.63	8	92	105-115
C	0.5	0.59	0.75	0.88	1.07	348	55	8.13	1.92	81	19	74-103
D	0.5	0.59	1.00	0.88	1.32	378	59	13.04	-0.10	100	0	70-105
	acetone (g)	30% HP (g)	Added water (mL)	37wt% HCl (g)	total water (g)	yield (mg)	% yield	mg TATP	mg DADP	% TATP	% DADP	m.p. (°C)
E	0.5	0.98	0.00	0.85	1.22	92	14	8.06		81		77-87
F	0.5	0.98	0.25	0.85	1.47	99	15	8.28		83		86-91
G	0.5	0.98	0.50	0.85	1.72	92	14	8.71		87		85-92
H	0.5	0.98	0.75	0.85	1.97	99	16	9.39		94		94-96
	acetone (g)	30% HP (g)	Added water (mL)	97wt% H ₂ SO ₄ (g)	total water (g)	yield (mg)	% yield	mg TATP	mg DADP	% TATP	% DADP	m.p. (°C)
I	0.5	0.98		0.88	0.71	218	34	0.86	6.69	11	89	80-105
J	0.5	0.98	0.25	0.88	0.96	140	22	6.23	2.40	72	28	72-83
K	0.5	0.98	0.50	0.88	1.21	265	42	6.22	2.40	72	28	74-100
L	0.5	0.98	0.75	0.88	1.46	161	25	9.51	1.13	89	11	74-108

Note: The rate of TATP formation is highest when water is at a minimum but the rate of formation of DADP is also highest under these conditions. With added water the rate of TATP formation is slower but the rate of formation of DADP is slowed to a greater extent. If a solvent is used in addition to the acetone, HP and acid the TATP will decompose and form DADP.

Mechanism details

FigureA10: Formation of 2,2-dihydroperoxypropane via Criegee intermediate.

Figure A11: Formation of 2,2-dihydroperoxy-2,2'-diisopropylperoxide via Criegee intermediate.

Note: Dihydroperoxy species are the major intermediates observed by GC-MS, LC-MS and NMR as hydrogen peroxide and acetone react to form TATP. In the presence of water the Criegee intermediate could react with water to form 2-hydroxy-2-hydroperoxypropane. This would limit progress towards 2,2-dihydroperoxypropane and subsequent formation of longer linear chain hydroperoxides. In the presence of more hydrogen peroxide (i.e. higher concentration HP) the progress towards longer linear chain hydroperoxides and TATP would be favored.

Appendix B: Data for manuscript 2

TATP decomposition in acetonitrile

All of the decomposition kinetics experiments were conducted by preparing 1 vial with 5 mL 20 mg/mL TATP in acetonitrile. A second vial was prepared with the appropriate amount of acetonitrile, water and acid totaling 5mL. Both vials were equilibrated to the experimental temperature and then mixed. Aliquots of the reaction mixture were taken, extracted in methylene chloride, rinsed once with sodium bicarbonate solution, once with water and dried over anhydrous magnesium sulfate. The extract was analyzed by GC-MS using electron impact ionization. External standards of TATP and DADP were used for quantification.

Table B1: Decomposition of TATP in 10 mL acetonitrile using 20 μL 97wt% H_2SO_4 and varying the amount of water at 26°C

TATP (mg)	Acid	time (minutes)	TATP RT (min)	peak area	concentration TATP (mg/mL)	ln concentration	DADP RT (min)	peak area	concentration DADP (mg/mL)	ln concentration
100.8	20 μL 97wt% H_2SO_4 in 10 mL acetonitrile	0	4.00	2.0E+08	11.3	2.43				
100.8		1.5	3.99	1.3E+08	7.0	1.94				
100.8		8	3.98	6.6E+07	2.9	1.08	2.91	6.3E+07	0.58	-0.54
100.8		11	3.98	5.2E+07	2.1	0.74	2.96	9.8E+07	1.45	0.37
100.8		15	3.98	3.7E+07	1.1	0.14	2.95	1.2E+08	2.05	0.72
100.8		20	3.98	2.5E+07	0.4	-0.84	2.90	1.5E+08	2.85	1.05
100.8		30	3.98	2.3E+06	-0.9		2.91	1.7E+08	3.31	1.20
100.8		40	3.98	7.7E+06	-0.6		2.91	2.0E+08	3.93	1.37
100.8		50	3.98	4.9E+06	-0.8		2.91	2.1E+08	4.31	1.46
100.8							2.91	2.1E+08	4.40	1.48
100.4	20 μL 97wt% H_2SO_4 in 9.75 mL acetonitrile with 0.25 mL water	0	no rxn							
100.4		1.5	no rxn							
100.4		8	no rxn							
100.4		11	no rxn							
100.4		15	no rxn							
100.4		20	no rxn							
100.4		30	no rxn							
100.4		40	no rxn							
100.4		50	no rxn							
100.4		90	no rxn							
100.1	20 μL 97wt% H_2SO_4 in 9.5 mL acetonitrile with 0.5 mL water	0	no rxn							
100.1		1.5	no rxn							
100.1		8	no rxn							
100.1		11	no rxn							
100.1		15	no rxn							
100.1		20	no rxn							
100.1		30	no rxn							
100.1		40	no rxn							
100.1		50	no rxn							
100.1

Figure B1: ln concentration vs time for decomposition of TATP in acetonitrile using 20 μL 97wt% H_2SO_4 with different amounts of added water at 25°C

Table B2: 100 mgTATP in acetonitrile using 20 μ L 97wt% H₂SO₄ at 25°C

TATP (mg)	Acid	time (minutes)	TATP RT (min)	peak area	concentration TATP (mg/mL)	ln concentration	DADP RT (min)	peak area	concentration DADP (mg/mL)	ln concentration
100	20 μ L 97wt% SA	2	4.00	1.9E+08	13.8	2.6				
100		7	4.00	1.9E+08	14.1	2.6				
100		15	4.00	1.7E+08	12.3	2.5				
100		26	3.99	1.6E+08	11.7	2.5	2.95	1.0E+07	0.51	
100		47	3.99	1.5E+08	10.4	2.3

Figure B2: ln concentration vs time for decomposition of 100 mgTATP in acetonitrile using 20 μ L 97wt% H₂SO₄ at 25°C

Table B3: 100 mgTATP in acetonitrile using 50 μ L 97wt% H₂SO₄ at 25°C

TATP (mg)	Acid	time (minutes)	TATP RT (min)	peak area	concentration TATP (mg/mL)	ln concentration	DADP RT (min)	peak area	concentration DADP (mg/mL)	ln concentration
100	50 μ L 97wt% H ₂ SO ₄	3	4.00	1.8E+08	12.7	2.5	2.95	9.7E+06	0.50	
100		8	3.99	1.6E+08	11.2	2.4				
100		16	3.99	1.3E+08	8.7	2.2				
100		28	3.98	7.2E+07	4.4	1.5	2.96	2.3E+06	0.32	
100		48	3.98	3.3E+07	1.3	0.3

Figure B3: ln concentration vs time for decomposition of 100 mgTATP in acetonitrile using 50 μ L 97wt% H₂SO₄ at 25°C

Table B4: 100 mgTATP in acetonitrile using 100 μ L 97wt% H₂SO₄ at 25°C

TATP (mg)	Acid	time (minutes)	TATP RT (min)	peak area	concentration TATP (mg/mL)	ln concentration	DADP RT (min)	peak area	concentration DADP (mg/mL)	ln concentration
100	SA 100 μ L 97%	4	3.99	1E+08	6.9	1.9	2.96	9.8E+06	0.51	-0.68
100		9	3.98	2.8E+07	0.9	-0.1	2.96	4.3E+06	0.37	-1.00
100		17	3.98	6204549	-0.8		2.95	5.1E+06	0.39	-0.94
100		31	3.99	3181375	-1.1		2.96	9.8E+06	0.51	-0.68
100		49	3.99	2435801	-1.1		2.96	1.6E+07	0.66	-0.42

Figure B4: ln concentration vs time for decomposition of 100 mgTATP in acetonitrile using 100 μ L 97wt% H₂SO₄ at 25°C

Table B5: 100 mgTATP in acetonitrile using 150 μ L 97wt% H₂SO₄ at 25°C

TATP (mg)	Acid	time (minutes)	TATP RT (min)	peak area	concentration TATP (mg/mL)	ln concentration	DADP RT (min)	peak area	concentration DADP (mg/mL)	ln concentration
100	SA 150 μ L 97%	1	4.00	1.7E+08	12.2	2.5	2.96	5.9E+06	0.41	
100		6	3.99	9.2E+07	6.0	1.8	2.96	1.6E+07	0.67	
100		12	3.98	6E+07	3.4	1.2	2.96	3.8E+06	0.36	
100		25								
100		35

Figure B5: ln concentration vs time for decomposition of 100 mgTATP in acetonitrile using 150 μ L 97wt% H₂SO₄ at 25°C

Table B6: 100 mgTATP in acetonitrile using 200 μ L 97wt% H₂SO₄ at 25°C

TATP (mg)	Acid	time (minutes)	TATP RT (min)	peak area	concentration TATP (mg/mL)	ln concentration	DADP RT (min)	peak area	concentration DADP (mg/mL)	ln concentration
100	200 μ L 97% SA	2	4.00	1.4E+08	10.0	2.3				
100		6	3.99	6.3E+07	3.7	1.3				
100		13	3.98	1.4E+07	-0.2		2.96	3.4E+06	0.34	
100		25								
100		35								

Table B7: 100 mgTATP in 90:10 acetonitrile/water using 200 μ L 97wt% H_2SO_4 at 25°C

TATP (mg)	Acid	time (seconds)	TATP RT (min)	peak area	concentration TATP (mg/mL)	ln concentration	DADP RT (min)	peak area	concentration DADP (mg/mL)	ln concentration
100	9 mL acetonitrile, 1 mL water and 200 μ L 96.5% SA	60	4.00	1.7E+08	12.4	2.5				
100		300	4.00	1.9E+08	14.1	2.6				
100		600	4.00	1.8E+08	13.6	2.6				
100		1200	4.00	1.5E+08	10.5	2.4				
100		1800	3.99	1.5E+08	11.1	2.4				
100		3000	3.99	1.2E+08	8.2	2.1				
100		4200	3.99	9.5E+07	6.3	1.8				
100		5400	3.98	8.4E+07	5.4	1.7				
100		7200	3.98	6.4E+07	3.8	1.3

Figure B6: ln concentration vs time for decomposition of 100 mgTATP in 90:10 acetonitrile/water using 200 μ L 97wt% H_2SO_4 at 25°C

Table B8: 100 mgTATP in 80:20 acetonitrile/water using 200 μ L 97wt% H₂SO₄ at 25°C

TATP (mg)	Acid	time (seconds)	TATP RT (min)	peak area	concentration TATP (mg/mL)	ln concentration	DADP RT (min)	peak area	concentration DADP (mg/mL)	ln concentration
100	8 mL acetonitrile, 2 mL water and 200 μ L 96.5% SA	60	4.00	2.1E+08	15.3	2.7				
100		300	4.00	1.9E+08	14.0	2.6				
100		600	4.03	2.1E+08	15.8	2.8				
100		1200	4.00	1.9E+08	14.3	2.7				
100		1800	4.00	1.9E+08	14.1	2.6				
100		3000	4.00	2E+08	14.7	2.7				
100		4200	3.99	1.7E+08	12.6	2.5				
100		5400	3.99	1.6E+08	11.7	2.5				
100		7200	3.99	1.5E+08	10.7	2.4

Figure B7: ln concentration vs time for decomposition of 100 mgTATP in 80:20 acetonitrile/water using 200 μ L 97wt% H₂SO₄ at 25°C

Table B9: 100 mgTATP in 70:30 acetonitrile/water using 200 μ L 97wt% H₂SO₄ at 25°C

TATP (mg)	Acid	time (seconds)	TATP RT (min)	peak area	concentration TATP (mg/mL)	ln concentration	DADP RT (min)	peak area	concentration DADP (mg/mL)	ln concentration
100	7 mL acetonitrile, 3 mL water and 200 μ L 96.5% SA	60	4.00	2E+08	13.9	2.6				
100		300	4.00	2.1E+08	14.0	2.6				
100		600	4.00	2E+08	13.7	2.6				
100		1200	4.00	2E+08	13.3	2.6				
100		1800	4.00	2E+08	13.7	2.6				
100		3000	4.00	2E+08	13.6	2.6				
100		4200	4.00	1.9E+08	13.1	2.6				
100		5400	4.00	1.9E+08	12.6	2.5				
100		7200	4.00	1.8E+08	12.1	2.5

Figure B8: ln concentration vs time for decomposition of 100 mgTATP in 70:30 acetonitrile/water using 200 μ L 97wt% H₂SO₄ at 25°C

TATP decomposition in alcohols

All of the decomposition kinetics experiments were conducted by preparing 1 vial with 5 mL 20 mg/mL TATP in methanol, ethanol, isopropanol, n-propanol and t-butanol. A second vial was prepared with the appropriate amount of alcohol, water and acid totaling 5mL. Both vials were equilibrated to the experimental temperature and then mixed. Aliquots of the reaction mixture were taken, extracted in methylene chloride, rinsed once with sodium bicarbonate solution, once with water and dried over anhydrous magnesium sulfate. The extract was analyzed by GC-MS using electron impact ionization. External standards of TATP and DADP were used for quantification.

Table B10: 100 mgTATP in methanol using 200 μ L 97wt% H₂SO₄ at 45°C

TATP (mg)	Acid	time (seconds)	TATP RT (min)	peak area	concentration TATP (mg/mL)	ln concentration	DADP RT (min)	peak area	concentration DADP (mg/mL)	ln concentration
100	10 mL methanol, 200 μ L 96.5% SA	60	3.99	1.5E+08	10.0	2.3				
100		300	3.99	1.0E+08	6.4	1.9				
100		600	3.98	6.0E+07	3.7	1.3				
100		900	3.98	3.2E+07	2.0	0.7				
100		1200	3.98	1.7E+07	1.1	0.1				
100		1500	3.98	9.3E+06	0.6	-0.6				
100		1800	3.98	5.4E+06	0.3	-1.1	2.98	2.1E+06	0.2	
100		2400	3.98	2.6E+06	0.2	-1.9				
100		3000	3.99	1.4E+06	0.1	-2.5				
100		3600	3.98	1.2E+06	0.1	-2.7

Figure B9: ln concentration vs time for decomposition of 100mg TATP in methanol using 200 μL 97wt% H_2SO_4 at 45°C

Table B11: 7.5 mgTATP in methanol using 356 μL 10.3M H_2SO_4 at 23°C

TATP (mg)	Acid	time (seconds)	concentration TATP ($\mu\text{g/mL}$)	ln concentration
7.5	356 μL 10.3M SA	1740	517	6.2
7.5		3660	456	6.1
7.5		7200	257	5.5
7.5		10800	152	5.0
7.5		14310	68	4.2
7.5		18540	33	3.5
7.5		23130

Figure B10: ln concentration vs time for decomposition of 7.5mg TATP in methanol using 356 μL 10.3M H_2SO_4 at 23°C

Table B12: 7.5 mgTATP in methanol using 790 μL 4.7M H_2SO_4 at 23°C

TATP (mg)	Acid	time (seconds)	concentration TATP ($\mu\text{g/mL}$)	ln concentration
7.5	790 μL 4.6M SA	1800	642	6.5
7.5		3750	607	6.4
7.5		7260	482	6.2
7.5		10950	365	5.9
7.5		14550	319	5.8
7.5		18630	229	5.4
7.5		23340	149	5.0

Figure B11: ln concentration vs time for decomposition of 7.5mg TATP in methanol using 790 μL 4.7M H_2SO_4 at 23°C

Table B13: 7.5 mgTATP in methanol using 316 μ L 37wt% HCl at 23°C

TATP (mg)	Acid	time (seconds)	concentration TATP (μ g/mL)	ln concentration
7.5	316 μ L 37% HCl	1890	511	6.2
7.5		3840	477	6.2
7.5		7350	217	5.4
7.5		11040	107	4.7
7.5		14640	44	3.8
7.5		18750	8	2.1
7.5		23430

Figure B12: ln concentration vs time for decomposition of 7.5mg TATP in methanol using 316 μ L 37wt% HCl at 23°C

Table B14: 7.5 mgTATP in methanol using 685 μ L 5.4M HCl at 23°C

TATP (mg)	Acid	time (seconds)	concentration TATP (μ g/mL)	ln concentration
7.5	685 μ L 5.4M HCl	2010	685	6.5
7.5		3930	602	6.4
7.5		7410	551	6.3
7.5		11130	458	6.1
7.5		14730	352	5.9
7.5		18810	329	5.8
7.5		23520	240	5.5

Figure B13: ln concentration vs time for decomposition of 7.5mg TATP in methanol using 685 μ L 5.4M HCl at 23°C

Table B15: 100 mgTATP in 90:10 v/v methanol/water using 200 μ L 97wt% H₂SO₄ at 25°C

TATP (mg)	Acid	time (seconds)	TATP RT (min)	peak area	concentration TATP (mg/mL)	ln concentration	DADP RT (min)	peak area	concentration DADP (mg/mL)	ln concentration
100	9 mL methanol, 1 mL water, 200 μ L 96.5% SA	60	4.00	1.8E+08	11.9	2.5	3.02	2.3E+06	0.2	
100		300	4.00	1.7E+08	11.0	2.4				
100		600	3.99	1.6E+08	10.5	2.3				
100		900	3.99	1.5E+08	10.0	2.3				
100		1200	4.00	1.5E+08	9.5	2.3	3.03	1.6E+06	0.2	
100		1500	3.99	1.4E+08	9.2	2.2	3.01	1.5E+06	0.2	
100		1800	3.99	1.4E+08	8.7	2.2				
100		2400	3.99	1.1E+08	6.9	1.9				
100		3000	3.99	1.1E+08	6.8	1.9				
100		3600	3.99	8.3E+07	5.3	1.7

Figure B14: ln concentration vs time for decomposition of 100mg TATP in 90:10 v/v methanol/water using 200 μ L 97wt% H₂SO₄ at 45°C

Table B16: 100 mgTATP in 80:20 v/v methanol/water using 200 μ L 97wt% H₂SO₄ at 45°C

TATP (mg)	Acid	time (seconds)	TATP RT (min)	peak area	concentration TATP (mg/mL)	ln concentration	DADP RT (min)	peak area	concentration DADP (mg/mL)	ln concentration
100	SA 8 mL methanol, 2 mL water, 200 μ L 96.5%	60	4.00	1.7E+08	10.8	2.4				
100		300	4.00	1.5E+08	9.5	2.2				
100		600	3.99	1.4E+08	8.8	2.2				
100		900	3.99	1.3E+08	8.4	2.1				
100		1200	3.99	1.1E+08	7.3	2.0				
100		1500	3.99	1.1E+08	6.9	1.9				
100		1800	3.99	1.0E+08	6.3	1.8				
100		2400	3.98	8.6E+07	5.5	1.7				
100		3000	3.98	6.8E+07	4.3	1.5				
100		3600	3.98	5.8E+07	3.7	1.3

Figure B15: ln concentration vs time for decomposition of 100mg TATP in 80:20 v/v methanol/water using 200 μ L 97wt% H₂SO₄ at 45°C

Table B17: 7.5 mgTATP in 50wt% methanol/water using 200 μ L 97wt% H₂SO₄ at 23°C

TATP (mg)	Acid	time (seconds)	concentration TATP (μ g/mL)	ln concentration
7.5	200 μ L 97wt% SA	300	645	6.5
7.5		630	629	6.4
7.5		1200	597	6.4
7.5		2400	576	6.4
7.5		3600	533	6.3
7.5		7320	448	6.1
7.5		10800	351	5.9
7.5

Figure B16: ln concentration vs time for decomposition of 7.5mg TATP in 50wt% methanol/water using 200 μ L 97wt% H₂SO₄ at 23°C

Table B18: 7.5 mgTATP in 50wt% methanol/water using 356 μ L 10.3M H₂SO₄ at 23°C

TATP (mg)	Acid	time (seconds)	concentration TATP (μ g/mL)	ln concentration
7.5	356 μ L 10.3M SA	300	564	6.3
7.5		600	581	6.4
7.5		1200	627	6.4
7.5		2400	546	6.3
7.5		3600	517	6.2
7.5		7320	464	6.1
7.5		10800	324	5.8
7.5

Figure B17: ln concentration vs time for decomposition of 7.5mg TATP in 50wt% methanol/water using 356 μ L 10.3M H₂SO₄ at 23°C

Table B19: 7.5 mgTATP in 50wt% methanol/water using 790 μ L 4.7M H₂SO₄ at 23°C

TATP (mg)	Acid	time (seconds)	concentration TATP (μ g/mL)	ln concentration
7.5	790 μ L 4.66M SA	300	526	6.3
7.5		600	621	6.4
7.5		1230	530	6.3
7.5		2400	542	6.3
7.5		3600	519	6.3
7.5		7200	499	6.2
7.5		10800	365	5.9
7.5

Figure B18: ln concentration vs time for decomposition of 7.5mg TATP in 50wt% methanol/water using 790 μ L 4.7M H₂SO₄ at 23°C

Table B20: 7.5 mgTATP in 50wt% methanol/water using 316 μ L 37wt% HCl at 23°C

TATP (mg)	Acid	time (seconds)	concentration TATP (μ g/mL)	ln concentration
7.5	316 μ L 37% HCl	300	692	6.5
7.5		600	790	6.7
7.5		1200	635	6.5
7.5		2400	608	6.4
7.5		3600	621	6.4
7.5		7200	481	6.2

Figure B19: ln concentration vs time for decomposition of 7.5mg TATP in 50wt% methanol/water using 316 μ L 37wt% HCl at 23°C

Table B21: 7.5 mgTATP in 50wt% methanol/water using 685 μ L 5.4M HCl at 23°C

TATP (mg)	Acid	time (seconds)	concentration TATP (μ g/mL)	ln concentration
7.5	685 μ L 5.4M HCl	300	655	6.5
7.5		600	642	6.5
7.5		1200	621	6.4
7.5		2400	590	6.4
7.5		3600	483	6.2
7.5		6960	347	5.8

Figure B20: ln concentration vs time for decomposition of 7.5mg TATP in 50wt% methanol/water using 685 μ L 5.4M HCl at 23°C

Table B22: 7.5 mgTATP in 50wt% methanol/water using 200 μ L 97wt% H₂SO₄ at 45°C

TATP (mg)	Acid	time (seconds)	concentration TATP (μ g/mL)	ln concentration
7.5	97wt% SA in 10 mL 200 μ L	300	538	6.3
7.5		1020	305	5.7
7.5		1800	121	4.8
7.5		3660		
7.5		5220

Figure B21: ln concentration vs time for decomposition of 7.5mg TATP in 50wt% methanol/water using 200 μ L 97wt% H₂SO₄ at 45°C

Table B23: 7.5 mgTATP in 50wt% methanol/water using 200 μ L 97wt% H₂SO₄ at 45°C

TATP (mg)	Acid	time (seconds)	concentration TATP (μ g/mL)	ln concentration
7.5	97wt% SA in 10 mL 50wt% 200 μ L	360	350	5.9
7.5		720	386	6.0
7.5		1260	237	5.5
7.5		2400	58	4.1
7.5		3660

Figure B22: ln concentration vs time for decomposition of 7.5mg TATP in 50wt% methanol/water using 200 μ L 97wt% H₂SO₄ at 45°C

Table B24: 7.5 mgTATP in 60wt% methanol/water using 200 μ L 97wt% H₂SO₄ at 45°C

TATP (mg)	Acid	time (seconds)	concentration TATP (μ g/mL)	ln concentration
7.5	200 μ L 97wt% SA in 10 mL 60wt% MeOH at 45°C	300	695	6.5
7.5		660	312	5.7
7.5		1200	273	5.6
7.5		2400	126	4.8
7.5		3600	28	3.3

Figure B23: ln concentration vs time for decomposition of 7.5mg TATP in 60wt% methanol/water using 200 μ L 97wt% H₂SO₄ at 45°C

Table B25: 100 mgTATP in ethanol using 200 μ L 97wt% H₂SO₄ at 45°C

TATP (mg)	Acid	time (seconds)	TATP RT (min)	peak area	concentration TATP (mg/mL)	ln concentration	DADP RT (min)	peak area	concentration DADP (mg/mL)	ln concentration
100	10 mL reagent alcohol, 200 μ L 96.5% SA	60	3.99	1.8E+08	12.0	2.5				
100		300	3.99	1.6E+08	10.6	2.4				
100		600	3.98	1.4E+08	9.2	2.2				
100		900	3.98	1.1E+08	7.5	2.0				
100		1200	3.98	9.6E+07	6.4	1.8				
100		1500	3.97	8.1E+07	5.3	1.7				
100		1800	3.98	6.3E+07	4.2	1.4				
100		2400	3.98	4.3E+07	2.8	1.0				
100		3000	3.97	3.0E+07	1.9	0.7				
100		3600	3.98	1.9E+07	1.3	0.2

Figure B24: ln concentration vs time for decomposition of 100mg TATP in ethanol using 200 μ L 97wt% H₂SO₄ at 45°C

Table B26: 100 mgTATP in 90:10 ethanol/water using 200 μ L 97wt% H₂SO₄ at 45°C

TATP (mg)	Acid	time (seconds)	TATP RT (min)	peak area	concentration TATP (mg/mL)	ln concentration	DADP RT (min)	peak area	concentration DADP (mg/mL)	ln concentration
100	9 mL reagent alcohol, 1 mL water, 200 μ L 96.5% SA	60	3.99	1.9E+08	13.1	2.6				
100		300	3.99	1.8E+08	12.5	2.5				
100		600	3.99	1.8E+08	12.2	2.5				
100		900	3.99	1.8E+08	12.2	2.5				
100		1200	3.99	1.7E+08	11.7	2.5				
100		1500	3.99	1.8E+08	12.0	2.5				
100		1800	3.98	1.7E+08	11.4	2.4				
100		2400	3.99	1.6E+08	10.4	2.3				
100		3000	3.98	1.5E+08	10.0	2.3				
100		3600	3.98	1.4E+08	9.5	2.3

Figure B25: ln concentration vs time for decomposition of 100mg TATP in 90:10 ethanol/water using 200 μ L 97wt% H₂SO₄ at 45°C

Table B27: 100 mgTATP in 80:20 ethanol/water using 200 μ L 97wt% H₂SO₄ at 45°C

TATP (mg)	Acid	time (seconds)	TATP RT (min)	peak area	concentration TATP (mg/mL)	ln concentration	DADP RT (min)	peak area	concentration DADP (mg/mL)	ln concentration
100	8 mL reagent alcohol, 2 mL water, 200 μ L 96.5% SA	60	4.62	8.5E+07	14.2	2.7				
100		300	4.63	2.4E+08	32.0					
100		600	4.62	1.0E+08	16.6	2.8				
100		900	4.62	9.0E+07	14.9	2.7				
100		1200	4.62	8.4E+07	14.2	2.7				
100		1500	4.62	8.1E+07	13.7	2.6				
100		1800	4.62	7.6E+07	13.1	2.6				
100		2400	4.62	7.9E+07	13.6	2.6				
100		3000	4.62	7.2E+07	12.6	2.5				
100		3600	4.62	6.1E+07	11.0	2.4

Figure B26: ln concentration vs time for decomposition of 100mg TATP in 80:20 ethanol/water using 200 μ L 97wt% H₂SO₄ at 45°C

Table B28: 100 mgTATP in 70:30 ethanol/water using 200 μ L 97wt% H₂SO₄ at 45°C

TATP (mg)	Acid	time (seconds)	TATP RT (min)	peak area	concentration TATP (mg/mL)	ln concentration	DADP RT (min)	peak area	concentration DADP (mg/mL)	ln concentration
100	7 mL reagent alcohol, 3 mL water, 200 μ L 96.5% SA	60	4.62	9.2E+07	15.2	2.7				
100		300	4.63	9.0E+07	14.9	2.7				
100		600	4.62	8.7E+07	14.5	2.7				
100		900	4.62	8.2E+07	13.9	2.6				
100		1200	4.62	8.1E+07	13.7	2.6				
100		1500	4.62	8.3E+07	14.0	2.6				
100		1800	4.62	7.0E+07	12.2	2.5				
100		2400	4.62	6.1E+07	11.1	2.4				
100		3000	4.62	6.0E+07	10.9	2.4				
100		3600	4.61	5.1E+07	9.7	2.3

Figure B27: ln concentration vs time for decomposition of 100mg TATP in 70:30 ethanol/water using 200 μ L 97wt% H₂SO₄ at 45°C

Table B29: 7.5 mgTATP in 50wt% ethanol/water using 200 μ L 97wt% H₂SO₄ at 45°C

TATP (mg)	Acid	time (seconds)	concentration TATP (μ g/mL)	ln concentration
7.5	97wt% SA in 10 mL 200 μ L	300	896	6.8
7.5		600	682	6.5
7.5		1200	604	6.4
7.5		2400	584	6.4
7.5		3600	269	5.6

Figure B28: ln concentration vs time for decomposition of 7.5mg TATP in 50wt% ethanol/water using 200 μ L 97wt% H₂SO₄ at 45°C

Table B30: 100 mgTATP in isopropanol using 200 μ L 97wt% H₂SO₄ at 45°C

TATP (mg)	Acid	time (seconds)	TATP RT (min)	peak area	concentration TATP (mg/mL)	ln concentration	DADP RT (min)	peak area	concentration DADP (mg/mL)	ln concentration
100	10 mL isopropanol, 96.5% SA	60	3.99	1.7E+08	11.8	2.5				
100		300	3.99	1.7E+08	11.8	2.5				
100		600	3.99	1.7E+08	11.3	2.4				
100		900	3.99	1.7E+08	11.4	2.4				
100		1200	3.98	1.5E+08	10.3	2.3				
100		1500	3.99	1.5E+08	10.0	2.3				
100		1800	3.98	1.6E+08	10.4	2.3				
100		2400	3.99	1.5E+08	10.3	2.3				
100		3000	3.98	1.4E+08	9.1	2.2				
100		3600	3.98	1.3E+08	8.5	2.1

Figure B29: ln concentration vs time for decomposition of 100mg TATP in isopropanol using 200 μ L 97wt% H₂SO₄ at 45°C

Table B31: 100 mgTATP in 90:10 isopropanol/water using 200 μ L 97wt% H₂SO₄ at 45°C

TATP (mg)	Acid	time (seconds)	TATP RT (min)	peak area	concentration TATP (mg/mL)	ln concentration	DADP RT (min)	peak area	concentration DADP (mg/mL)	ln concentration
100	9 mL isopropanol, 1 mL water, 200 μ L 96.5% SA	60	3.98	1.2E+08	7.8	2.1				
100		300	3.98	1.1E+08	7.6	2.0				
100		600	3.98	1.2E+08	7.9	2.1				
100		900	3.98	1.2E+08	8.2	2.1				
100		1200	3.98	1.1E+08	7.5	2.0				
100		1500	3.98	1.1E+08	7.6	2.0				
100		1800	3.98	1.1E+08	7.6	2.0				
100		2400	3.98	1.1E+08	7.4	2.0				
100		3000	3.98	1.1E+08	7.2	2.0				
100		3600	3.98	1.1E+08	7.1	2.0

Figure B30: ln concentration vs time for decomposition of 100mg TATP in 90:10 isopropanol/water using 200 μ L 97wt% H₂SO₄ at 45°C

Table B32: 100 mgTATP in 80:20 isopropanol/water using 200 μ L 97wt% H₂SO₄ at 45°C

TATP (mg)	Acid	time (seconds)	TATP RT (min)	peak area	concentration TATP (mg/mL)	ln concentration	DADP RT (min)	peak area	concentration DADP (mg/mL)	ln concentration
100	8 mL isopropanol, 2 mL water, 200 μ L 96.5% SA	60	4.62	5.5E+07	10.1	2.3				
100		900	4.62	5.7E+07	10.3	2.3				
100		1800	4.62	5.1E+07	9.4	2.2				
100		2700	4.62	4.3E+07	8.1	2.1				
100		3600	4.62	4.3E+07	8.1	2.1				
100		5400	4.61	2.8E+07	5.7	1.7				
100		7200	4.61	9.8E+04	0.0					
100		14400	4.60	1.3E+07	3.0	1.1				
100		21600	4.60	5.1E+06	1.3	0.3				
100		28800	4.60	1.7E+06	0.5	-0.6

Figure B31: ln concentration vs time for decomposition of 100mg TATP in 80:20 isopropanol/water using 200 μ L 97wt% H₂SO₄ at 45°C

Table B33: 100 mgTATP in 70:30 isopropanol/water using 200 μ L 97wt% H₂SO₄ at 45°C

TATP (mg)	Acid	time (seconds)	TATP RT (min)	peak area	concentration TATP (mg/mL)	ln concentration	DADP RT (min)	peak area	concentration DADP (mg/mL)	ln concentration
100	7 mL isopropanol, 3 mL water, 200 μ L 96.5% SA	60	4.62	5.7E+07	10.3	2.3				
100		900	4.62	5.0E+07	9.2	2.2				
100		1800	4.62	5.9E+07	10.7	2.4				
100		2700	4.62	4.9E+07	9.2	2.2				
100		3600	4.62	4.3E+07	8.2	2.1				
100		5400	4.62	5.4E+07	9.9	2.3				
100		7200	4.61	4.0E+07	7.7	2.0				
100		14400	4.60	1.8E+07	3.9	1.4				
100		21600	4.60	1.1E+07	2.5	0.9				
100		28800	4.60	5.8E+06	1.5	0.4

Figure B32: ln concentration vs time for decomposition of 100mg TATP in isopropanol using 200 μ L 97wt% H₂SO₄ at 45°C

Table B34: 100 mgTATP in 90:10 isopropanol/water using 200 μ L 97wt% H₂SO₄ at 45°C

TATP (mg)	Acid	time (seconds)	TATP RT (min)	peak area	concentration TATP (mg/mL)	ln concentration	DADP RT (min)	peak area	concentration DADP (mg/mL)	ln concentration
100	9 mL isopropanol, 1 mL water, 200 μ L 96.5% SA	60	3.98	1.2E+08	7.8	2.1				
100		300	3.98	1.1E+08	7.6	2.0				
100		600	3.98	1.2E+08	7.9	2.1				
100		900	3.98	1.2E+08	8.2	2.1				
100		1200	3.98	1.1E+08	7.5	2.0				
100		1500	3.98	1.1E+08	7.6	2.0				
100		1800	3.98	1.1E+08	7.6	2.0				
100		2400	3.98	1.1E+08	7.4	2.0				
100		3000	3.98	1.1E+08	7.2	2.0				
100		3600	3.98	1.1E+08	7.1	2.0

Figure B33: ln concentration vs time for decomposition of 100mg TATP in 90:10 isopropanol/water using 200 μ L 97wt% H₂SO₄ at 45°C

Table B35: 100 mgTATP in 80:20 isopropanol/water using 200 μL 97wt% H_2SO_4 at 45°C

TATP (mg)	Acid	time (seconds)	TATP RT (min)	peak area	concentration TATP (mg/mL)	ln concentration	DADP RT (min)	peak area	concentration DADP (mg/mL)	ln concentration
100	8 mL isopropanol, 2 mL water, 200 μL 96.5% SA	60	4.62	5.5E+07	10.1	2.3				
100		900	4.62	5.7E+07	10.3	2.3				
100		1800	4.62	5.1E+07	9.4	2.2				
100		2700	4.62	4.3E+07	8.1	2.1				
100		3600	4.62	4.3E+07	8.1	2.1				
100		5400	4.61	2.8E+07	5.7	1.7				
100		7200	4.61	9.8E+04	0.0					
100		14400	4.60	1.3E+07	3.0	1.1				
100		21600	4.60	5.1E+06	1.3	0.3				
100		28800	4.60	1.7E+06	0.5	-0.6

Figure B34: ln concentration vs time for decomposition of 100mg TATP in 80:20 isopropanol/water using 200 μL 97wt% H_2SO_4 at 45°C

Table B36: 100 mgTATP in 70:30 isopropanol/water using 200 μ L 97wt% H₂SO₄ at 45°C

TATP (mg)	Acid	time (seconds)	TATP RT (min)	peak area	concentration TATP (mg/mL)	ln concentration	DADP RT (min)	peak area	concentration DADP (mg/mL)	ln concentration
100	7 mL isopropanol, 3 mL water, 200 μ L 96.5% SA	60	4.62	5.7E+07	10.3	2.3				
100		900	4.62	5.0E+07	9.2	2.2				
100		1800	4.62	5.9E+07	10.7	2.4				
100		2700	4.62	4.9E+07	9.2	2.2				
100		3600	4.62	4.3E+07	8.2	2.1				
100		5400	4.62	5.4E+07	9.9	2.3				
100		7200	4.61	4.0E+07	7.7	2.0				
100		14400	4.60	1.8E+07	3.9	1.4				
100		21600	4.60	1.1E+07	2.5	0.9				
100		28800	4.60	5.8E+06	1.5	0.4

Figure B35: ln concentration vs time for decomposition of 100mg TATP in 70:30 isopropanol/water using 200 μ L 97wt% H₂SO₄ at 45°C

Table B37: 7.5 mgTATP in 50wt% isopropanol/water using 200 μ L 97wt% H₂SO₄ at 45°C

TATP (mg)	Acid	time (seconds)	concentration TATP (μ g/mL)	ln concentration
9	97wt% SA in 200 μ L 10 mL	300	1190	7.1
9		600	742	6.6
9		1200	917	6.8
9		2400	580	6.4
9		3600	457	6.1

Figure B36: ln concentration vs time for decomposition of 7.5mg TATP in 50wt% isopropanol/water using 200 μ L 97wt% H₂SO₄ at 45°C

Table B38: 7.5 mgTATP in 50wt% isopropanol/water using 200μL 97wt% H₂SO₄ at 45°C

TATP (mg)	Acid	time (seconds)	concentration TATP (μg/mL)	ln concentration
7	97wt% SA in 50wt% 200 uL	300	904	6.8
7		600	894	6.8
7		1200		
7		2400		
7				

Table B39: 100 mgTATP in n-propanol using 200 μ L 97wt% H₂SO₄ at 45°C

TATP (mg)	Acid	time (seconds)	TATP RT (min)	peak area	concentration TATP (mg/mL)	ln concentration	DADP RT (min)	peak area	concentration DADP (mg/mL)	ln concentration
100	10 mL n-propyl alcohol, 200 μ L 96.5% SA	60	3.99	1.7E+08	11.5	2.4				
100		300	3.99	1.6E+08	10.8	2.4				
100		600	3.98	1.4E+08	9.3	2.2				
100		900	3.98	1.3E+08	8.8	2.2				
100		1200	3.98	1.2E+08	8.1	2.1				
100		1500	3.98	1.1E+08	7.4	2.0				
100		1800	3.98	1.1E+08	7.4	2.0				
100		2400	3.98	9.2E+07	6.0	1.8				
100		3000	3.97	7.2E+07	4.7	1.6				
100		3600	3.97	5.9E+07	3.9	1.3

Figure B37: ln concentration vs time for decomposition of 100mg TATP in n-propanol using 200 μ L 97wt% H₂SO₄ at 45°C

Table B40: 100 mgTATP in 90:10 n-propanol/water using 200 μ L 97wt% H₂SO₄ at 45°C

TATP (mg)	Acid	time (seconds)	TATP RT (min)	peak area	concentration TATP (mg/mL)	ln concentration	DADP RT (min)	peak area	concentration DADP (mg/mL)	ln concentration
100	9 mL n-propyl alcohol, 1 mL water, 200 μ L 96.5% SA	60	3.98	1.6E+08	10.7	2.4				
100		300	3.99	1.7E+08	11.7	2.5				
100		600	3.99	1.7E+08	11.2	2.4				
100		900	3.99	1.7E+08	11.3	2.4				
100		1200	3.99	1.6E+08	11.0	2.4				
100		1500	3.99	1.6E+08	11.0	2.4				
100		1800	3.99	1.7E+08	11.5	2.4				
100		2400	3.98	1.5E+08	10.3	2.3				
100		3000	3.99	1.7E+08	11.6	2.4				
100		3600	3.98	1.5E+08	10.1	2.3

Figure B38: ln concentration vs time for decomposition of 100mg TATP in 90:10 n-propanol/water using 200 μ L 97wt% H₂SO₄ at 45°C

TATP decomposition with aqueous acid

All of the decomposition kinetics experiments were conducted by weighing 5mg solid TATP into a 14mL vial. To the vial 1 mL of aqueous acid was added with a volumetric pipet. At recorded intervals, the decomposition reaction was quenched by adding approximately 3mL sodium bicarbonate solution and 5mL methylene chloride. The extract was rinsed with water and dried over anhydrous magnesium sulfate. The extract was analyzed by GC-MS using electron impact ionization. External standards of TATP and DADP were used for quantification.

Table B41: Aqueous 37wt% HCl added to 5 mg TATP at 22°C

TATP (mg)	reagent	Molarity	time (seconds)	mg TATP	% TATP remaining	mg DADP	1,3 - dichloroacetone peak area	ln % TATP remaining
4.9	1 mL 37 wt% HCl	12.2	600	3.37	68.8		1.1E+06	4.23
5.1		12.2	600	3.17	62.1		2.9E+06	4.13
5.1		12.2	1200	2.27	44.6		6.0E+06	3.80
4.9		12.2	1200	1.88	38.3		8.0E+06	3.65
5.1		12.2	1800	0.63	12.3		1.6E+07	2.51
4.9		12.2	1800	0.78	15.9		1.2E+07	2.76
4.9		12.2	2700	0.34	6.8			1.92
4.9		12.2	2700	0.17	3.5			1.25
5.4		12.2	3600	0.065	1.2			0.18
5.0		12.2	3600	0.051	1.0			0.01

Figure B39: ln % TATP remaining vs time for decomposition of 5mg TATP using 1mL 37wt% HCl at 22°C

Table B42: Aqueous 10M HCl added to 5 mgTATP at 22°C

TATP (mg)	reagent	Molarity	time (seconds)	mg TATP	% TATP remaining	mg DADP	1,3 - dichloroacetone peak area	ln % TATP remaining
4.9	1 mL 10 M HCl	10	300	4.53	92.4			4.53
5.2		10	300	4.64	89.2			4.49
5.1		10	600	4.41	86.5			4.46
5.1		10	600	4.21	82.5			4.41
4.8		10	900	3.25	67.7			4.22
5.0		10	900	4.25	85.0		2.1E+05	4.44
4.8		10	1200	3.405	70.9		7.0E+05	4.26
5.0		10	1200	3.525	70.5		7.7E+05	4.26
5.2		10	1800	3.23	62.1		1.6E+06	4.13
5.0		10	1800	3.07	61.4		2.3E+06	4.12

Figure B40: ln % TATP remaining vs time for decomposition of 5mg TATP using 1mL 10M HCl at 22°C

Table B43: Aqueous 8.8M HCl added to 5 mgTATP at 22°C

TATP (mg)	reagent	Molarity	time (seconds)	mg TATP	% TATP remaining	mg DADP	1,3 - dichloroacetone peak area	ln % TATP remaining
4.9	1 mL 8.8M HCl	8.8	600	4.69	95.6			4.56
5.2		8.8	600	4.56	87.7			4.47
5.0		8.8	1200	broken vial				
5.1		8.8	1200	4.22	82.7			4.42
5.0		8.8	1800	3.83	76.5			4.34
5.1		8.8	1800	3.78	74.0			4.30
5.3		8.8	2700	3.19	60.2		7.4E+05	4.10
5.0		8.8	2700	2.99	59.7		7.3E+05	4.09
5.2		8.8	3600	2.87	55.2		2.1E+06	4.01
5.1		8.8	3600	3.46	67.7		2.0E+06	4.22

Figure B41: ln % TATP remaining vs time for decomposition of 5mg TATP using 1mL 8.8M HCl at 22°C

Table B44: Aqueous 18wt% HCl added to 5 mgTATP at 22°C

TATP (mg)	reagent	Molarity	time (seconds)	mg TATP	% TATP remaining	mg DADP	1,3 - dichloroacetone peak area	ln % TATP remaining
4.9	1 mL 18 wt% HCl	5.4	2700	4.37	89.2			4.49
5.3		5.4	2700	4.32	81.4			4.40
5.2		5.4	5400	4.24	81.5			4.40
5.4		5.4	5400	4.21	77.9			4.36
5.2		5.4	7200	4.11	78.9			4.37
5.1		5.4	7200	4.30	84.3			4.43
5.1		5.4	14400	4.11	80.5			4.39
4.9		5.4	14400	3.63	74.1			4.31
4.9		5.4	21600	3.00	61.1			4.11
4.9		5.4	21600	3.3	67.3			4.21

Figure B42: ln % TATP remaining vs time for decomposition of 5mg TATP using 1mL 18wt% HCl at 22°C

Table B45: Aqueous 14.1M H₂SO₄ added to 5 mgTATP at 22°C

TATP (mg)	reagent	Molarity	time (seconds)	mg TATP	% TATP remaining	mg DADP	byproducts	ln % TATP remaining
5.1	1 mL 80 wt% sulfuric acid	14.1	300	1.92	37.5	1.92		3.63
5.2		14.1	300	2.25	43.2	1.77		3.77
5.1		14.1	600	0.84	16.5	2.29		2.80
4.8		14.1	600	1.07	22.2	2.01		3.10
5.0		14.1	900	0.15	2.9	2.23		1.06
5.2		14.1	900	0.58	11.1	2.26		2.40
5.2		14.1	1200	0.18	3.4	1.75		1.21
4.8		14.1	1200	0.26	5.4	0.93		1.69
5.2		14.1	1800	0.11	2.1	0.74		0.75
5.2		14.1	1800	0.16	3.1	1.15		1.12

Figure B43: ln % TATP remaining vs time for decomposition of 5mg TATP using 1mL 14.1M H₂SO₄ at 22°C

Table B46: Aqueous 12.5M H₂SO₄ added to 5 mgTATP at 22°C

TATP (mg)	reagent	Molarity	time (seconds)	mg TATP	% TATP remaining	mg DADP	byproducts	ln % TATP remaining
5.1	1 mL 12.5M Sulfuric	12.5	600	0.735	14.4	2.60		2.67
4.9		12.5	600	0.885	18.1	1.96		2.89
5.1		12.5	1200	0.245	4.8	2.07		1.57
5.2		12.5	1200	0.11	2.1	1.54		0.75
5.1		12.5	1800	0.46	9.0	0.91		2.20
5.1		12.5	1800	0.19	3.7	1.21		1.32
5.0		12.5	2700	0.080	1.6	0.15		0.47
5.1		12.5	2700	0.095	1.9	0.26		0.62
5.3		12.5	3600	0.092	1.7			0.55
5.1		12.5	3600	0.065	1.3			0.24
5.2		12.5	300	1.97	37.9	0.385		3.63
5.2		12.5	300	1.55	29.8	1.47		3.39
5.1		12.5	900	0.15	2.8			1.04
4.8		12.5	900	0.13	2.7			1.00

Figure B44: ln % TATP remaining vs time for decomposition of 5mg TATP using 1mL 12.5M H₂SO₄ at 22°C

Table B47: Aqueous 10.3M H₂SO₄ added to 5 mgTATP at 22°C

TATP (mg)	reagent	Molarity	time (seconds)	mg TATP	% TATP remaining	mg DADP	byproducts	ln % TATP remaining
5.3	1 mL 65 wt% sulfuric acid	10.3	600	4.36	82.3			4.41
5.1		10.3	1200	3.34	65.4	0.16		4.18
5.0		10.3	1800	3.35	66.9	0.055		4.20
5.0		10.3	600	3.86	77.1			4.35
5.0		10.3	600	4.11	82.2			4.41
5.1		10.3	1200	4.01	78.6	0.008		4.36
5.0		10.3	1200	4.25	85.0	0.013		4.44
5.2		10.3	1800	3.88	74.5	0.021		4.31
4.9		10.3	1800	3.91	79.8	0.013		4.38
5.2		10.3	2700	3.60	69.1	0.015		4.24
5.1		10.3	2700	3.27	64.1	0.013		4.16
4.9		10.3	3600	2.11	43.1	0.024		3.76
5.2		10.3	3600	2.89	55.5	0.023		4.02
5.0		10.3	5400	1.71	34.1	0.036		3.53
5.0		10.3	5400	1.25	25.0	0.029		3.22
5.0		10.3	7200	1.21	24.1	0.022		3.18
4.9		10.3	7200	1.74	35.5	0.032		3.57

Figure B45: ln % TATP remaining vs time for decomposition of 5mg TATP using 1mL 10.3M H₂SO₄ at 22°C

Table B48: Aqueous 8.1M H₂SO₄ added to 5 mgTATP at 22°C

TATP (mg)	reagent	Molarity	time (seconds)	mg TATP	% TATP remaining	mg DADP	byproducts	ln % TATP remaining
5.2	1 mL 8.1M Sulfuric	8.1	900	3.77	72.5			4.28
5.1		8.1	900	3.41	66.8			4.20
4.8		8.1	1800	2.77	57.7			4.06
4.9		8.1	1800	3.36	68.6			4.23
5.1		8.1	2700	2.47	48.3			3.88
4.9		8.1	2700	2.43	49.6			3.90
5.2		8.1	3600	2.55	49.0			3.89
4.9		8.1	3600	3.13	63.9			4.16
5.1		8.1	5400	2.33	45.6			3.82
5.2		8.1	5400	2.15	41.3			3.72

Figure B46: ln % TATP remaining vs time for decomposition of 5mg TATP using 1mL 8.1M H₂SO₄ at 22°C

Table B49: Aqueous 13.1M HNO₃ added to 5 mgTATP at 22°C

TATP (mg)	reagent	Molarity	time (seconds)	mg TATP	% TATP remaining	mg DADP	byproducts	ln % TATP remaining
5.1	nitric 1 mL 13.1M	13.1	60	3.22	63.0	0.11		4.14
5.0		13.1	60	3.40	67.9	0.04		4.22
5.2		13.1	120	1.58	30.4	0.68		3.41
4.8		13.1	120	1.32	27.4	0.18		3.31
5.0		13.1	180	0.35	6.9	0.98		1.93
4.8		13.1	180	0.44	9.1	0.52		2.20

Figure B47: ln % TATP remaining vs time for decomposition of 5mg TATP using 1mL 13.1M HNO₃ at 22°C

Table B50: Aqueous 10M HNO₃ added to 5 mgTATP at 22°C

TATP (mg)	reagent	Molarity	time (seconds)	mg TATP	% TATP remaining	mg DADP	byproducts	ln % TATP remaining
5.0	1 mL 10M nitric	10	120	3.39	67.7			4.22
5.2		10	120	4.14	79.5	0.039		4.38
5.2		10	240	3.15	60.5	0.084		4.10
5.0		10	240	3.94	78.7	0.054		4.37
5.2		10	360	2.46	47.2	0.18		3.85
4.9		10	360	2.02	41.1	0.071		3.72
4.8		10	480	1.49	30.9	0.067		3.43
5.1		10	480	1.36	26.6	0.11		3.28
5.1		10	600	1.04	20.4	0.12		3.02
5.0		10	600	1.13	22.5	0.12		3.11

Figure B48: ln % TATP remaining vs time for decomposition of 5mg TATP using 1mL 10M HNO₃ at 22°C

Table B51: Aqueous 8.1M HNO₃ added to 5 mgTATP at 22°C

TATP (mg)	reagent	Molarity	time (seconds)	mg TATP	% TATP remaining	mg DADP	byproducts	ln % TATP remaining
4.8	1 mL 8.1M nitric	8.1	300	4.49	93.5			4.54
5.1		8.1	300	5.08	99.5			4.60
5.2		8.1	600	5.52	106.2			4.66
5.1		8.1	1200	4.50	88.2			4.48
4.9		8.1	900	4.86	99.1			4.60
5.1		8.1	1200	4.81	94.2			4.55
4.9		8.1	1500	3.81	77.8			4.35
4.8		8.1	600	4.82	100.3			4.61
5.1		8.1	1800	4.93	96.6			4.57
4.8		8.1	900	4.87	101.5			4.62

Figure B49: ln % TATP remaining vs time for decomposition of 5mg TATP using 1mL 8.1M HNO₃ at 22°C

Table B52: Aqueous 11.6M HClO₄ added to 5 mgTATP at 22°C

TATP (mg)	reagent	Molarity	time (seconds)	mg TATP	% TATP remaining	mg DADP	byproducts	ln % TATP remaining
5.2	1 mL 11.6M perchloric	11.6	60	0.28	5.4	3.46		1.68
5.2		11.6	60	0.30	5.7	3.15		1.74
4.8		11.6	120	0.47	9.8	1.41		2.28
5.0		11.6	120	0.15	2.9	1.60		1.06
5.2		11.6	180	0.07	1.3	0.73		0.22
4.9		11.6	180	0.22	4.4	0.75		1.48
4.8		11.6	240	0.05	1.0	0.29		0.04
5.1		11.6	240	0.26	5.1	0.76		1.63

Figure B50: ln % TATP remaining vs time for decomposition of 5mg TATP using 1mL 11.6M HClO₄ at 22°C

Table B53: Aqueous 9.3M HClO₄ added to 5 mgTATP at 22°C

TATP (mg)	reagent	Molarity	time (seconds)	mg TATP	% TATP remaining	mg DADP	byproducts	ln % TATP remaining
5.2	1 mL 9.3M perchloric	9.3	60		0.0	0.16		
5.1		9.3	60		0.0	0.10		
4.9		9.3	120	3.94	80.4	0.19		4.39
5.2		9.3	120	3.69	70.9	0.43		4.26
5		9.3	180	2.69	53.8	0.46		3.99
4.8		9.3	180	2.48	51.7	0.78		3.94
4.8		9.3	240	1.31	27.3	1.83		3.31
5.2		9.3	240	1.65	31.7	0.04		3.46

Figure B51: ln % TATP remaining vs time for decomposition of 5mg TATP using 1mL 9.3M HClO₄ at 22°C

Table B54: Aqueous 8.4M HClO₄ added to 5 mgTATP at 22°C

TATP (mg)	reagent	Molarity	time (seconds)	mg TATP	% TATP remaining	mg DADP	byproducts	ln % TATP remaining
4.8	1 mL 8.4M perchloric	8.4	60	3.90	81.3			4.40
5.0		8.4	60	4.11	82.1			4.41
5.2		8.4	180	3.77	72.5	0.16		4.28
5.1		8.4	180	3.69	72.4	0.02		4.28
4.8		8.4	300	3.00	62.6	0.02		4.14
5.2		8.4	300	2.51	48.3	0.01		3.88
4.8		8.4	420	2.35	48.9	0.03		3.89
4.9		8.4	420	2.13	43.5	0.03		3.77

Figure B52: ln % TATP remaining vs time for decomposition of 5mg TATP using 1mL 8.4M HClO₄ at 22°C

Table B55: Specific heats of acids

Acid	kJ/kgK
Hydrochloric (32%)	2.5
Sulfuric (98%)	1.5
Sulfuric (60%)	2.2
Nitric (95%)	2.1
Nitric (60%)	2.7

Table B56: Data for ternary diagram, Figure 2.2 (sulfuric acid & ethanol)

hours	solvent (mL)	solvent (wt%)	acid mL	acid (wt%)	total water (g)	total organic solvent (g)	total acid (g)	solvent wt%	water wt%	% acid	% remaining
18	1	EtOH 100%	3	H2SO4 50%	2.11	0.79	2.11	0.2	0.4	42.14	1
18	1	EtOH 100%	3	H2SO4 50%	2.11	0.79	2.11	0.2	0.4	42.14	5
18	1	EtOH 100%	2	H2SO4 65%	1.09	0.79	2.03	0.2	0.3	51.91	0
18	1	EtOH 100%	2	H2SO4 65%	1.09	0.79	2.03	0.2	0.3	51.91	0
18	2	EtOH 100%	2	H2SO4 65%	1.09	1.58	2.03	0.3	0.2	43.20	0
18	2	EtOH 100%	2	H2SO4 65%	1.09	1.58	2.03	0.3	0.2	43.20	0
18	1	EtOH 50%	3	H2SO4 50%	2.57	0.46	2.11	0.1	0.5	41.11	19
18	1	EtOH 50%	3	H2SO4 50%	2.57	0.46	2.11	0.1	0.5	41.11	20
18	2	EtOH 50%	3	H2SO4 50%	3.03	0.91	2.11	0.2	0.5	34.91	21
18	2	EtOH 50%	3	H2SO4 50%	3.03	0.91	2.11	0.2	0.5	34.91	28
18	1	EtOH 50%	2	H2SO4 65%	1.55	0.46	2.03	0.1	0.4	50.30	0
18	1	EtOH 50%	2	H2SO4 65%	1.55	0.46	2.03	0.1	0.4	50.30	0
18	2	EtOH 50%	2	H2SO4 65%	2.01	0.91	2.03	0.2	0.4	41.02	1
18	2	EtOH 50%	2	H2SO4 65%	2.01	0.91	2.03	0.2	0.4	41.02	6
3	1	EtOH 50%	2	H2SO4 65%	1.55	0.46	2.03	0.1	0.4	50.30	17
24	1	EtOH 50%	1	H2SO4 80%	0.80	0.46	1.38	0.2	0.3	52.34	4
24	1	EtOH 50%	1	H2SO4 80%	0.80	0.46	1.38	0.2	0.3	52.34	4
21	1	EtOH 90%	2	H2SO4 50%	1.49	0.74	1.41	0.2	0.4	38.75	0
21	1	EtOH 90%	2	H2SO4 50%	1.49	0.74	1.41	0.2	0.4	38.75	0
21	2	EtOH 90%	2	H2SO4 50%	1.57	1.47	1.41	0.3	0.4	31.64	1
21	2	EtOH 90%	2	H2SO4 50%	1.57	1.47	1.41	0.3	0.4	31.64	1
21	1	EtOH 90%	2	H2SO4 65%	1.18	0.74	2.03	0.2	0.3	51.52	0
21	2	EtOH 90%	2	H2SO4 65%	1.26	1.47	2.03	0.3	0.3	42.68	0
21	1	EtOH 90%	2	H2SO4 65%	1.18	0.74	2.03	0.2	0.3	51.52	0
21	2	EtOH 90%	2	H2SO4 65%	1.26	1.47	2.03	0.3	0.3	42.68	0
18	1	EtOH 90%	1	H2SO4 65%	0.63	0.74	1.02	0.3	0.3	42.68	0
18	1	EtOH 90%	1	H2SO4 65%	0.63	0.74	1.02	0.3	0.3	42.68	0
18	2	EtOH 100%	3	H2SO4 50%	2.11	1.58	2.11	0.3	0.4	36.41	25
18	2	EtOH 100%	3	H2SO4 50%	2.11	1.58	2.11	0.3	0.4	36.41	33
3	1	EtOH 50%	2	H2SO4 65%	1.55	0.46	2.03	0.1	0.4	50.30	31
21	2	EtOH 90%	2	H2SO4 35%	1.79	1.47	0.88	0.4	0.4	21.19	28
21	2	EtOH 90%	2	H2SO4 35%	1.79	1.47	0.88	0.4	0.4	21.19	29
21	1	EtOH 90%	2	H2SO4 35%	1.71	0.74	0.88	0.2	0.5	26.40	42
21	1	EtOH 90%	2	H2SO4 35%	1.71	0.74	0.88	0.2	0.5	26.40	42
18	1	EtOH 90%	1	H2SO4 50%	0.79	0.74	0.70	0.3	0.4	31.64	31
18	1	EtOH 90%	1	H2SO4 50%	0.79	0.74	0.70	0.3	0.4	31.64	35
18	2	EtOH 100%	9	H2SO4 20%	7.92	1.58	1.98	0.1	0.7	17.25	81
18	1	EtOH 100%	9	H2SO4 20%	7.92	0.79	1.98	0.1	0.7	18.52	87
18	2	EtOH 100%	9	H2SO4 20%	7.92	1.58	1.98	0.1	0.7	17.25	88
18	1	EtOH 100%	9	H2SO4 20%	7.92	0.79	1.98	0.1	0.7	18.52	90
18	1	EtOH 100%	5	H2SO4 35%	4.08	0.79	2.20	0.1	0.6	31.09	67
18	2	EtOH 100%	5	H2SO4 35%	4.08	1.58	2.20	0.2	0.5	27.97	67
18	2	EtOH 100%	5	H2SO4 35%	4.08	1.58	2.20	0.2	0.5	27.97	67
18	1	EtOH 100%	5	H2SO4 35%	4.08	0.79	2.20	0.1	0.6	31.09	71
18	2	EtOH 50%	9	H2SO4 20%	8.84	0.91	1.98	0.1	0.8	16.88	87
18	2	EtOH 50%	9	H2SO4 20%	8.84	0.91	1.98	0.1	0.8	16.88	95
18	1	EtOH 50%	9	H2SO4 20%	8.38	0.46	1.98	0.0	0.8	18.31	97
18	1	EtOH 50%	9	H2SO4 20%	8.38	0.46	1.98	0.0	0.8	18.31	101
18	2	EtOH 50%	5	H2SO4 35%	4.99	0.91	2.20	0.1	0.6	27.10	59
18	1	EtOH 50%	5	H2SO4 35%	4.53	0.46	2.20	0.1	0.6	30.55	67
18	2	EtOH 50%	5	H2SO4 35%	4.99	0.91	2.20	0.1	0.6	27.10	75
18	1	EtOH 50%	5	H2SO4 35%	4.53	0.46	2.20	0.1	0.6	30.55	93
~24	2	EtOH 50%	2	H2SO4 65%	2.01	0.91	2.03	0.2	0.4	41.02	88
~24	2	EtOH 50%	2	H2SO4 65%	2.01	0.91	2.03	0.2	0.4	41.02	90
21	2	EtOH 90%	2	H2SO4 20%	1.92	1.47	0.44	0.4	0.5	11.47	65
21	1	EtOH 90%	2	H2SO4 20%	1.84	0.74	0.44	0.2	0.6	14.58	73
21	1	EtOH 90%	2	H2SO4 20%	1.84	0.74	0.44	0.2	0.6	14.58	74
21	2	EtOH 90%	2	H2SO4 20%	1.92	1.47	0.44	0.4	0.5	11.47	98
18	1	EtOH 90%	1	H2SO4 35%	0.90	0.74	0.44	0.4	0.4	21.19	74
18	1	EtOH 90%	1	H2SO4 35%	0.90	0.74	0.44	0.4	0.4	21.19	76

Table B57: Data for ternary diagram, Figure 2.2 (hydrochloric acid & ethanol)

hours	solvent (mL)	solvent (wt%)	acid mL	acid (wt%)	total water (g)	total organic solvent (g)	total acid (g)	solvent wt%	water wt%	% acid	% remaining
0.8	7	EtOH 100%	3	HCl 2M	2.88	5.52	0.21	0.6	0.3	2.46	11
2.9	9	EtOH 100%	1	HCL 5M	0.91	7.10	0.17	0.9	0.1	2.11	10
3	2	EtOH 50%	2	HCl 36%	2.42	0.91	0.85	0.2	0.6	20.28	0
	2	EtOH 50%	2	HCl 36%	2.42	0.91	0.85	0.2	0.6	20.28	0
3	1	EtOH 50%	2	HCl 36%	1.97	0.46	0.85	0.1	0.6	25.94	0
3	1	EtOH 50%	2	HCl 36%	1.97	0.46	0.85	0.1	0.6	25.94	0
5	1	EtOH 50%	2	HCl 36%	1.97	0.46	0.85	0.1	0.6	25.94	0
5	2	EtOH 50%	4	HCl 36%	3.93	0.91	1.70	0.1	0.6	25.94	0
5	2	EtOH 50%	4	HCl 36%	3.93	0.91	1.70	0.1	0.6	25.94	0
5	1	EtOH 50%	4	HCl 36%	3.48	0.46	1.70	0.1	0.6	30.16	0
5	1	EtOH 50%	4	HCl 36%	3.48	0.46	1.70	0.1	0.6	30.16	0
6	2	EtOH 50%	4	HCl 36%	3.93	0.91	1.70	0.1	0.6	25.94	1
5	1	EtOH 50%	2	HCl 36%	1.97	0.46	0.85	0.1	0.6	25.94	2
5	2	EtOH 50%	2	HCl 36%	2.42	0.91	0.85	0.2	0.6	20.28	4
6	2	EtOH 50%	4	HCl 36%	3.93	0.91	1.70	0.1	0.6	25.94	6
5	2	EtOH 50%	2	HCl 36%	2.42	0.91	0.85	0.2	0.6	20.28	13
5	1	EtOH 70%	2	HCl 36%	1.77	0.61	0.85	0.2	0.5	26.31	0
5	1	EtOH 70%	2	HCl 36%	1.77	0.61	0.85	0.2	0.5	26.31	0
5	2	EtOH 70%	4	HCl 36%	3.54	1.22	1.70	0.2	0.5	26.31	0
5	2	EtOH 70%	4	HCl 36%	3.54	1.22	1.70	0.2	0.5	26.31	0
5	1	EtOH 70%	4	HCl 36%	3.28	0.61	1.70	0.1	0.6	30.40	0
5	1	EtOH 70%	4	HCl 36%	3.28	0.61	1.70	0.1	0.6	30.40	0
3	1	EtOH 70%	2	HCl 36%	1.77	0.61	0.85	0.2	0.5	26.31	0
5	2	EtOH 70%	2	HCl 36%	2.03	1.22	0.85	0.3	0.5	20.73	0
3	1	EtOH 70%	2	HCl 36%	1.77	0.61	0.85	0.2	0.5	26.31	0
5	2	EtOH 70%	2	HCl 36%	2.03	1.22	0.85	0.3	0.5	20.73	2
3	9	EtOH 100%	1	HCl 3M	0.94	7.10	0.10	0.9	0.1	1.27	45
6	2	EtOH 50%	2	HCl 36%	2.42	0.91	0.85	0.2	0.6	20.28	31
5	1	EtOH 50%	1	HCl 36%	1.21	0.46	0.42	0.2	0.6	20.28	34
5	1	EtOH 50%	1	HCl 36%	1.21	0.46	0.42	0.2	0.6	20.28	36
6	2	EtOH 50%	2	HCl 36%	2.42	0.91	0.85	0.2	0.6	20.28	37
5	1	EtOH 70%	1	HCl 36%	1.01	0.61	0.42	0.3	0.5	20.73	32
5	1	EtOH 70%	1	HCl 36%	1.01	0.61	0.42	0.3	0.5	20.73	33
3	1	EtOH 70%	1	HCl 36%	1.01	0.61	0.42	0.3	0.5	20.73	35
3	1	EtOH 70%	1	HCl 36%	1.01	0.61	0.42	0.3	0.5	20.73	40
5	2	EtOH 70%	1	HCl 36%	1.28	1.22	0.42	0.4	0.4	14.56	70
5	2	EtOH 70%	1	HCl 36%	1.28	1.22	0.42	0.4	0.4	14.56	83
0.75	7	EtOH 100%	3	HCl 1M	2.94	5.52	0.12	0.6	0.3	1.35	74
6	2	EtOH 50%	4	HCl 18%	4.48	0.91	0.78	0.1	0.7	12.68	91
6	2	EtOH 50%	2	HCl 18%	2.70	0.91	0.39	0.2	0.7	9.78	93
6	2	EtOH 50%	4	HCl 18%	4.48	0.91	0.78	0.1	0.7	12.68	96
6	2	EtOH 50%	2	HCl 18%	2.70	0.91	0.39	0.2	0.7	9.78	97
5	1	EtOH 50%	1	HCl 36%	1.21	0.46	0.42	0.2	0.6	20.28	56
5	2	EtOH 50%	1	HCl 36%	1.67	0.91	0.42	0.3	0.6	14.12	60
3	1	EtOH 70%	1	HCl 18%	1.15	0.61	0.20	0.3	0.6	10.01	83
3	1	EtOH 70%	2	HCl 18%	2.04	0.61	0.39	0.2	0.7	12.87	89
3	1	EtOH 70%	1	HCl 18%	1.15	0.61	0.20	0.3	0.6	10.01	91
3	1	EtOH 70%	2	HCl 18%	2.04	0.61	0.39	0.2	0.7	12.87	93

Table B58: Data for ternary diagram, Figure 2.2 (sulfuric acid & isopropanol)

hours	solvent (mL)	solvent (wt%)	acid mL	acid (wt%)	total water (g)	total organic solvent (g)	total acid (g)	solvent wt%	water wt%	% acid	% remaining
20	1	IPA 100%	1	H2SO4 20%	0.88	0.79	0.22	0.4	0.5	11.7	34
20	1	IPA 100%	1	H2SO4 20%	0.88	0.79	0.22	0.4	0.5	11.7	34
20	2	IPA 100%	2	H2SO4 20%	1.76	1.57	0.44	0.4	0.5	11.7	34
20	2	IPA 100%	2	H2SO4 20%	1.76	1.57	0.44	0.4	0.5	11.7	35
17	2	IPA 100%	2	H2SO4 20%	1.76	1.57	0.44	0.4	0.5	11.7	88
17	2	IPA 100%	2	H2SO4 20%	1.76	1.57	0.44	0.4	0.5	11.7	90
17	1	IPA 100%	1	H2SO4 20%	0.88	0.79	0.22	0.4	0.5	11.7	93
17	1	IPA 100%	1	H2SO4 20%	0.88	0.79	0.22	0.4	0.5	11.7	95
17	2	IPA 100%	2	H2SO4 35%	1.63	1.57	0.88	0.4	0.4	21.5	58
17	2	IPA 100%	2	H2SO4 35%	1.63	1.57	0.88	0.4	0.4	21.5	59
17	1	IPA 100%	1	H2SO4 35%	0.82	0.79	0.44	0.4	0.4	21.5	69
17	1	IPA 100%	1	H2SO4 35%	0.82	0.79	0.44	0.4	0.4	21.5	70
20	2	IPA 100%	2	H2SO4 50%	1.41	1.57	1.41	0.4	0.3	32.1	0
20	1	IPA 100%	1	H2SO4 50%	0.70	0.79	0.70	0.4	0.3	32.1	0
20	2	IPA 100%	2	H2SO4 50%	1.41	1.57	1.41	0.4	0.3	32.1	2
17	2	IPA 100%	2	H2SO4 50%	1.41	1.57	1.41	0.4	0.3	32.1	6
20	1	IPA 100%	1	H2SO4 50%	0.70	0.79	0.70	0.4	0.3	32.1	15
17	2	IPA 100%	2	H2SO4 50%	1.41	1.57	1.41	0.4	0.3	32.1	21
17	1	IPA 100%	1	H2SO4 50%	0.70	0.79	0.70	0.4	0.3	32.1	22
17	1	IPA 100%	1	H2SO4 50%	0.70	0.79	0.70	0.4	0.3	32.1	43
17	1	IPA 100%	1	H2SO4 65%	0.55	0.79	1.02	0.3	0.2	43.3	0
17	1	IPA 100%	1	H2SO4 65%	0.55	0.79	1.02	0.3	0.2	43.3	0
17	2	IPA 100%	2	H2SO4 65%	1.09	1.57	2.03	0.3	0.2	43.3	0
17	2	IPA 100%	2	H2SO4 65%	1.09	1.57	2.03	0.3	0.2	43.3	0
20	1	IPA 100%	1	H2SO4 65%	0.55	0.79	1.02	0.3	0.2	43.3	0
20	1	IPA 100%	1	H2SO4 65%	0.55	0.79	1.02	0.3	0.2	43.3	0
20	2	IPA 100%	2	H2SO4 65%	1.09	1.57	2.03	0.3	0.2	43.3	0
20	2	IPA 100%	2	H2SO4 65%	1.09	1.57	2.03	0.3	0.2	43.3	0
19	1	IPA 90%	1	H2SO4 20%	0.96	0.73	0.22	0.4	0.5	11.5	85
19	1	IPA 90%	1	H2SO4 20%	0.96	0.73	0.22	0.4	0.5	11.5	89
19	1	IPA 90%	2	H2SO4 20%	1.84	0.73	0.44	0.2	0.6	14.6	92
19	1	IPA 90%	2	H2SO4 20%	1.84	0.73	0.44	0.2	0.6	14.6	96
19	1	IPA 90%	2	H2SO4 35%	1.71	0.73	0.88	0.2	0.5	26.5	69
19	1	IPA 90%	2	H2SO4 35%	1.71	0.73	0.88	0.2	0.5	26.5	70
19	1	IPA 90%	1	H2SO4 35%	0.90	0.73	0.44	0.4	0.4	21.3	72
19	1	IPA 90%	1	H2SO4 35%	0.90	0.73	0.44	0.4	0.4	21.3	72
19	1	IPA 90%	2	H2SO4 50%	1.49	0.73	1.41	0.2	0.4	38.9	8
19	1	IPA 90%	2	H2SO4 50%	1.49	0.73	1.41	0.2	0.4	38.9	9
19	1	IPA 90%	1	H2SO4 50%	0.79	0.73	0.70	0.3	0.4	31.8	58
19	1	IPA 90%	1	H2SO4 50%	0.79	0.73	0.70	0.3	0.4	31.8	59
19	1	IPA 90%	1	H2SO4 65%	0.63	0.73	1.02	0.3	0.3	42.9	0
19	1	IPA 90%	1	H2SO4 65%	0.63	0.73	1.02	0.3	0.3	42.9	0
19	1	IPA 90%	2	H2SO4 65%	1.18	0.73	2.03	0.2	0.3	51.7	0
19	1	IPA 90%	2	H2SO4 65%	1.18	0.73	2.03	0.2	0.3	51.7	0

Table B59: Data for ternary diagram, Figure 2.2 (hydrochloric acid & isopropanol)

hours	solvent (mL)	solvent (wt%)	acid mL	acid (wt%)	total water (g)	total organic solvent (g)	total acid (g)	solvent wt%	water wt%	% acid	% remaining
20	2	IPA 100%	2	HCl 18%	1.78	1.57	0.39	0.4	0.5	10.5	2
20	1	IPA 100%	1	HCl 18%	0.89	0.79	0.20	0.4	0.5	10.5	9
20	2	IPA 100%	2	HCl 18%	1.78	1.57	0.39	0.4	0.5	10.5	12
20	1	IPA 100%	1	HCl 18%	0.89	0.79	0.20	0.4	0.5	10.5	16
17	2	IPA 100%	2	HCl 18%	1.78	1.57	0.39	0.4	0.5	10.5	27
17	1	IPA 100%	1	HCl 18%	0.89	0.79	0.20	0.4	0.5	10.5	46
17	1	IPA 100%	1	HCl 18%	0.89	0.79	0.20	0.4	0.5	10.5	47
17	1	IPA 100%	1	HCl 18%	0.89	0.79	0.20	0.4	0.5	10.5	52
20	1	IPA 100%	1	HCl 36%	0.75	0.79	0.42	0.4	0.4	21.6	0
20	1	IPA 100%	1	HCl 36%	0.75	0.79	0.42	0.4	0.4	21.6	0
20	2	IPA 100%	2	HCl 36%	1.51	1.57	0.85	0.4	0.4	21.6	0
20	2	IPA 100%	2	HCl 36%	1.51	1.57	0.85	0.4	0.4	21.6	0
19	1	IPA 90%	2	HCl 18%	1.87	0.73	0.39	0.2	0.6	13.1	30
19	1	IPA 90%	2	HCl 18%	1.87	0.73	0.39	0.2	0.6	13.1	33
19	1	IPA 90%	1	HCl 18%	0.97	0.73	0.20	0.4	0.5	10.3	58
19	1	IPA 90%	1	HCl 36%	0.84	0.73	0.42	0.4	0.4	21.4	0
19	1	IPA 90%	1	HCl 36%	0.84	0.73	0.42	0.4	0.4	21.4	0
19	1	IPA 90%	2	HCl 36%	1.59	0.73	0.85	0.2	0.5	26.8	0

Table B60: Data for ternary diagram in acetone (hydrochloric acid & sulfuric acid)

hours	solvent (mL)	solvent	acid mL	acid (wt%)	%H ₂ O	% acetone	% acid	% remaining
3	0.5	Acetone	1	H ₂ SO ₄ 20%	59	26	15	89
3	0.5	Acetone	1	H ₂ SO ₄ 20%	59	26	15	92
3	1	Acetone	1	H ₂ SO ₄ 20%	47	42	12	96
3	1	Acetone	1	H ₂ SO ₄ 20%	47	42	12	99
17	0.5	Acetone	0.5	H ₂ SO ₄ 35%	40	39	21	89
17	0.5	Acetone	0.5	H ₂ SO ₄ 35%	40	39	21	90
17	1	Acetone	0.5	H ₂ SO ₄ 35%	29	56	15	95
17	1	Acetone	0.5	H ₂ SO ₄ 35%	29	56	15	96
3	0.5	Acetone	1	H ₂ SO ₄ 35%	49	24	27	92
3	0.5	Acetone	1	H ₂ SO ₄ 35%	49	24	27	93
3	1	Acetone	1	H ₂ SO ₄ 35%	40	39	21	97
3	1	Acetone	1	H ₂ SO ₄ 35%	40	39	21	97
3	0.5	Acetone	1	H ₂ SO ₄ 50%	39	22	39	93
3	0.5	Acetone	1	H ₂ SO ₄ 50%	39	22	39	93
3	1	Acetone	1	H ₂ SO ₄ 50%	32	36	32	95
3	1	Acetone	1	H ₂ SO ₄ 50%	32	36	32	95
17	0.5	Acetone	0.5	H ₂ SO ₄ 65%	23	34	43	0
17	0.5	Acetone	0.5	H ₂ SO ₄ 65%	23	34	43	0
17	1	Acetone	0.5	H ₂ SO ₄ 65%	17	50	32	5
17	1	Acetone	0.5	H ₂ SO ₄ 65%	17	50	32	9
3	0.5	Acetone	1	H ₂ SO ₄ 65%	28	20	52	12
3	0.5	Acetone	1	H ₂ SO ₄ 65%	28	20	52	23
3	1	Acetone	1	H ₂ SO ₄ 65%	23	34	43	50
3	1	Acetone	1	H ₂ SO ₄ 65%	23	34	43	61
17	0.5	Acetone	0.5	HCl 18%	47	42	10	84
17	0.5	Acetone	0.5	HCl 18%	47	42	10	94
17	1	Acetone	0.5	HCl 18%	33	59	7	95
17	1	Acetone	0.5	HCl 18%	33	59	7	95
3	0.5	Acetone	1	HCl 18%	60	27	13	96
3	0.5	Acetone	1	HCl 18%	60	27	13	96
3	1	Acetone	1	HCl 18%	47	42	10	97
3	1	Acetone	1	HCl 18%	47	42	10	98

Table B61: Data for ternary diagram in ethylene glycol (hydrochloric acid & sulfuric acid)

hours	solvent (mL)	solvent (v/v)	acid mL	acid (wt%)	water wt%	EG wt%	% acid	% remaining
20	1	EG / water (1:1)	4	HCl 18%	76	10	14	38
20	2	EG / water (1:1)	4	HCl 18%	71	17	12	77
20	2	EG / water (1:1)	4	HCl 18%	71	17	12	78
20	1	EG / water (1:1)	4	HCl 18%	76	10	14	84
20	1	EG / water (1:1)	4	HCl 36%	61	9	29	0
20	1	EG / water (1:1)	4	HCl 36%	61	9	29	0
20	1	EG / water (1:1)	2	HCl 36%	60	16	25	5
20	1	EG / water (1:1)	2	HCl 36%	60	16	25	7
20	2	EG / water (1:1)	2	HCl 36%	57	24	19	39
20	2	EG / water (1:1)	2	HCl 36%	57	24	19	44

Table B62: Data for ternary diagram in ethyl acetate (hydrochloric acid & sulfuric acid)

hours	solvent (mL)	solvent (v/v)	acid mL	acid (wt%)	water wt%	EtOAc wt%	% acid	% remaining
20	2	Ethyl Acetate	9	H2SO4 20%	68	15	17	94
20	2	Ethyl Acetate	9	H2SO4 20%	68	15	17	102
20	2	Ethyl Acetate	5	H2SO4 35%	51	22	27	90
20	2	Ethyl Acetate	5	H2SO4 35%	51	22	27	91
20	2	Ethyl Acetate	3	H2SO4 50%	35	30	35	37
20	2	Ethyl Acetate	3	H2SO4 50%	35	30	35	48
20	2	Ethyl Acetate	2	H2SO4 65%	22	36	41	0
20	2	Ethyl Acetate	2	H2SO4 65%	22	36	41	0
20	2	Ethyl Acetate	4	HCl 18%	58	29	13	23
20	2	Ethyl Acetate	4	HCl 18%	58	29	13	31
20	2	Ethyl Acetate	2	HCl 36%	36	43	20	0
20	2	Ethyl Acetate	2	HCl 36%	36	43	20	0

Figure B53: Ternary diagram for decomposition of 0.5g TATP using acetone, ethylene glycol and ethyl acetate with hydrochloric acid [Reaction time 3-20 hours; specific times can be found in tables B60-B62]

Figure B54: Ternary diagram for decomposition of 0.5g TATP using acetone, ethylene glycol and ethyl acetate with sulfuric acid [Reaction time 3-20 hours; specific times can be found in tables B60-B62]

Determination of activation energy for decomposition of TATP in alcohol with hydrochloric and sulfuric acids.

Table B63: 100 mg TATP, 7mL ethanol, 3mL 1.5M HCl added, 60°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	2.0E+06	195.47	1	5.3
100	3.35	1.8E+06	177.72	4	5.2
100	3.36	1.2E+06	129.87	11	4.9
100	3.35	7.4E+05	92.77	18	4.5
100	3.35	3.5E+05	44.72	26	3.8
100	3.35	1.8E+05	24.23	35	3.2
100	3.35	8.6E+04	12.95	46	2.6
100	3.35	2.9E+04	5.90	60	1.8

Figure B55: ln concentration vs time for decomposition of 100 mg TATP, 7mL ethanol, 3mL 1.5M HCl added, 60°C

Table B64: 100 mg TATP, 7mL ethanol, 3mL 1.5M HCl added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.358	2308407.5	223.11	1	5.41
100	3.358	2290058.7	221.51	4	5.40
100	3.356	2022635.6	198.18	10	5.29
100	3.354	1652936.6	165.93	26	5.11
100	3.352	1049640.6	113.30	51	4.73
100	3.349	667540.3	77.27	80	4.35
100	3.349	337116.9	41.47	116	3.72
100	3.349	259508.9	33.06	142	3.50

Figure B56: ln concentration vs time for decomposition of 100 mg TATP, 7mL ethanol, 3mL 1.5M HCl added, 45°C

Table B65: 100 mg TATP, 7mL ethanol, 3mL 1.5M HCl added, 30°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	2.3E+06	202.08	1	5.3
100	3.36	2.2E+06	196.08	12	5.3
100	3.36	2.1E+06	188.51	32	5.2
100	3.36	2.0E+06	181.41	51	5.2
100	3.31	1.7E+06	162.99	109	5.1
100	3.36	1.6E+06	150.52	184	5.0
100	3.36	1.4E+06	136.28	235	4.9
100	3.36	1.2E+06	126.88	296	4.8

Figure B57: ln concentration vs time for decomposition of 100 mg TATP, 7mL ethanol, 3mL 1.5M HCl added, 30°C

Table B66: 100 mg TATP, 7mL ethanol, 3mL 1.5M H₂SO₄ added, 60°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	2.2E+06	213.93	1	5.4
100	3.36	1.7E+06	169.27	3	5.1
100	3.36	1.4E+06	144.66	7	5.0
100	3.35	7.3E+05	92.23	14	4.5
100	3.35	3.6E+05	46.69	22	3.8
100	3.35	1.6E+05	21.94	31	3.1
100	3.35	6.9E+04	10.89	42	2.4
100	3.35	1.7E+04	4.49	56	1.5

Figure B58: ln concentration vs time for decomposition of 100 mg TATP, 7mL ethanol, 3mL 1.5M H₂SO₄ added, 60°C

Table B67: 100 mg TATP, 7mL ethanol, 3mL 1.5M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	2.1E+06	179.0	6	5.2
100	3.36	1.9E+06	168.3	14	5.1
100	3.36	1.7E+06	150.8	26	5.0
100	3.36	1.2E+06	120.6	44	4.8
100	3.36	8.3E+05	93.7	64	4.5
100	3.36	6.0E+05	68.4	84	4.2
100	3.35	3.3E+05	39.5	116	3.7
100	3.35	1.7E+05	21.4	157	3.1
100	3.35	8.6E+04	12.4	208	2.5

Figure B59: ln concentration vs time for decomposition of 100 mg TATP, 7mL ethanol, 3mL 1.5M H₂SO₄ added, 45°C

Table B68: Data for calculating activation energy

TATP (mg)	acid	moles acid	mass acid (g)	alcohol (mL)	water (g)	Temp (°C)	k(sec ⁻¹)	1/T(K)	ln k
100	3 mL 1.5M HCl	0.0045	0.16	7	3.0	30	0.096	0.00330	-2.34
100	3 mL 1.5M H ₂ SO ₄	0.0045	0.44	7	3.1	30	0.096	0.00330	-2.34
100	3 mL 1.5M H ₂ SO ₄	0.0045	0.44	7	3.1	45	0.834	0.00314	-0.18
100	3 mL 1.5M HCl	0.0045	0.16	7	3.0	45	0.846	0.0031	-0.17
100	3 mL 1.5M HCl	0.0045	0.16	7	3.0	60	3.714	0.00300	1.31
100	3 mL 1.5M H ₂ SO ₄	0.0045	0.44	7	3.1	60	4.278	0.00300	1.45

Figure B60: Arrhenius plot for decomposition of TATP in ethanol using sulfuric and hydrochloric acid

Table B69: Activation energy and pre-exponential factor for decomposition of TATP in ethanol using hydrochloric and sulfuric acid

	Ea (kJ/mole)	A (sec-1)
HCl	103	3.2 x 10 ¹⁶
H ₂ SO ₄	106	2.5 x 10 ¹⁷

Additional decomposition data for TATP decomposition in alcohols

Table B70: 100 mg TATP, 10mL ethanol, 500 μ L 80wt% H₂SO₄ added, 35°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (μ g/mL)	time (min)	ln(concentration)
100	3.77	1.4E+06	8358.0	3	9.0
100	3.77	1.4E+06	8230.1	6	9.0
100	3.77	1.4E+06	7894.1	10	9.0
100	3.77	1.2E+06	7232.4	14	8.9
100	3.77	1.2E+06	6846.9	20	8.8
100	3.77	1.0E+06	6116.3	28	8.7
100	3.77	8.8E+05	5293.6	40	8.6
100	3.77	6.8E+05	4157.1	52	8.3
100	3.77	5.9E+05	3708.2	64	8.2
100	3.77	5.1E+05	3227.3	72	8.1

Figure B61: ln concentration vs time for decomposition of 100 mg TATP, 10mL ethanol, 500 μ L 80wt% H₂SO₄ added, 35°C

Table B71: 50 mg TATP, 10mL ethanol, 500µL 80wt% H₂SO₄ added, 35°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.77	7.5E+05	4585.5	3	8.4
100	3.77	7.9E+05	4780.1	6	8.5
100	3.77	7.0E+05	4283.0	10	8.4
100	3.77	6.4E+05	3982.6	14	8.3
100	3.77	4.8E+05	3063.0	20	8.0
100	3.77	5.4E+05	3402.7	23	8.1
100	3.77	4.0E+05	2634.4	31	7.9
100	3.77	4.0E+05	2660.7	36	7.9
100	3.77	3.5E+05	2354.8	42	7.8
100	3.77	2.9E+05	2002.0	54	7.6

Figure B62: ln concentration vs time for decomposition of 50 mg TATP, 10mL ethanol, 500µL 80wt% H₂SO₄ added, 35°C

Table B72: 100 mg TATP, 10mL ethanol, 500µL 80wt% H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.77	1.4E+06	8202.9	2	9.0
100	3.77	1.2E+06	7016.7	5	8.9
100	3.77	1.0E+06	5928.0	8	8.7
100	3.77	7.8E+05	4729.2	12	8.5
100	3.77	6.1E+05	3772.8	16	8.2
100	3.77	4.9E+05	3111.4	22	8.0
100	3.77	2.8E+05	1927.6	30	7.6
100	3.77	1.7E+05	1343.9	33	7.2
100	3.77	9.1E+04	910.3	42	6.8

Figure B63: ln concentration vs time for decomposition of 100 mg TATP, 10mL ethanol, 500µL 80wt% H₂SO₄ added, 45°C

Table B73: 50 mg TATP, 10mL ethanol, 500µL 80wt% H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.77	5.5E+05	3420.7	2	8.1
100	3.77	4.9E+05	3121.9	5	8.0
100	3.77	3.9E+05	2541.6	10	7.8
100	3.77	3.3E+05	2247.9	13	7.7
100	3.77	2.5E+05	1809.0	19	7.5
100	3.77	2.1E+05	1577.5	24	7.4
100	3.77	1.3E+05	1113.6	35	7.0
100	3.77	9.2E+04	916.2	41	6.8
100	3.77	6.4E+04	761.5	50	6.6

Figure B64: ln concentration vs time for decomposition of 50 mg TATP, 10mL ethanol, 500µL 80wt% H₂SO₄ added, 45°C

Table B74: 100 mg TATP, 9mL ethanol, 1mL water, 500 μ L 80wt% H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (μ g/mL)	time (min)	ln(concentration)
100	3.77	1.4E+06	8303.2	2	9.0
100	3.77	1.3E+06	7688.8	5	8.9
100	3.77	1.4E+06	8300.3	9	9.0
100	3.77	1.2E+06	6890.2	13	8.8
100	3.77	1.1E+06	6342.6	18	8.8
100	3.77	9.2E+05	5508.1	25	8.6
100	3.77	8.1E+05	4856.1	32	8.5
100	3.77	6.5E+05	3996.9	40	8.3
100	3.77	5.6E+05	3522.3	47	8.2
100	3.77	4.5E+05	2869.7	58	8.0

Figure B65: ln concentration vs time for decomposition of 100 mg TATP, 9mL ethanol, 1mL water, 500 μ L 80wt% H₂SO₄ added, 45°C

Table B75: 100 mg TATP, 8mL ethanol, 2mL water, 500 μ L 80wt% H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (μ g/mL)	time (min)	ln(concentration)
100	3.77	1.5E+06	8723.5	2	9.1
100	3.77	1.5E+06	8540.4	5	9.1
100	3.77	1.4E+06	7995.3	9	9.0
100	3.77	1.3E+06	7563.9	13	8.9
100	3.77	1.1E+06	6559.0	18	8.8
100	3.77	9.3E+05	5528.7	25	8.6
100	3.77	8.0E+05	4836.4	32	8.5
100	3.77	7.1E+05	4346.9	40	8.4
100	3.77	5.4E+05	3388.3	50	8.1
100	3.77	3.8E+05	2478.8	63	7.8

Figure B66: ln concentration vs time for decomposition of 100 mg TATP, 8mL ethanol, 2mL water, 500 μ L 80wt% H₂SO₄ added, 45°C

Table B76: 100 mg TATP, 10mL ethanol, 500µL 18wt% HCl added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.77	1.6E+06	9236.7	2	9.1
100	3.77	1.6E+06	8848.1	5	9.1
100	3.77	1.6E+06	8841.8	8	9.1
100	3.77	1.5E+06	8752.5	11	9.1
100	3.77	1.4E+06	8273.6	15	9.0
100	3.77	1.4E+06	8116.1	20	9.0
100	3.77	1.4E+06	8098.0	25	9.0
100	3.77	1.4E+06	7809.3	32	9.0
100	3.77	1.2E+06	6844.5	41	8.8
100	3.77	1.1E+06	6184.1	50	8.7

Figure B67: ln concentration vs time for decomposition of 100 mg TATP, 10mL ethanol, 500µL 18wt% HCl added, 45°C

Table B77: 100 mg TATP, 10mL ethanol, 500µL 18wt% HCl added, 40°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.77	1.6E+06	8858.7	3	9.1
100	3.77	1.5E+06	8657.2	5	9.1
100	3.77	1.5E+06	8446.0	8	9.0
100	3.78	2.4E+06	13503.4		
100	3.77	1.5E+06	8292.3	15	9.0
100	3.77	1.4E+06	8236.7	20	9.0
100	3.77	1.4E+06	7907.6	26	9.0
100	3.77	1.3E+06	7878.3	35	9.0
100	3.77	1.4E+06	7653.3	45	8.9
100	3.77	1.2E+06	7073.8	53	8.9

Figure B68: ln concentration vs time for decomposition of 100 mg TATP, 10mL ethanol, 500µL 18wt% HCl added, 40°C

Table B78: 100 mg TATP, 10mL ethanol, 500µL 18wt% HCl added, 35°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.77	1.6E+06	8909.0	2	9.1
100	3.77	1.5E+06	8712.5	5	9.1
100	3.77	1.5E+06	8333.1	10	9.0
100	3.77	1.6E+06	8789.7	16	9.1
100	3.77	1.5E+06	8547.5	25	9.1
100	3.77	1.5E+06	8240.9	32	9.0
100	3.77	1.4E+06	8090.4	40	9.0
100	3.77	1.4E+06	8077.6	50	9.0
100	3.77	1.4E+06	7901.9	60	9.0
100	3.77	1.3E+06	7484.5	71	8.9

Figure B69: ln concentration vs time for decomposition of 100 mg TATP, 10mL ethanol, 500µL 18wt% HCl added, 35°C

Table B79: 100 mg TATP, 9.15mL ethanol, 0.75mL water, 600µL 18wt% HCl added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.77	5.7E+05	4277.6	2	8.4
100	3.77	1.1E+06	6453.1	5	8.8
100	3.77	9.6E+05	5960.9	8	8.7
100	3.77	1.1E+06	6472.1	12	8.8
100	3.77	1.0E+06	6303.3	17	8.7
100	3.77	9.8E+05	6030.5	23	8.7
100	3.77	8.4E+05	5411.1	30	8.6
100	3.77	6.3E+05	4076.0	43	8.3
100	3.77	5.0E+05	3280.8	51	8.1
100	3.77	4.6E+05	3045.1	55	8.0

Figure B70: ln concentration vs time for decomposition of 100 mg TATP, 9.15mL ethanol, 0.75mL water, 600µL 18wt% HCl added, 45°C

Table B80: 100 mg TATP, 9.15mL ethanol, 0.15mL water, 1.2mL 18wt% HCl added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.77	1.4E+06	7680.6	2	8.9
100	3.77	1.0E+06	6304.0	5	8.7
100	3.77	7.9E+05	5191.3	8	8.6
100	3.77	6.5E+05	4203.1	11	8.3
100	3.77	5.7E+05	3722.9	14	8.2
100	3.77	4.7E+05	3051.2	17	8.0
100	3.77	3.6E+05	2405.0	21	7.8
100	3.77	2.3E+05	1532.0	27	7.3
100	3.77	1.5E+05	1033.5	33	6.9
100	3.77	3.3E+05	2192.8	37	7.7

Figure B71: ln concentration vs time for decomposition of 100 mg TATP, 9.15mL ethanol, 0.15mL water, 1.2mL 18wt% HCl added, 45°C

Table B81: 100 mg TATP, 9mL ethanol, 1mL 10.4mM ZnSO₄ in water, 500μL 80wt% H₂SO₄ added, 35°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (μg/mL)	time (min)	ln(concentration)
100	3.77	1.9E+06	9189.5	2	9.1
100	3.77	1.9E+06	9187.7	5	9.1
100	3.77	1.8E+06	8964.8	9	9.1
100	3.77	1.7E+06	8611.7	14	9.1
100	3.77	1.6E+06	8097.6	21	9.0
100	3.77	1.5E+06	7678.5	30	8.9
100	3.77	1.9E+06	9182.8		
100	3.77	1.4E+06	7309.8	50	8.9
100	3.77	1.3E+06	6934.6	60	8.8
100	3.76	1.1E+06	6097.2	70	8.7

Figure B72: ln concentration vs time for decomposition of 100 mg TATP, 9mL ethanol, 1mL 10.4mM ZnSO₄ in water, 500μL 80wt% H₂SO₄ added, 35°C

Table B82: 100 mg TATP, 9mL ethanol, 1mL 10.4mM ZnSO₄ in water, 500μL 80wt% H₂SO₄ added, 40°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (μg/mL)	time (min)	ln(concentration)
100	3.77	1.8E+06	8987.9	2	9.1
100	3.77	1.7E+06	8744.4	5	9.1
100	3.77	1.8E+06	8924.8	9	9.1
100	3.77	1.5E+06	7824.4	14	9.0
100	3.77	1.4E+06	7349.6	20	8.9
100	3.76	1.1E+06	6130.5	28	8.7
100	3.77	1.2E+06	6487.0	36	8.8
100	3.77	1.0E+06	5933.1	44	8.7
100	3.76	1.1E+06	6322.4	50	8.8
100	3.76	9.1E+05	5449.0	60	8.6

Figure B73: ln concentration vs time for decomposition of 100 mg TATP, 9mL ethanol, 1mL 10.4mM ZnSO₄ in water, 500μL 80wt% H₂SO₄ added, 40°C

Table B83: 100 mg TATP, 9mL ethanol, 1mL 10.4mM ZnSO₄ in water, 500μL 80wt% H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (μg/mL)	time (min)	ln(concentration)
100	3.77	1.6E+06	8356.9	2	9.0
100	3.77	1.4E+06	7189.6	8	8.9
100	3.77	1.3E+06	7028.5	12	8.9
100	3.77	1.2E+06	6575.7	17	8.8
100	3.76	1.1E+06	5997.2	23	8.7
100	3.76	9.0E+05	5395.6	30	8.6
100	3.76	7.8E+05	4563.5	36	8.4
100	3.76	7.4E+05	4362.3	42	8.4
100	3.76	5.4E+05	3123.3	50	8.0

Figure B74: ln concentration vs time for decomposition of 100 mg TATP, 9mL ethanol, 1mL 10.4mM ZnSO₄ in water, 500μL 80wt% H₂SO₄ added, 45°C

Table B84: 100 mg TATP, 10mL ethanol, 500µL 36wt% HCl added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.77	1.3E+06	8106.0	3	9.0
100	3.77	1.1E+06	7197.5	6	8.9
100	3.77	1.1E+06	7186.0	9	8.9
100	3.77	1.0E+06	6506.6	13	8.8
100	3.77	8.5E+05	5795.4	17	8.7
100	3.77	7.1E+05	4837.9	22	8.5
100	3.77	5.0E+05	3459.5	32	8.1
100	3.77	4.8E+05	3282.9	36	8.1
100	3.76	3.4E+05	2379.9	43	7.8
100	3.77	2.8E+05	1957.0	50	7.6

Figure B75: ln concentration vs time for decomposition of 100 mg TATP, 10mL ethanol, 500µL 36wt% HCl added, 45°C

Table B85: 100 mg TATP, 10mL ethanol, 365 μ Lwater, 160 μ L 97wt% H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (μ g/mL)	time (min)	ln(concentration)
100	3.77	1.4E+06	8655.2	2	9.1
100	3.77	1.3E+06	8091.8	5	9.0
100	3.77	1.2E+06	7657.9	8	8.9
100	3.77	1.2E+06	7315.6	12	8.9
100	3.77	1.1E+06	6941.7	16	8.8
100	3.77	1.2E+06	7375.3	22	8.9
100	3.77	1.0E+06	6629.8	32	8.8
100	3.77	9.2E+05	6122.3	36	8.7
100	3.77	8.3E+05	5694.6	43	8.6
100	3.77	7.5E+05	5347.2	50	8.6

Figure B76: ln concentration vs time for decomposition of 100 mg TATP, 10mL ethanol, 365 μ Lwater, 160 μ L 97wt% H₂SO₄ added, 45°C

Table B86: 100 mg TATP, 10mL ethanol, 365 μ Lwater, 380 μ L 99% methanesulfonic acid added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (μ g/mL)	time (min)	ln(concentration)
100	3.77	1.4E+06	8565.2	2	9.1
100	3.77	1.4E+06	8506.3	5	9.0
100	3.77	1.3E+06	8049.6	8	9.0
100	3.77	1.1E+06	7229.5	12	8.9
100	3.77	1.1E+06	6978.4	16	8.9
100	3.77	8.6E+05	5854.8	25	8.7
100	3.77	7.3E+05	4964.5	32	8.5
100	3.77	6.4E+05	4394.0	36	8.4
100	3.77	5.7E+05	3935.6	43	8.3
100	3.77	4.6E+05	3165.5	50	8.1

Figure B77: ln concentration vs time for decomposition of 100 mg TATP, 10mL ethanol, 365 μ Lwater, 380 μ L 99% methanesulfonic acid added, 45°C

Table B87: 100 mg TATP, 9mL ethanol, 1 mL 10.4mM ZnSO₄ in water,65mg Zn powder added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.78	1.8E+06	9286.9	1	9.1
100	3.78	1.7E+06	9067.7	17	9.1
100	3.79	1.7E+06	9098.0	25	9.1
100	3.78	1.7E+06	8821.9	39	9.1
100	3.78	1.7E+06	8846.8	46	9.1
100	3.78	1.6E+06	8677.0	59	9.1
100	3.78	1.7E+06	8847.2	74	9.1
100	3.78	1.6E+06	8649.2	82	9.1
100	3.78	1.6E+06	8604.0	91	9.1
100	3.78	1.6E+06	8572.8	99	9.1
100	3.78	1.6E+06	8769.1	109	9.1
100	3.78	1.6E+06	8558.3	120	9.1

Figure B78: ln concentration vs time for decomposition of 100 mg TATP, 9mL ethanol, 1 mL 10.4mM ZnSO₄ in water,65mg Zn powder added, 45°C

Table B88: 100 mg TATP, 9mL ethanol, 1 mL 1M ZnSO₄ in water, 653mg Zn powder added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.78	1.6E+06	8126.51	2	9.0
100	3.78	1.6E+06	8218.38	19	9.0
100	3.78	1.6E+06	8084.37	34	9.0
100	3.78	1.7E+06	8512.45	59	9.0
100	3.78	1.6E+06	8074.80	75	9.0
100	3.78	1.7E+06	8508.04	96	9.0
100	3.78	1.6E+06	8248.78	119	9.0
100	3.78	1.8E+06	9006.03	159	9.1
100	3.78	1.6E+06	8370.39	204	9.0
100	3.78	1.6E+06	8154.13	249	9.0

Figure B79: ln concentration vs time for decomposition of 100 mg TATP, 9mL ethanol, 1 mL 1M ZnSO₄ in water, 653mg Zn powder added, 45°C

Table B89: 100 mg TATP, 9mL ethanol, 1 mL 1M ZnSO₄ in water, 659mg Zn powder, 55µL 96% H₂SO₄, added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.78	1.7E+06	9672.86	3	9.2
100	3.78	1.5E+06	8717.57	20	9.1
100	3.78	1.4E+06	8207.80	35	9.0
100	3.78	1.3E+06	7635.88	60	8.9
100	3.78	1.2E+06	7183.79	76	8.9
100	3.78	1.2E+06	7248.81	97	8.9
100	3.78	1.0E+06	6529.32	120	8.8
100	3.78	9.1E+05	6012.24	160	8.7
100	3.77	8.6E+05	5767.11	205	8.7
100	3.78	7.8E+05	5426.87	250	8.6

Figure B80: ln concentration vs time for decomposition of 100 mg TATP, 9mL ethanol, 1 mL 1M ZnSO₄ in water, 659mg Zn powder, 55µL 96% H₂SO₄, added, 45°C

Table B90: 100 mg TATP, 10mL ethanol, 350µL water, 530µL 96% H₂SO₄, added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.78	1.6E+06	9272.82	2	9.1
100	3.78	1.5E+06	8819.94	5	9.1
100	3.78	1.3E+06	7820.82	8	9.0
100	3.78	1.1E+06	7102.32	12	8.9
100	3.77	9.3E+05	6103.38	17	8.7
100	3.77	8.3E+05	5637.12	24	8.6
100	3.77	6.7E+05	4902.73	30	8.5
100	3.77	5.1E+05	3759.50	36	8.2
100	3.77	4.5E+05	3341.08	42	8.1
100	3.77	3.3E+05	2451.45	50	7.8

Figure B81: ln concentration vs time for decomposition of 100 mg TATP, 10mL ethanol, 350µL water, 530µL 96% H₂SO₄, added, 45°C

Table B91: 100 mg TATP, 9mL ethanol, 1mL 0.5M HCl added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.77	2.1E+06	10393.9	4	9.2
100	3.77	1.7E+06	8862.2	214	9.1
100	3.77	5.0E+05	3297.4	1794	8.1
100	3.77	2.6E+05	1783.0	2811	7.5
100	3.74	5.9E+04	479.5	5605	6.2

Figure B82: ln concentration vs time for decomposition of 100 mg TATP, 9mL ethanol, 1mL 0.5M HCl, 45°C

Table B92: 100 mg TATP, 9mL ethanol, 1mL 0.1M HCl added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.77	2.1E+06	10412.4	6	9.3
100	3.77	2.0E+06	10254.2	245	9.2
100	3.78	2.0E+06	9930.1	1798	9.2
100	3.77	1.4E+06	7640.7	2813	8.9
100	3.74	9.6E+05	5826.2	5609	8.7
100	3.76	6.5E+05	4853.2	8676	8.5

Figure B83: ln concentration vs time for decomposition of 100 mg TATP, 9mL ethanol, 1mL 0.1M HCl, 45°C

Table B93: 100 mg TATP, 9mL ethanol, 1mL 0.43M HCl added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.74	2013152.3	10101.3	2	9.220
100	3.742	322268.7	2164.7	2611	7.680
100	3.743	278854.9	1886.6	2817	7.543
100	3.754	41127.1	322.6	5854	5.776

Figure B84: ln concentration vs time for decomposition of 100 mg TATP, 9mL ethanol, 1mL 0.43M HCl, 45°C

Table B94: 100 mg TATP, 9mL ethanol, 1mL 5M HCl added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.77	2.0E+06	10366.8	6	9.2
100	3.76	1.5E+06	7915.1	26	9.0
100	3.76	7.4E+05	4793.1	63	8.5
100	3.76	4.1E+05	2696.5	100	7.9
100	3.76	1.4E+05	1008.4	173	6.9
100	3.77	5.5E+04	476.4	249	6.2
100	3.76	2.8E+05	1867.4	332	7.5

Figure B85: ln concentration vs time for decomposition of 100 mg TATP, 9mL ethanol, 1mL 5M HCl, 45°C

Table B95: 100 mg TATP, 9mL ethanol, 1mL 4M HCl added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.77	2.1E+06	10406.8	8	9.3
100	3.77	1.6E+06	8617.9	28	9.1
100	3.77	1.2E+06	7012.7	65	8.9
100	3.76	7.4E+05	4786.0	101	8.5
100	3.76	3.2E+05	2179.2	175	7.7
100	3.76	1.6E+05	1170.0	250	7.1
100	3.76	7.9E+04	627.6	334	6.4

Figure B86: ln concentration vs time for decomposition of 100 mg TATP, 9mL ethanol, 1mL 4M HCl, 45°C

Table B96: 100 mg TATP, 9mL ethanol, 1mL 3M HCl added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.766	2005988	10214.0	10	9.232
100	3.765	2044531.9	10374.5	29	9.247
100	3.767	1717673.8	9013.1	66	9.106
100	3.765	1128542.7	6559.2	103	8.789
100	3.76	696841.4	4531.8	177	8.419
100	3.762	459993.3	3035.5	252	8.018
100	3.77	30013.4	319.0	335	5.765

Figure B87: ln concentration vs time for decomposition of 100 mg TATP, 9mL ethanol, 1mL 3M HCl, 45°C

Table B97: 100 mg TATP, 8mL ethanol, 2mL 5M HCl added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.76	1.8E+06	9439.5	3	9.2
100	3.76	6.4E+05	4323.7	23	8.4
100	3.76	9.6E+04	748.4	61	6.6
100	3.77	1.3E+04	208.8	124	5.3

Figure B88: ln concentration vs time for decomposition of 100 mg TATP, 8mL ethanol, 2mL 5M HCl, 45°C

Table B98: 100 mg TATP, 8mL ethanol, 2mL 4M HCl added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.77	2.7E+06	13120.2	6	9.5
100	3.77	1.8E+06	9259.1	24	9.1
100	3.77	1.4E+06	7584.1	63	8.9
100	3.76	8.4E+05	5522.5	125	8.6
100	3.76	2.3E+05	1646.6	239	7.4

Figure B89: ln concentration vs time for decomposition of 100 mg TATP, 8mL ethanol, 2mL 4M HCl, 45°C

Table B99: 100 mg TATP, 8mL ethanol, 2mL 3M HCl added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.77	2.1E+06	10691.3	9	9.3
100	3.77	1.6E+06	8686.7	64	9.1
100	3.76	1.1E+06	6748.9	126	8.8
100	3.76	7.5E+05	5152.5	240	8.5

Figure B90: ln concentration vs time for decomposition of 100 mg TATP, 8mL ethanol, 2mL 3M HCl, 45°C

Table B100: 100 mg TATP, 7mL ethanol, 3mL 3M HCl added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.77	2.5E+06	11420.2	3	9.3
100	3.76	1.3E+06	6768.0	10	8.8
100	3.76	5.9E+05	3333.2	25	8.1
100	3.76	1.7E+05	1058.9	48	7.0

Figure B91: ln concentration vs time for decomposition of 100 mg TATP, 7mL ethanol, 3mL 3M HCl, 45°C

Table B101: 100 mg TATP, 7mL ethanol, 3mL 2M HCl added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.77	2.5E+06	11573.1	4	9.4
100	3.76	2.0E+06	9668.7	12	9.2
100	3.76	8.4E+05	4722.4	34	8.5

Figure B92: ln concentration vs time for decomposition of 100 mg TATP, 7mL ethanol, 3mL 2M HCl, 45°C

Table B102: 100 mg TATP, 7mL ethanol, 3mL 1M HCl added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.76	2.3E+06	10759.0	5	9.3
100	3.76	2.0E+06	9620.2	14	9.2
100	3.76	1.5E+06	7439.8	44	8.9

Figure B93: ln concentration vs time for decomposition of 100 mg TATP, 7mL ethanol, 3mL 1M HCl, 45°C

Table B103: 100 mg TATP, 9mL ethanol, 1mL 1.5M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.37	3.5E+06	245.5	1	5.5
100	3.37	3.4E+06	237.0	4	5.5
100	3.37	3.1E+06	222.1	11	5.4
100	3.36	2.8E+06	203.9	19	5.3
100	3.36	2.7E+06	195.2	36	5.3
100	3.36	2.5E+06	185.8	56	5.2
100	3.36	2.2E+06	169.5	87	5.1
100	3.36	2.1E+06	161.2	120	5.1

Figure B94: ln concentration vs time for decomposition of 100 mg TATP, 9mL ethanol, 1mL 1.5M H₂SO₄ added, 45°C

Table B104: 100 mg TATP, 8mL ethanol, 2mL 0.75M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	2.9E+06	208.26	4	5.3
100	3.36	2.7E+06	197.46	11	5.3
100	3.36	2.6E+06	192.87	24	5.3
100	3.36	2.4E+06	179.22	42	5.2
100	3.36	2.3E+06	171.21	60	5.1
100	3.36	2.2E+06	167.14	75	5.1

Figure B95: ln concentration vs time for decomposition of 100 mg TATP, 8mL ethanol, 2mL 0.75M H₂SO₄ added, 45°C

Table B105: 100 mg TATP, 7mL ethanol, 3mL 0.36M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	2.9E+06	206.99	6	5.3
100	3.36	2.8E+06	204.22	13	5.3
100	3.36	2.6E+06	192.90	26	5.3
100	3.36	2.4E+06	181.49	44	5.2
100	3.36	2.7E+06	195.39	62	5.3
100	3.36	2.1E+06	164.52	77	5.1

Figure B96: ln concentration vs time for decomposition of 100 mg TATP, 7mL ethanol, 3mL 0.36M H₂SO₄ added, 45°C

Table B106: 100 mg TATP, 9mL ethanol, 1mL 1.5M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.37	2.5E+06	200.8	2	5.3
100	3.36	2.0E+06	171.3	10	5.1
100	3.36	2.0E+06	173.5	22	5.2
100	3.36	1.9E+06	163.0	40	5.1
100	3.36	1.7E+06	155.5	60	5.0
100	3.36	1.7E+06	154.8	80	5.0
100	3.36	1.5E+06	142.4	112	5.0
100	3.36	1.3E+06	131.7	151	4.9
100	3.36	1.1E+06	116.0	204	4.8

Figure B97: ln concentration vs time for decomposition of 100 mg TATP, 9mL ethanol, 1mL 1.5M H₂SO₄ added, 45°C

Table B107: 100 mg TATP, 8mL ethanol, 2mL 1.5M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	1.9E+06	167.3	4	5.1
100	3.36	2.1E+06	177.8	12	5.2
100	3.36	1.9E+06	168.5	24	5.1
100	3.36	1.7E+06	153.5	42	5.0
100	3.36	1.4E+06	136.8	62	4.9
100	3.36	1.2E+06	121.1	82	4.8
100	3.36	1.0E+06	113.0	114	4.7
100	3.36	6.4E+05	73.3	154	4.3
100	3.36	4.8E+05	55.9	206	4.0

Figure B98: ln concentration vs time for decomposition of 100 mg TATP, 8mL ethanol, 2mL 1.5M H₂SO₄ added, 45°C

Table B108: 100 mg TATP, 7mL ethanol, 3mL 0.75M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	1.9E+06	168.8	8	5.1
100	3.36	2.0E+06	171.6	16	5.1
100	3.36	1.9E+06	164.9	28	5.1
100	3.36	1.7E+06	153.5	46	5.0
100	3.36	1.4E+06	137.7	66	4.9
100	3.36	1.3E+06	126.2	86	4.8
100	3.36	9.8E+05	108.5	118	4.7
100	3.36	7.2E+05	81.7	160	4.4
100	3.35	5.0E+05	57.8	210	4.1

Figure B99: ln concentration vs time for decomposition of 100 mg TATP, 7mL ethanol, 3mL 0.75M H₂SO₄ added, 45°C

Table B109: 100 mg TATP, 7mL ethanol, 3mL 1.5M H₂SO₄ added, 30°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	2.1E+06	192.75	4	5.3
100	3.36	2.3E+06	201.05	14	5.3
100	3.36	1.9E+06	177.08	35	5.2
100	3.36	1.9E+06	171.93	53	5.1
100	3.34	1.6E+06	156.04	112	5.1
100	3.36	1.5E+06	143.40	187	5.0
100	3.36	1.4E+06	140.99	238	4.9
100	3.36	1.1E+06	115.12	299	4.7

Figure B100: ln concentration vs time for decomposition of 100 mg TATP, 7mL ethanol, 3mL 1.5M H₂SO₄ added, 30°C

Table B110: 100 mg TATP, 9mL ethanol, 1mL 8.7M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	1.9E+06	185.4	1	5.2
100	3.36	1.5E+06	152.3	10	5.0
100	3.36	6.7E+05	82.7	23	4.4
100	3.35	3.6E+05	47.1	38	3.9
100	3.35	9.8E+04	17.0	74	2.8
100	3.35	1.7E+04	7.8	131	2.0
100	3.35	8.3E+03	6.7	177	1.9
100	3.35	5.2E+03	6.4	233	1.9

Figure B101: ln concentration vs time for decomposition of 100 mg TATP, 9mL ethanol, 1mL 8.7M H₂SO₄ added, 45°C

Table B111: 100 mg TATP, 9mL ethanol, 1mL 6M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	1.9E+06	185.8	3	5.2
100	3.36	1.3E+06	134.4	12	4.9
100	3.36	1.2E+06	127.1	25	4.8
100	3.35	7.2E+05	89.1	40	4.5
100	3.35	3.2E+05	42.2	76	3.7
100	3.35	7.7E+04	14.7	133	2.7
100	3.35	4.2E+04	10.6	179	2.4
100	3.35	1.2E+04	7.1	236	2.0

Figure B102: ln concentration vs time for decomposition of 100 mg TATP, 9mL ethanol, 1mL 6M H₂SO₄ added, 45°C

Table B112: 100 mg TATP, 8mL ethanol, 2mL 4.4M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	1.9E+06	186.1	5	5.2
100	3.36	1.2E+06	132.3	14	4.9
100	3.36	7.4E+05	91.4	27	4.5
100	3.35	3.9E+05	51.0	42	3.9
100	3.35	9.5E+04	16.7	78	2.8
100	3.35	1.5E+04	7.5	135	2.0
100	3.35	7.9E+03	6.7	181	1.9
100	3.35	5.0E+03	6.3	239	1.8

Figure B103: ln concentration vs time for decomposition of 100 mg TATP, 8mL ethanol, 2mL 4.4M H₂SO₄ added, 45°C

Table B113: 100 mg TATP, 8mL ethanol, 2mL 1M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	2.0E+06	191.4	7	5.3
100	3.36	2.1E+06	201.2	16	5.3
100	3.36	2.0E+06	194.0	29	5.3
100	3.36	1.9E+06	185.8	44	5.2
100	3.36	1.7E+06	171.4	80	5.1
100	3.36	1.3E+06	137.5	137	4.9
100	3.35	1.0E+06	115.8	183	4.8
100	3.35	8.5E+05	102.5	242	4.6

Figure B014: ln concentration vs time for decomposition of 100 mg TATP, 8mL ethanol, 2mL 1M H₂SO₄ added, 45°C

Table B114: 100 mg TATP, 9mL ethanol, 1mL 8.7M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	1.8E+06	173.8	1	5.2
100	3.35	1.2E+06	126.4	11	4.8
100	3.35	6.3E+05	76.6	28	4.3
100	3.35	3.0E+05	38.4	45	3.6
100	3.35	1.1E+05	16.2	73	2.8
100	3.35	1.9E+04	6.2	115	1.8
100	3.35	6.2E+03	4.7	173	1.6
100	3.35	1.5E+04	5.7	248	1.7

Figure B105: ln concentration vs time for decomposition of 100 mg TATP, 9mL ethanol, 1mL 8.7M H₂SO₄ added, 45°C

Table B115: 100 mg TATP, 8mL ethanol, 2mL 4.4M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	1.5E+06	149.0	3	5.0
100	3.35	1.3E+06	132.0	13	4.9
100	3.35	5.9E+05	71.8	30	4.3
100	3.35	2.9E+05	37.3	47	3.6
100	3.35	9.1E+04	14.5	75	2.7
100	3.35	1.6E+04	5.9	117	1.8
100	3.35	4.5E+03	4.5	175	1.5
100	3.35	5.3E+03	4.6	250	1.5

Figure B106: ln concentration vs time for decomposition of 100 mg TATP 8mL ethanol, 2mL 4.4M H₂SO₄ added, 45°C

Table B116: 100 mg TATP, 7mL ethanol, 3mL 2.9M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	2.0E+06	190.6	5	5.3
100	3.36	1.2E+06	131.2	15	4.9
100	3.35	5.6E+05	69.1	32	4.2
100	3.35	2.5E+05	33.1	49	3.5
100	3.35	7.2E+04	12.4	77	2.5
100	3.35	1.4E+04	5.6	119	1.7
100	3.35	6.0E+03	4.7	177	1.5
100	3.35	4.5E+03	4.5	252	1.5

Figure B107: ln concentration vs time for decomposition of 100 mg TATP 7mL ethanol, 3mL 2.9M H₂SO₄ added, 45°C

Table B117: 100 mg TATP, 7mL ethanol, 3mL 1.5M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	2.0E+06	194.0	7	5.3
100	3.35	1.3E+06	136.0	34	4.9
100	3.35	9.9E+05	111.4	51	4.7
100	3.35	5.8E+05	70.9	79	4.3
100	3.35	3.1E+05	39.7	121	3.7
100	3.35	1.2E+05	18.1	179	2.9
100	3.35	4.4E+04	9.1	254	2.2

Figure B108: ln concentration vs time for decomposition of 100 mg TATP 7mL ethanol, 3mL 1.5M H₂SO₄ added, 45°C

Table B118: 100 mg TATP, 9mL ethanol, 1mL 18.2M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.35	1.1E+06	121.1	1	4.8
100	3.35	2.5E+05	35.5	9	3.6
100	3.35	7.2E+04	11.9	17	2.5
100	3.35	1.5E+04	3.9	33	1.4

Figure B109: ln concentration vs time for decomposition of 100 mg TATP 9mL ethanol, 1mL 18.2M H₂SO₄ added, 45°C

Table B119: 100 mg TATP, 9mL ethanol, 1mL 12.2M HCl added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	2.2E+06	201.6	3	5.3
100	3.36	1.6E+06	160.7	11	5.1
100	3.35	7.8E+05	91.8	19	4.5
100	3.35	4.7E+04	60.5	27	4.1
100	3.35	2.8E+05	38.5	35	3.7

Figure B110: ln concentration vs time for decomposition of 100 mg TATP 9mL ethanol, 1mL 12.2M HCl added, 45°C

Table B120: 100 mg TATP, 8mL ethanol, 2mL 12.2M HCl added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	1.6E+06	163.7	0.3	5.1
100	3.36	1.3E+06	144.2	0.6	5.0
100	3.36	1.8E+06	131.2	0.8	4.9
100	3.36	1.1E+06	127.5	1.0	4.8

Figure B111: ln concentration vs time for decomposition of 100 mg TATP 8mL ethanol, 2mL 12.2M HCl added, 45°C

Table B121: 100 mg TATP, 9mL ethanol, 1mL 18.2M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	1.6E+06	162.1	0.4	5.1
100	3.36	1.6E+06	163.3	0.6	5.1
100	3.36	1.2E+06	132.3	0.8	4.9
100	3.35	1.1E+06	125.2	1.0	4.8

Figure B112: ln concentration vs time for decomposition of 100 mg TATP 9mL ethanol, 1mL 18.2M H₂SO₄ added, 45°C

Table B122: 100 mg TATP, 8mL ethanol, 2mL 12.2M HCl added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.35	7.7E+05	89.5	3	4.5
100	3.35	5.4E+05	66.1	5	4.2
100	3.35	3.4E+05	43.9	7	3.8
100	3.35	2.0E+05	26.8	9	3.3
100	3.35	1.5E+05	21.6	11	3.1

Figure B113: ln concentration vs time for decomposition of 100 mg TATP 8mL ethanol, 2mL 12.2M HCl added, 45°C

Table B123: 100 mg TATP, 6mL ethanol, 4mL 6.1M HCl added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.35	1.1E+05	15.3	3	2.7
100	3.35	4.4E+04	6.6	5	1.9
100	3.35	3.4E+04	5.3	7	1.7
100	3.35	3.5E+04	5.4	9	1.7
100	3.35	3.8E+04	5.8	11	1.8

Figure B114: ln concentration vs time for decomposition of 100 mg TATP 6mL ethanol, 4mL 6.1M HCl added, 45°C

Table B124: 100 mg TATP, 9mL ethanol, 1mL 18.2M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.35	3.5E+05	44.9	3	3.8
100	3.35	2.2E+05	30.1	4	3.4
100	3.35	1.5E+05	21.1	6	3.0
100	3.35	1.0E+05	14.4	8	2.7
100	3.36	8.3E+04	12.1	10	2.5

Figure B115: ln concentration vs time for decomposition of 100 mg TATP 9mL ethanol, 1mL 18.2M H₂SO₄ added, 45°C

Table B125: 100 mg TATP, 7mL ethanol, 3mL 6.1M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	7.6E+05	88.3	3	4.5
100	3.36	6.5E+05	77.2	4	4.3
100	3.36	4.1E+05	52.4	6	4.0
100	3.35	2.8E+05	37.4	8	3.6
100	3.35	1.8E+05	25.3	10	3.2

Figure B116: ln concentration vs time for decomposition of 100 mg TATP 7mL ethanol, 3mL 6.1M H₂SO₄ added, 45°C

Table B126: 100 mg TATP, 6mL ethanol, 4mL 9.1M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	5.2E+03	1.2	2	0.2
100	3.36	4.8E+03	1.2	3	0.2
100	3.36	4.2E+03	1.1	4	0.1
100	3.36	4.4E+03	1.1	5	0.1
100	3.36	3.6E+03	1.0	6	0.0

Figure B117: ln concentration vs time for decomposition of 100 mg TATP 6mL ethanol, 4mL 9.1M H₂SO₄ added, 45°C

Table B127: 100 mg TATP, 9mL isopropanol, 1mL 0.36M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	2.3E+06	215.6	3	5.4
100	3.36	2.2E+06	205.6	15	5.3
100	3.36	2.2E+06	205.8	45	5.3
100	3.36	2.0E+06	195.8	92	5.3
100	3.36	2.1E+06	198.4	138	5.3
100	3.36	1.9E+06	187.8	230	5.2
100	3.36	1.9E+06	192.9	320	5.3
100	3.36	1.5E+06	154.0	1440	5.0

Figure B118: ln concentration vs time for decomposition of 100 mg TATP 9mL isopropanol, 1mL 0.36M H₂SO₄ added, 45°C

Table B128: 100 mg TATP, 9mL isopropanol, 1mL 0.75M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	2.2E+06	211.1	5	5.4
100	3.36	2.4E+06	220.0	17	5.4
100	3.36	2.2E+06	204.3	47	5.3
100	3.36	2.0E+06	191.5	94	5.3
100	3.36	2.0E+06	190.0	140	5.2
100	3.36	1.9E+06	188.9	233	5.2
100	3.36	1.9E+06	185.1	323	5.2
100	3.36	1.3E+06	135.0	1443	4.9

Figure B119: ln concentration vs time for decomposition of 100 mg TATP 9mL isopropanol, 1mL 0.75M H₂SO₄ added, 45°C

Table B129: 100 mg TATP, 9mL isopropanol, 1mL 1.1M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	2.3E+06	212.7	7	5.4
100	3.36	2.2E+06	211.1	19	5.4
100	3.36	2.2E+06	212.3	49	5.4
100	3.36	2.1E+06	210.0	96	5.3
100	3.36	2.0E+06	193.2	142	5.3
100	3.36	1.9E+06	182.0	236	5.2
100	3.36	1.8E+06	177.2	325	5.2
100	3.35	7.3E+05	82.8	1445	4.4

Figure B120: ln concentration vs time for decomposition of 100 mg TATP 9mL isopropanol, 1mL 1.1M H₂SO₄ added, 45°C

Table B130: 100 mg TATP, 9mL isopropanol, 1mL 1.8M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	2.0E+06	190.1	9	5.25
100	3.37	3.5E+06	296.3	21	5.7
100	3.36	1.9E+06	188.3	51	5.2
100	3.36	2.0E+06	191.1	98	5.3
100	3.36	1.9E+06	182.2	144	5.2
100	3.36	1.6E+06	159.2	239	5.1
100	3.36	1.4E+06	148.1	327	5.0
100	3.35	3.1E+05	38.6	1447	3.7

Figure B121: ln concentration vs time for decomposition of 100 mg TATP 9mL isopropanol, 1mL 1.8M H₂SO₄ added, 45°C

Table B131: 100 mg TATP, 9mL isopropanol, 1mL 2.9M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	2.3E+06	213.9	11	5.4
100	3.36	2.4E+06	223.9	23	5.4
100	3.36	1.9E+06	183.8	53	5.2
100	3.36	1.7E+06	169.6	100	5.1
100	3.36	1.7E+06	168.8	146	5.1
100	3.36	1.2E+06	129.5	242	4.9
100	3.36	9.9E+05	107.7	329	4.7
100	3.35	8.3E+04	11.5	1449	2.4

Figure B122: ln concentration vs time for decomposition of 100 mg TATP 9mL isopropanol, 1mL 2.9M H₂SO₄ added, 45°C

Table B132: 100 mg TATP, 9mL ethanol, 1mL 0.75M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	1.9E+06	187.0	2	5.2
100	3.36	1.9E+06	190.4	23	5.2
100	3.36	1.9E+06	189.1	52	5.2
100	3.36	1.7E+06	174.0	91	5.2
100	3.36	1.7E+06	170.9	125	5.1

Figure B123: ln concentration vs time for decomposition of 100 mg TATP 9mL ethanol, 1mL 0.75M H₂SO₄ added, 45°C

Table B133: 100 mg TATP, 9mL ethanol, 1mL 1.1M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	1.9E+06	189.2	4	5.2
100	3.36	1.8E+06	177.2	25	5.2
100	3.36	1.7E+06	175.3	54	5.2
100	3.36	1.6E+06	167.9	93	5.1
100	3.36	1.6E+06	164.7	127	5.1

Figure B124: ln concentration vs time for decomposition of 100 mg TATP 9mL ethanol, 1mL 1.1M H₂SO₄ added, 45°C

Table B134: 100 mg TATP, 9mL ethanol, 1mL 1.8M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	1.8E+06	181.8	6	5.2
100	3.36	1.8E+06	179.0	27	5.2
100	3.36	1.6E+06	162.8	56	5.1
100	3.36	1.4E+06	151.7	95	5.0
100	3.35	1.2E+06	135.7	129	4.9

Figure B125: ln concentration vs time for decomposition of 100 mg TATP 9mL ethanol, 1mL 1.8M H₂SO₄ added, 45°C

Table B135: 100 mg TATP, 9mL ethanol, 1mL 2.9M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	1.9E+06	189.3	8	5.2
100	3.36	1.6E+06	165.6	29	5.1
100	3.36	1.5E+06	154.0	58	5.0
100	3.35	1.0E+06	115.4	97	4.7
100	3.35	8.8E+05	103.7	131	4.6

Figure B126: ln concentration vs time for decomposition of 100 mg TATP 9mL ethanol, 1mL 2.9M H₂SO₄ added, 45°C

Table B136: 100 mg TATP, 7mL isopropanol, 3mL 0.25M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	2.3E+06	211.9	1	5.4
100	3.35	2.0E+06	190.6	95	5.3
100	3.35	1.8E+06	174.6	164	5.2
100	3.35	1.6E+06	163.2	271	5.1
100	3.36	1.5E+06	154.1	346	5.0
100	3.35	5.8E+05	68.4	1420	4.2

Figure B127: ln concentration vs time for decomposition of 100 mg TATP 7mL isopropanol, 3mL 0.25M H₂SO₄ added, 45°C

Table B137: 100 mg TATP, 7mL isopropanol, 3mL 0.37M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	2.2E+06	204.3	4	5.3
100	3.35	2.0E+06	187.5	98	5.2
100	3.36	1.6E+06	160.3	167	5.1
100	3.35	1.4E+06	143.8	274	5.0
100	3.35	1.2E+06	126.1	349	4.8
100	3.35	2.9E+05	37.2	1422	3.6

Figure B128: ln concentration vs time for decomposition of 100 mg TATP 7mL isopropanol, 3mL 0.37M H₂SO₄ added, 45°C

Table B138: 100 mg TATP, 7mL isopropanol, 3mL 0.6M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	2.3E+06	211.8	6	5.4
100	3.35	1.6E+06	164.1	100	5.1
100	3.35	1.4E+06	142.8	170	5.0
100	3.35	9.8E+05	108.4	277	4.7
100	3.35	7.7E+05	89.0	352	4.5
100	3.35	6.6E+04	8.4	1424	2.1

Figure B129: ln concentration vs time for decomposition of 100 mg TATP 7mL isopropanol, 3mL 0.6M H₂SO₄ added, 45°C

Table B139: 100 mg TATP, 7mL isopropanol, 3mL 0.97M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.35	2.2E+06	203.9	9	5.3
100	3.35	1.4E+06	140.6	102	4.9
100	3.35	1.5E+06	151.0	172	5.0
100	3.34	5.9E+05	71.0	279	4.3
100	3.35	4.2E+05	52.5	354	4.0
100	3.35	6.4E+03	0.0	1426	-3.4

Figure B130: ln concentration vs time for decomposition of 100 mg TATP 7mL isopropanol, 3mL 0.97M H₂SO₄ added, 45°C

Table B140: 100 mg TATP, 7mL ethanol, 3mL 0.25M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	2.0E+06	184.6	1	5.2
100	3.36	2.0E+06	183.4	31	5.2
100	3.36	1.9E+06	174.9	76	5.2
100	3.36	1.6E+06	156.0	146	5.0
100	3.36	1.2E+06	128.6	237	4.9

Figure B131: ln concentration vs time for decomposition of 100 mg TATP 7mL ethanol, 3mL 0.25M H₂SO₄ added, 45°C

Table B141: 100 mg TATP, 7mL ethanol, 3mL 0.73M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	2.2E+06	194.8	4	5.3
100	3.36	2.0E+06	187.4	34	5.2
100	3.36	1.8E+06	168.4	79	5.1
100	3.36	1.3E+06	129.5	149	4.9
100	3.35	9.6E+05	104.3	239	4.6

Figure B132: ln concentration vs time for decomposition of 100 mg TATP 7mL ethanol, 3mL 0.37M H₂SO₄ added, 45°C

Table B142: 100 mg TATP, 7mL ethanol, 3mL 0.6M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	2.0E+06	184.2	7	5.2
100	3.36	1.8E+06	169.7	37	5.1
100	3.36	1.2E+06	124.3	82	4.8
100	3.35	7.4E+06	84.2	153	4.4
100	3.35	4.2E+05	51.2	241	3.9

Figure B133: ln concentration vs time for decomposition of 100 mg TATP 7mL ethanol, 3mL 0.6M H₂SO₄ added, 45°C

Table B143: 100 mg TATP, 7mL ethanol, 3mL 0.97M H₂SO₄ added, 45°C

TATP (mg)	TATP RT (min)	peak area	Concentration of aliquot (µg/mL)	time (min)	ln(concentration)
100	3.36	2.0E+06	187.1	10	5.2
100	3.36	1.6E+06	157.9	40	5.1
100	3.36	1.5E+06	120.9	85	4.8
100	3.35	5.3E+05	63.3	156	4.1
100	3.35	2.2E+05	28.8	243	3.4

Figure B134: ln concentration vs time for decomposition of 100 mg TATP 7mL ethanol, 3mL 0.97M H₂SO₄ added, 45°C

Table B144: Summary of TATP decomposition experiments using ethanol, isopropanol and sulfuric acid

TATP (mg)	acid	ethanol (mL)	isopropanol (mL)	added water (mL)	Temp °C	k(sec ⁻¹)
100	3mL 1.5M H ₂ SO ₄	7			30	2.68E-05
100	500 µL 80wt% H ₂ SO ₄	10			35	2.33E-04
50	500 µL 80wt% H ₂ SO ₄	10			35	1.93E-04
100	500 µL 80wt% H ₂ SO ₄	10			45	9.28E-04
50	500 µL 80wt% H ₂ SO ₄	10			45	5.33E-04
100	500 µL 80wt% H ₂ SO ₄	9		1	45	3.28E-04
100	500 µL 80wt% H ₂ SO ₄	8		2	45	3.47E-04
100	160 µL 97wt% H ₂ SO ₄	10		0.365	45	1.48E-04
100	530 µL 97wt% H ₂ SO ₄	10		0.35	45	4.43E-04
100	1mL 1.5M H ₂ SO ₄	9			45	4.58E-05
100	2mL 0.75M H ₂ SO ₄	8			45	5.07E-05
100	3mL 0.36M H ₂ SO ₄	7			45	4.22E-05
100	1mL 1.5M H ₂ SO ₄	9			45	3.82E-05
100	2mL 1.5M H ₂ SO ₄	8			45	9.58E-05
100	3mL 1.5M H ₂ SO ₄	7			45	2.32E-04
100	3mL 0.75M H ₂ SO ₄	7			45	8.93E-05
100	1mL 8.7M H ₂ SO ₄	9			45	4.17E-04
100	1mL 6M H ₂ SO ₄	9			45	3.22E-04
100	2mL 4.4M H ₂ SO ₄	8			45	5.50E-04
100	2mL 1M H ₂ SO ₄	8			45	4.97E-05
100	1mL 8.7M H ₂ SO ₄	9			45	4.97E-04
100	2mL 4.4M H ₂ SO ₄	8			45	4.98E-04
100	3mL 2.9M H ₂ SO ₄	7			45	5.32E-04
100	3mL 1.5M H ₂ SO ₄	7			45	2.13E-04
100	1mL 18.2M H ₂ SO ₄	9			45	1.75E-03
100	1mL 18.2M H ₂ SO ₄	9			45	7.77E-03
100	1mL 18.2M H ₂ SO ₄	9			45	3.05E-03
100	3mL 6.1M H ₂ SO ₄	7			45	3.00E-03
100	1mL 0.36M H ₂ SO ₄		9		45	3.42E-06
100	1mL 0.75M H ₂ SO ₄		9		45	5.02E-06
100	1mL 1.1M H ₂ SO ₄		9		45	1.11E-05
100	1mL 1.8M H ₂ SO ₄		9		45	2.02E-05
100	1mL 2.9M H ₂ SO ₄		9		45	3.38E-05
100	1mL 0.75M H ₂ SO ₄	9			45	1.51E-05
100	1mL 1.1M H ₂ SO ₄	9			45	1.72E-05
100	1mL 1.8M H ₂ SO ₄	9			45	4.02E-05
100	1mL 2.9M H ₂ SO ₄	9			45	8.33E-05
100	3mL 0.25M H ₂ SO ₄		7		45	1.29E-05
100	3mL 0.37M H ₂ SO ₄		7		45	2.00E-05
100	3mL 0.6M H ₂ SO ₄		7		45	3.77E-05
100	3mL 0.97M H ₂ SO ₄		7		45	6.62E-05
100	3mL 0.25M H ₂ SO ₄	7			45	2.62E-05
100	3mL 0.73M H ₂ SO ₄	7			45	4.67E-05
100	3mL 0.6M H ₂ SO ₄	7			45	9.35E-05
100	3mL 0.97M H ₂ SO ₄	7			45	1.36E-04
100	3mL 1.5M H ₂ SO ₄	7			60	1.19E-03

Table B145: Summary of TATP decomposition experiments using ethanol, sulfuric acid, zinc and zinc sulfate

TATP (mg)	acid	ethanol (mL)	isopropanol (mL)	added water (mL)	Temp °C	k(sec ⁻¹)
100	500 µL 80wt% H ₂ SO ₄ , 1mL 10.4mM ZnSO ₄	9		1	35	9.20E-05
100	500 µL 80wt% H ₂ SO ₄ , 1mL 10.4mM ZnSO ₄	9		1	40	1.44E-04
100	500 µL 80wt% H ₂ SO ₄ , 1mL 10.4mM ZnSO ₄	9		1	45	3.08E-04
100	65mg Zn powder 1 mL 10.4mM ZnSO ₄	9		1	45	9.95E-06
100	653mg Zn powder 1 mL 10.4mM ZnSO ₄	9		1	45	no rxn
100	653mg Zn powder,55 µL 97wt% H ₂ SO ₄	9		1	45	3.72E-05

Table B146: Summary of TATP decomposition experiments using ethanol and hydrochloric acid

TATP (mg)	acid	ethanol (mL)	isopropanol (mL)	added water (mL)	Temp °C	k(sec ⁻¹)
100	500 µL 18wt% HCl	10			45	1.27E-04
100	500 µL 18wt% HCl	10			40	6.23E-05
100	500 µL 18wt% HCl	10			35	3.52E-05
100	600 µL 18wt% HCl	9.15		0.75	45	2.55E-04
100	1.2 mL 18wt% HCl	9.15		0.15	45	1.07E-03
100	500 µL 37wt% HCl	10			45	5.08E-04
100	1mL 0.5M HCl	9			45	9.18E-06
100	1mL 0.1M HCl	9			45	1.57E-06
100	1mL 0.43M HCl	9			45	9.80E-06
100	1mL 5M HCl	9			45	2.15E-04
100	1mL 4M HCl	9			45	1.48E-04
100	1mL 3M HCl	9			45	1.56E-04
100	2mL 5M HCl	8			45	5.28E-04
100	2mL 4M HCl	8			45	1.39E-04
100	2mL 3M HCl	8			45	5.27E-05
100	3mL 3M HCl	7			45	8.60E-04
100	3mL 2M HCl	7			45	5.08E-04
100	3mL 1M HCl	7			45	1.54E-04
100	3mL 1.5M HCl	7			60	1.03E-03
100	3mL 1.5M HCl	7			30	2.60E-05
100	3mL 1.5M HCl	7			45	2.35E-04
100	1mL 12.2M HCl	9			45	8.93E-04
100	2mL 12.2M HCl	8			45	6.05E-03
100	2mL 12.2M HCl	8			45	3.12E-03

Mechanism details

Figure B135: TATP decomposition mechanism details

Appendix C: Data for Manuscript 3

Table C1: Carbon analysis using elemental analyzer coupled with isotopic ratio mass spectrometer

	Mass C (ug)	%C m/m	Average %C	Stand Dev
UOP GB220 copper carbonate as received	38.1 44.4 42.1 118.8 115.8 118.1	4.10 4.16 4.35 3.90 3.90 3.89	4.05	
UOP GB220 copper carbonate exposed to C ₂ H ₂ /H ₂ O	220.1 186.3 171.2	18.81 19.20 18.87	18.96	
UOP GB 220 copper carbonate exposed to dry C ₂ H ₂	130.01 133.90 133.27 138.64 121.71	17.47 16.91 17.72 17.80 16.16	17.21	0.68
UOP GB238 copper oxide as received	none none none none none none	none none none none none none	none	
UOP GB238 copper oxide exposed to C ₂ H ₂ /H ₂ O	86.0 70.5 92.6	7.98 7.76 8.04	7.92	
UOP GB 238 copper oxide exposed to dry C ₂ H ₂	88.92 88.43 82.50 74.73 87.01	8.18 8.69 8.61 8.45 8.51	8.49	0.19
UOP GB562S copper sulfide (from carbonate) as received	none none none none none none	none none none none none none	none	
UOP GB562S copper sulfide (from carbonate) exposed to C ₂ H ₂ /H ₂ O	20.0 17.5 15.9 41.4 42.7 41.9	1.74 1.73 1.77 1.41 1.46 1.42	1.59	
UOP GB562S copper sulfide exposed to dry C ₂ H ₂	47.42 47.41 50.63 45.05 52.75	1.60 1.58 1.65 1.64 1.62	1.62	0.03
UOP GB 562S copper sulfide (not from carbonate) as received	none none none none none	none none none none none	none	
UOP GB562S (not from carbonate) exposed to dry C ₂ H ₂	63.4 77.8 69.0 67.8	2.12 2.31 2.25 2.20	2.22	0.08
GB562S (not from carbonate) exposed to C ₂ H ₂ /H ₂ O	34.6 39.0 40.0 34.7 37.2	1.14 1.30 1.29 1.17 1.20	1.22	0.07

Appendix D: Data for Manuscript 4

Hydrogen peroxide added to sodium borohydride solution (65mg in 20mL 3wt% NaOH)

In a 50mL 3-neck round bottom flask 20 mL of 3wt% NaOH was added to 65mg sodium borohydride. The flask was connected to the manometer followed by injection of 2 mL 30wt% hydrogen peroxide. At recorded intervals the volume of gas produced was recorded.

Table D1: 20mL 3wt% NaOH, 65mg NaBH₄, 2mL 30wt% HP, 18°C

time (sec)	<u>Total evolved</u> <u>gas (mL)</u>	<u>% total gas</u> <u>evolved</u>	<u>ln % total gas evolved</u>
180	1.4	96	4.57E+00
300	2.9	92	4.53E+00
420	4.2	89	4.49E+00
540	5.7	85	4.44E+00
660	7.1	81	4.40E+00
735	8	79	4.37E+00
840	8.9	76	4.34E+00
1140	11.6	69	4.24E+00
1440	13.4	65	4.17E+00
1740	15.2	60	4.09E+00
2475	18.6	51	3.93E+00
3300	21.7	43	3.75E+00
3900	22	42	3.73E+00
4800	23.5	38	3.63E+00
9720	24.5	35	3.56E+00

Figure: ln % total gas evolved vs time for reaction of 65mg NaBH₄ in 20mL 3wt% NaOH with 2mL 30wt% hydrogen peroxide

Table D2: 20mL 3wt% NaOH, 66mg NaBH₄, 2mL 30wt% HP, 17°C

time (sec)	Total evolved gas (mL)	% total gas evolved	ln % total gas evolved
180	1.4	96	4.57E+00
360	3.2	92	4.52E+00
540	4.6	88	4.48E+00
780	6.2	84	4.43E+00
1080	9.7	74	4.31E+00
1560	12.9	66	4.19E+00
2280	17.2	54	4.00E+00
2820	19.5	48	3.88E+00
3780	22.5	40	3.70E+00
4200	23.5	38	3.63E+00
4440	24.3	36	3.58E+00
4740	24.5	35	3.56E+00
4980	25.6	32	3.47E+00
5280	26.2	31	3.42E+00
5520	26.6	30	3.39E+00
6000	26.5	30	3.40E+00

Figure: ln % total gas evolved vs time for reaction of 66mg NaBH₄ in 20mL 3wt% NaOH with 2mL 30wt% hydrogen peroxide at 17°C

Table D3: 20mL 3wt% NaOH, 65mg NaBH₄, 2mL 30wt% HP, 17°C

time (sec)	<u>Total evolved</u> <u>gas (mL)</u>	<u>% total gas</u> <u>evolved</u>	<u>ln % total gas</u> <u>evolved</u>
144	0.5	99	4.59E+00
192	1	97	4.58E+00
281	2	95	4.55E+00
368	3	92	4.52E+00
505	4.6	88	4.48E+00
670	6	84	4.43E+00
817	7.5	80	4.38E+00
916	8.5	78	4.35E+00
1155	10.5	72	4.28E+00
1333	12	68	4.22E+00
1516	13.5	64	4.16E+00
1684	15	60	4.10E+00
1916	17	55	4.01E+00
2151	19	50	3.91E+00
2340	20.5	46	3.82E+00
2645	22.5	40	3.70E+00
3545	26	31	3.44E+00
3945	28	26	3.26E+00
4553	29.5	22	3.09E+00
4930	32	15	2.73E+00
5880	35	7	2.00E+00

Figure: ln % total gas evolved vs time for reaction of 65mg NaBH₄ in 20mL 3wt% NaOH with 2mL 30wt% hydrogen peroxide at 17°C

Table D4: 20mL 3wt% NaOH, 65mg NaBH₄, 2mL 30wt% HP, 20°C

time (sec)	Total evolved gas (mL)	% total gas evolved	ln % total gas evolved
156	1	97	4.58E+00
214	2	95	4.55E+00
271	3	92	4.52E+00
327	4	89	4.49E+00
378	5	87	4.46E+00
438	6	84	4.43E+00
496	7	81	4.40E+00
555	8	79	4.37E+00
625	9	76	4.33E+00
688	10	74	4.30E+00
758	11	71	4.26E+00
834	12	68	4.22E+00
908	13	66	4.18E+00
983	14	63	4.14E+00
1367	18.5	51	3.93E+00
1770	22.5	40	3.70E+00

Figure: ln % total gas evolved vs time for reaction of 65mg NaBH₄ in 20mL 3wt% NaOH with 2mL 30wt% hydrogen peroxide at 20°C

Table D5: 20mL 3wt% NaOH, 64mg NaBH₄, 2mL 30wt% HP, 31°C

time (sec)	<u>Total evolved</u> <u>gas (mL)</u>	<u>% total gas</u> <u>evolved</u>	<u>ln % total gas</u> <u>evolved</u>
60	0.4	99	4.59E+00
90	1.9	95	4.55E+00
120	3.2	92	4.52E+00
150	4.5	88	4.48E+00
180	5.9	84	4.44E+00
210	7.1	81	4.40E+00
240	8.4	78	4.35E+00
270	9.7	74	4.31E+00
300	10.8	71	4.27E+00
360	13.1	65	4.18E+00
420	15.1	60	4.10E+00
480	17	55	4.01E+00
510	17.9	53	3.96E+00
540	18.7	51	3.92E+00
570	19.5	48	3.88E+00
600	20.3	46	3.84E+00
630	21	44	3.79E+00
660	21.7	43	3.75E+00
720	23	39	3.67E+00
780	24.3	36	3.58E+00
840	25.5	33	3.48E+00
900	26.5	30	3.40E+00
960	27.6	27	3.30E+00
1020	28.6	24	3.19E+00
1095	29.7	21	3.06E+00
1140	30.4	20	2.97E+00
1200	31.2	17	2.86E+00
1260	32	15	2.73E+00
1440	33.8	11	2.36E+00
1740	36.9	2	8.68E-01

Figure: ln % total gas evolved vs time for reaction of 64mg NaBH₄ in 20mL 3wt% NaOH with 2mL 30wt% hydrogen peroxide at 31°C

Table D6: 20mL 3wt% NaOH, 63mg NaBH₄, 2mL 30wt% HP, 31°C

time (sec)	<u>Total evolved</u> <u>gas (mL)</u>	<u>% total gas</u> <u>evolved</u>	<u>ln % total gas</u> <u>evolved</u>
60	1.7	96	4.56E+00
90	3.2	92	4.52E+00
120	4.7	88	4.47E+00
150	6.6	83	4.41E+00
210	10	74	4.30E+00
240	11.7	69	4.23E+00
270	13	66	4.18E+00
300	14.5	62	4.12E+00
330	15.7	58	4.07E+00
360	16.8	56	4.02E+00
390	17.9	53	3.96E+00
420	18.8	50	3.92E+00
450	19.7	48	3.87E+00
480	20.5	46	3.82E+00
510	21.2	44	3.78E+00
570	22.6	40	3.69E+00
600	23.4	38	3.64E+00
660	24.5	35	3.56E+00
720	25.5	33	3.48E+00
780	26.5	30	3.40E+00
840	27.4	28	3.31E+00
930	28.5	25	3.20E+00
1200	31.9	16	2.75E+00
1530	35.4	6	1.85E+00

Figure: ln % total gas evolved vs time for reaction of 63mg NaBH₄ in 20mL 3wt% NaOH with 2mL 30wt% hydrogen peroxide at 31°C

Table D7: 20mL 3wt% NaOH, 66mg NaBH₄, 2mL 30wt% HP, 30°C

time (sec)	<u>Total evolved</u> <u>gas (mL)</u>	<u>% total gas</u> <u>evolved</u>	<u>ln % total gas</u> <u>evolved</u>
69	1	97	4.58E+00
105	2	95	4.55E+00
136	3	92	4.52E+00
166	4	89	4.49E+00
196	5	87	4.46E+00
225	6	84	4.43E+00
254	7	81	4.40E+00
285	8	79	4.37E+00
316	9	76	4.33E+00
348	10	74	4.30E+00
380	11	71	4.26E+00
414	12	68	4.22E+00
449	13	66	4.18E+00
483	14	63	4.14E+00
519	15	60	4.10E+00
555	16	58	4.05E+00
592	17	55	4.01E+00
624	18	52	3.96E+00
658	19	50	3.91E+00
694	20	47	3.85E+00
728	21	44	3.79E+00
765	22	42	3.73E+00
805	23	39	3.67E+00
844	24	37	3.60E+00
884	25	34	3.52E+00
925	26	31	3.44E+00
972	27	29	3.35E+00
1125	30	21	3.03E+00
1293	33	13	2.54E+00
1494	36	5	1.56E+00

Figure: ln % total gas evolved vs time for reaction of 66mg NaBH₄ in 20mL 3wt% NaOH with 2mL 30wt% hydrogen peroxide at 30°C

Sodium borohydride added to hydrogen peroxide (30mg in 20mL 3wt% HP)

In a 50mL 3-neck round bottom flask 30 mg of sodium borohydride was added to 20 mL of 3wt% HP. At recorded intervals the volume of gas produced was recorded.

Table D8: 20mL 3wt% HP, 30mg NaBH₄, 0°C

<u>time</u> <u>(sec)</u>	<u>Total evolved</u> <u>gas (mL)</u>	<u>% total gas</u> <u>evolved</u>	<u>ln % total gas</u> <u>evolved</u>
12	1.5	96	4.56E+00
42	2.5	93	4.54E+00
71	3.5	91	4.51E+00
103	4.5	88	4.48E+00
138	5.5	85	4.45E+00
179	6.5	83	4.42E+00
225	7.5	80	4.38E+00
281	8.5	78	4.35E+00
597	12	68	4.22E+00
765	13	66	4.18E+00
1200	13.7	64	4.16E+00
1627	15	60	4.10E+00

Figure: ln % total gas evolved vs time for reaction of 30mg NaBH₄ in 20mL 3wt% hydrogen peroxide at 0°C

Table D9: 20mL 6wt% HP, 30mg NaBH₄, 0°C

time (sec)	Total evolved gas (mL)	% total gas evolved	ln % total gas evolved
5	2	95	4.55E+00
24	5	87	4.46E+00
41	6.5	83	4.42E+00
62	8.5	78	4.35E+00
85	10.5	72	4.28E+00
106	12	68	4.22E+00
123	13	66	4.18E+00
144	14	63	4.14E+00
179	15.5	59	4.08E+00
221	17	55	4.01E+00
255	18	52	3.96E+00
297	19	50	3.91E+00

Figure: ln % total gas evolved vs time for reaction of 30mg NaBH₄ in 20mL 6wt% hydrogen peroxide at 0°C

Table D10: 20mL 12wt% HP, 29mg NaBH₄, 0°C

time (sec)	Total evolved gas (mL)	% total gas evolved	ln % total gas evolved
4	3	92	4.52E+00
18	9	76	4.33E+00
34	12	68	4.22E+00
44	14	63	4.14E+00
58	16.5	56	4.03E+00
76	19	50	3.91E+00
85	20	47	3.85E+00
115	24	37	3.60E+00
132	26	31	3.44E+00
161	27.5	27	3.31E+00

Figure: ln % total gas evolved vs time for reaction of 30mg NaBH₄ in 20mL 12wt% hydrogen peroxide at 0°C

Table D11: 20mL 3wt% NaOH, 65mg NaBH₄, 2mL 30wt% HP, 40°C

time (sec)	<u>Total evolved</u> <u>gas (mL)</u>	<u>% total gas</u> <u>evolved</u>	<u>ln % total gas</u> <u>evolved</u>
36	1	97	4.58E+00
56	2	95	4.55E+00
71	3	92	4.52E+00
85	4	89	4.49E+00
98	5	87	4.46E+00
110	6	84	4.43E+00
122	7	81	4.40E+00
134	8	79	4.37E+00
146	9	76	4.33E+00
170	11	71	4.26E+00
183	12	68	4.22E+00
194	13	66	4.18E+00
207	14	63	4.14E+00
220	15	60	4.10E+00
233	16	58	4.05E+00
253	17.5	54	3.98E+00
273	19	50	3.91E+00
289	20	47	3.85E+00
304	21	44	3.79E+00
327	22	42	3.73E+00
400	26	31	3.44E+00
460	29	23	3.15E+00
501	31	18	2.89E+00
555	33.5	11	2.43E+00

Figure: ln % total gas evolved vs time for reaction of 65mg NaBH₄ in 20mL 3wt% NaOH with 2mL 30wt% hydrogen peroxide at 40°C

Table D12: 20mL 3wt% NaOH, 64mg NaBH₄, 2mL 30wt% HP, 40°C

time (sec)	<u>Total evolved</u> <u>gas (mL)</u>	<u>% total gas</u> <u>evolved</u>	<u>ln % total gas</u> <u>evolved</u>
30	2.8	93	4.53E+00
60	6.5	83	4.42E+00
90	10.5	72	4.28E+00
120	14.5	62	4.12E+00
150	17.9	53	3.96E+00
180	21	44	3.79E+00
210	23.7	37	3.62E+00
240	26.2	31	3.42E+00
270	28.4	25	3.21E+00
300	30.4	20	2.97E+00
330	32.2	15	2.70E+00
360	33.7	11	2.38E+00
390	35.2	7	1.93E+00
420	36.7	3	1.07E+00

Figure: ln % total gas evolved vs time for reaction of 64mg NaBH₄ in 20mL 3wt% NaOH with 2mL 30wt% hydrogen peroxide at 40°C

Table D13: 20mL 3wt% HP, 33mg NaBH₄, 20°C

time (sec)	Total evolved gas (mL)	% total gas evolved	ln % total gas evolved
20	4	89	4.49E+00
30	5	87	4.46E+00
40	6	84	4.43E+00
60	8	79	4.37E+00
72	9	76	4.33E+00
85	10	74	4.30E+00
100	11	71	4.26E+00
118	12	68	4.22E+00
137	13	66	4.18E+00
163	14	63	4.14E+00
191	15	60	4.10E+00
224	16	58	4.05E+00
268	17	55	4.01E+00

Figure: ln % total gas evolved vs time for reaction of 33mg NaBH₄ in 20mL 3wt% hydrogen peroxide at 20°C

Table D14: 20mL 3wt% HP, 30mg NaBH₄, 20°C

<u>time</u> <u>(sec)</u>	<u>Total evolved</u> <u>gas (mL)</u>	<u>% total gas</u> <u>evolved</u>	<u>ln % total gas</u> <u>evolved</u>
13	3	92	4.52E+00
26	4	89	4.49E+00
43	5.5	85	4.45E+00
61	7	81	4.40E+00
75	8	79	4.37E+00
91	9	76	4.33E+00
110	10	74	4.30E+00
130	11	71	4.26E+00
157	12	68	4.22E+00
186	13	66	4.18E+00
220	14	63	4.14E+00

Figure: ln % total gas evolved vs time for reaction of 30mg NaBH₄ in 20mL 3wt% hydrogen peroxide at 20°C

Table D15: 20mL 3wt% HP, 32mg NaBH₄, 25°C

time (sec)	Total evolved gas (mL)	% total gas evolved	ln % total gas evolved
30	4.6	88	4.48E+00
60	8.2	78	4.36E+00
90	10.5	72	4.28E+00
120	12	68	4.22E+00
150	13.3	65	4.17E+00
180	14.2	62	4.13E+00
210	15	60	4.10E+00
240	15.5	59	4.08E+00
270	16	58	4.05E+00
300	16.3	57	4.04E+00
330	16.6	56	4.03E+00
390	17.1	55	4.00E+00
420	17.4	54	3.99E+00
450	17.6	53	3.98E+00
480	17.8	53	3.97E+00
570	18.1	52	3.95E+00
930	18.2	52	3.95E+00

Figure: ln % total gas evolved vs time for reaction of 32mg NaBH₄ in 20mL 3wt% hydrogen peroxide at 25°C

Table D16: 20mL 3wt% HP, 39mg NaBH₄, 25°C

time (sec)	Total evolved gas (mL)	% total gas evolved	ln % total gas evolved
15	3.6	90	4.51E+00
32	6	84	4.43E+00
56	9.1	76	4.33E+00
87	12	68	4.22E+00
118	14	63	4.14E+00
150	15.5	59	4.08E+00
188	17	55	4.01E+00
243	18.5	51	3.93E+00
292	19.5	48	3.88E+00
353	20.5	46	3.82E+00
399	21	44	3.79E+00
640	22.5	40	3.70E+00

Figure: ln % total gas evolved vs time for reaction of 39mg NaBH₄ in 20mL 3wt% hydrogen peroxide at 25°C

Table D17: 20mL 3wt% HP, 28mg NaBH₄, 25°C

time (sec)	Total evolved gas (mL)	% total gas evolved	ln % total gas evolved
16	3	92	4.52E+00
26	4	89	4.49E+00
41	5.5	85	4.45E+00
55	7	81	4.40E+00
75	8.5	78	4.35E+00
98	10	74	4.30E+00
130	11.5	70	4.24E+00
170	13	66	4.18E+00
207	14	63	4.14E+00
254	15	60	4.10E+00

Figure: ln % total gas evolved vs time for reaction of 28mg NaBH₄ in 20mL 3wt% hydrogen peroxide at 25°C

Table D18: 20mL 3wt% HP, 25mg NaBH₄, 25°C

time (sec)	Total evolved gas (mL)	% total gas evolved	ln % total gas evolved
20	4	89	4.49E+00
29	5	87	4.46E+00
38	6	84	4.43E+00
47	7	81	4.40E+00
59	8	79	4.37E+00
73	9	76	4.33E+00
91	10	74	4.30E+00
112	11	71	4.26E+00
139	12	68	4.22E+00
172	13	66	4.18E+00
218	14	63	4.14E+00
285	15	60	4.10E+00

Figure: ln % total gas evolved vs time for reaction of 25mg NaBH₄ in 20mL 3wt% hydrogen peroxide at 25°C

Table D19: 20mL 3wt% HP, 29mg NaBH₄, 25°C

time (sec)	Total evolved gas (mL)	% total gas evolved	ln % total gas evolved
12	3	92	4.52E+00
24	4	89	4.49E+00
34	5	87	4.46E+00
45	6	84	4.43E+00
56	7	81	4.40E+00
70	8	79	4.37E+00
86	9	76	4.33E+00
107	10	74	4.30E+00
132	11	71	4.26E+00
167	12	68	4.22E+00
210	13	66	4.18E+00

Figure: ln % total gas evolved vs time for reaction of 29mg NaBH₄ in 20mL 3wt% hydrogen peroxide at 25°C

Table D20: 20mL 6wt% HP, 30mg NaBH₄, 25°C

time (sec)	Total evolved gas (mL)	% total gas evolved	ln % total gas evolved
12	7	81	4.40E+00
22	10	74	4.30E+00
35	13	66	4.18E+00
49	15.5	59	4.08E+00
72	18	52	3.96E+00
88	19	50	3.91E+00
109	20	47	3.85E+00
144	21	44	3.79E+00
210	22	42	3.73E+00

Figure: ln % total gas evolved vs time for reaction of 30mg NaBH₄ in 20mL 6wt% hydrogen peroxide at 25°C

Table D21: 20mL 3wt% HP, 29mg NaBH₄, 25°C

<u>time</u> <u>(sec)</u>	<u>Total evolved</u> <u>gas (mL)</u>	<u>% total gas</u> <u>evolved</u>	<u>ln % total gas</u> <u>evolved</u>
10	4	89	4.49E+00
24	5.5	85	4.45E+00
38	7	81	4.40E+00
51	9	76	4.33E+00
66	10	74	4.30E+00
81	11	71	4.26E+00
95	12	68	4.22E+00
111	13	66	4.18E+00
128	14	63	4.14E+00
142	14.5	62	4.12E+00
159	15	60	4.10E+00

Figure: ln % total gas evolved vs time for reaction of 29mg NaBH₄ in 20mL 3wt% hydrogen peroxide at 25°C

Table D22: 20mL 3wt% HP, 29mg NaBH₄, 25°C

<u>time</u> <u>(sec)</u>	<u>Total evolved</u> <u>gas (mL)</u>	<u>% total gas</u> <u>evolved</u>	<u>ln % total gas</u> <u>evolved</u>
11	3	92	4.52E+00
22	4	89	4.49E+00
31	5	87	4.46E+00
43	5.5	85	4.45E+00
54	7.5	80	4.38E+00
74	9	76	4.33E+00
89	10	74	4.30E+00
104	11	71	4.26E+00
129	13	66	4.18E+00
152	14	63	4.14E+00
174	15	60	4.10E+00

Figure: ln % total gas evolved vs time for reaction of 29mg NaBH₄ in 20mL 3wt% hydrogen peroxide at 25°C

Table D23: 20mL 3wt% HP, 31mg NaBH₄, 25°C

time (sec)	Total evolved gas (mL)	% total gas evolved	ln % total gas evolved
11	3	92	4.52E+00
24	4	89	4.49E+00
39	5.5	85	4.45E+00
54	7	81	4.40E+00
73	8.5	78	4.35E+00
87	9.5	75	4.32E+00
103	10.5	72	4.28E+00
122	11.5	70	4.24E+00
145	12.5	67	4.20E+00
173	13.5	64	4.16E+00

Figure: ln % total gas evolved vs time for reaction of 31mg NaBH₄ in 20mL 3wt% hydrogen peroxide at 25°C

Table D24: 20mL 3wt% HP, 31mg NaBH₄, 30°C

time (sec)	Total evolved gas (mL)	% total gas evolved	ln % total gas evolved
20	4.5	88	4.48E+00
41	8	79	4.37E+00
68	11	71	4.26E+00
94	13	66	4.18E+00
122	14.5	62	4.12E+00
146	15.5	59	4.08E+00
161	16	58	4.05E+00
177	16.5	56	4.03E+00
194	17	55	4.01E+00
218	17.5	54	3.98E+00

Figure: ln % total gas evolved vs time for reaction of 31mg NaBH₄ in 20mL 3wt% hydrogen peroxide at 30°C

Table D25: 20mL 3wt% HP, 31mg NaBH₄, 30°C

time (sec)	Total evolved gas (mL)	% total gas evolved	ln % total gas evolved
5	3	92	4.52E+00
17	5	87	4.46E+00
27	7	81	4.40E+00
39	9	76	4.33E+00
47	10	74	4.30E+00
55	11	71	4.26E+00
65	12	68	4.22E+00
84	13.5	64	4.16E+00
99	14.5	62	4.12E+00
119	15.5	59	4.08E+00
146	16.5	56	4.03E+00
179	17.5	54	3.98E+00

Figure: ln % total gas evolved vs time for reaction of 31mg NaBH₄ in 20mL 3wt% hydrogen peroxide at 30°C

Table D26: 20mL 3wt% HP, 29mg NaBH₄, 30°C

time (sec)	Total evolved gas (mL)	% total gas evolved	ln % total gas evolved
14	4	89	4.49E+00
26	6	84	4.43E+00
37	8	79	4.37E+00
49	9.5	75	4.32E+00
67	11.5	70	4.24E+00
84	13	66	4.18E+00
99	14	63	4.14E+00
120	15	60	4.10E+00
142	16	58	4.05E+00
178	17	55	4.01E+00

Figure: ln % total gas evolved vs time for reaction of 29mg NaBH₄ in 20mL 3wt% hydrogen peroxide at 30°C

Table D27: 20mL 3wt% HP, 29mg NaBH₄, 35°C

time (sec)	Total evolved gas (mL)	% total gas evolved	ln % total gas evolved
19	4.5	88	4.48E+00
31	5.5	85	4.45E+00
53	9	76	4.33E+00
83	11	71	4.26E+00
123	12.5	67	4.20E+00
168	13.5	64	4.16E+00
210	14	63	4.14E+00

Figure: ln % total gas evolved vs time for reaction of 29mg NaBH₄ in 20mL 3wt% hydrogen peroxide at 35°C

Table D28: 20mL 3wt% HP, 30mg NaBH₄, 35°C

time (sec)	Total evolved gas (mL)	% total gas evolved	ln % total gas evolved
15	4	89	4.49E+00
26	6	84	4.43E+00
37	8	79	4.37E+00
48	9.5	75	4.32E+00
62	11	71	4.26E+00
73	12	68	4.22E+00
89	13	66	4.18E+00
130	15	60	4.10E+00
164	16	58	4.05E+00
210	17	55	4.01E+00

Figure: ln % total gas evolved vs time for reaction of 30mg NaBH₄ in 20mL 3wt% hydrogen peroxide at 35°C

Table D29: 20mL 3wt% HP, 30mg NaBH₄, 35°C

time (sec)	Total evolved gas (mL)	% total gas evolved	ln % total gas evolved
40	2	95	4.55E+00
45	3	92	4.52E+00
51	4	89	4.49E+00
81	9	76	4.33E+00
102	11	71	4.26E+00

Figure: ln % total gas evolved vs time for reaction of 30mg NaBH₄ in 20mL 3wt% hydrogen peroxide at 35°C

Table D30: 20mL 3wt% HP, 29mg NaBH₄, 35°C

time (sec)	Total evolved gas (mL)	% total gas evolved	ln % total gas evolved
9	4	89	4.49E+00
18	6	84	4.43E+00
30	8	79	4.37E+00
45	11	71	4.26E+00
65	12.5	67	4.20E+00
81	14	63	4.14E+00
99	15	60	4.10E+00
122	16	58	4.05E+00

Figure: ln % total gas evolved vs time for reaction of 29mg NaBH₄ in 20mL 3wt% hydrogen peroxide at 35°C

Sodium borohydride hydrolysis in water

Water was measured into a 50mL 3-neck round bottom flask. 70mg sodium borohydride was added. At recorded intervals the total gas evolved was measured.

Table D31: 20mL water, 70mg NaBH₄, 25°C

time (sec)	<u>Total evolved</u> <u>gas (mL)</u>	<u>% total gas</u> <u>evolved</u>	<u>ln % total gas</u> <u>evolved</u>
60	0.4	99	4.59E+00
120	1	97	4.58E+00
180	1.7	96	4.56E+00
240	2.4	94	4.54E+00
300	3	92	4.52E+00
360	3.7	90	4.50E+00
420	4.5	88	4.48E+00
480	5.2	86	4.46E+00
540	6	84	4.43E+00
600	6.5	83	4.42E+00
900	8.8	77	4.34E+00
1230	11	71	4.26E+00
1500	13.2	65	4.18E+00
1800	15.2	60	4.09E+00
2250	17.7	53	3.97E+00
2400	18.8	50	3.92E+00
2700	20.5	46	3.82E+00
3300	23.6	38	3.63E+00
4410	28.5	25	3.20E+00
5520	32.5	14	2.64E+00
6810	36.9	2	8.68E-01

Figure: ln % total gas evolved vs time for reaction of 70mg NaBH₄ in 20mL water at 25°C

Hydrogen peroxide decomposition

Hydrogen peroxide was added to aqueous sodium hydroxide solution. At recorded intervals the total gas evolved was noted.

Table D32: 20mL 3wt% NaOH, 2mL 30wt% HP, 20°C

time (sec)	Total evolved gas (mL)	fraction remaining	ln fraction remaining	1/fraction remaining
268	1.5	0.99	-0.008	1.0
422	3	0.98	-0.016	1.0
559	4.5	0.98	-0.024	1.0
699	6	0.97	-0.032	1.0
847	7.5	0.96	-0.041	1.0
1088	10	0.95	-0.054	1.1
1338	12.5	0.93	-0.069	1.1
1540	14.5	0.92	-0.080	1.1
1766	16.5	0.91	-0.092	1.1
2051	19	0.90	-0.106	1.1
2468	22.5	0.88	-0.13	1.1
2799	25	0.87	-0.14	1.2
3272	28.5	0.85	-0.16	1.2
3645	31	0.84	-0.18	1.2
4085	34	0.82	-0.20	1.2
4401	36	0.81	-0.21	1.2
4920	39	0.79	-0.23	1.3
5727	43.5	0.77	-0.26	1.3
7080	48.5	0.74	-0.30	1.3
8192	53	0.72	-0.33	1.4
9876	59	0.69	-0.38	1.5
12300	66	0.65	-0.43	1.5
13860	69.5	0.63	-0.46	1.6
15540	72.5	0.62	-0.49	1.6
20100	79.5	0.58	-0.55	1.7
24780	85.2	0.55	-0.60	1.8
27960	88.7	0.53	-0.64	1.9
64800	115.7	0.39	-0.95	2.6
82810	125.9	0.33	-1.10	3.0
259200	134	0.29	-1.24	3.5

Figure: ln fraction remaining for decomposition of 2mL 30wt% HP in 20mL 3wt% NaOH at 20°C

Figure: 1/fraction remaining for decomposition of 2mL 30wt% HP in 20mL 3wt% NaOH at 20°C

Table D33: 20mL 3wt% NaOH, 2mL 30wt% HP, 40°C

time (sec)	Total evolved gas (mL)	fraction remaining	ln fraction remaining	1/fraction remaining
43	1	0.99	-0.006	1.0
71	2	0.99	-0.012	1.0
93	3	0.98	-0.018	1.0
114	4	0.98	-0.024	1.0
132	5	0.97	-0.030	1.0
150	6	0.96	-0.036	1.0
168	7	0.96	-0.042	1.0
188	8	0.95	-0.048	1.0
206	9	0.95	-0.054	1.1
223	10	0.94	-0.060	1.1
241	11	0.94	-0.067	1.1
260	12	0.93	-0.073	1.1
278	13	0.92	-0.079	1.1
299	14	0.92	-0.086	1.1
318	15	0.91	-0.092	1.1
338	16	0.91	-0.098	1.1
379	18	0.89	-0.111	1.1
399	19	0.89	-0.118	1.1
417	20	0.88	-0.125	1.1
437	21	0.88	-0.131	1.1
457	22	0.87	-0.138	1.1
478	23	0.87	-0.145	1.2
498	24	0.86	-0.151	1.2
543	26	0.85	-0.165	1.2
566	27	0.84	-0.172	1.2
590	28	0.84	-0.179	1.2
615	29	0.83	-0.186	1.2
666	31	0.82	-0.200	1.2
695	32	0.81	-0.207	1.2
725	33	0.81	-0.215	1.2
753	34	0.80	-0.222	1.2
783	35	0.80	-0.229	1.3
813	36	0.79	-0.237	1.3
842	37	0.78	-0.244	1.3
873	38	0.78	-0.252	1.3
905	39	0.77	-0.259	1.3
935	40	0.77	-0.267	1.3
968	41	0.76	-0.274	1.3
1030	43	0.75	-0.290	1.3
1188	47	0.72	-0.322	1.4
1220	48	0.72	-0.330	1.4
1262	49	0.71	-0.338	1.4
1395	52	0.70	-0.363	1.4
1664	57	0.67	-0.406	1.5
2037	63	0.63	-0.460	1.6
2278	67	0.61	-0.498	1.6
2580	71	0.58	-0.537	1.7
2970	75	0.56	-0.578	1.8
3482	80	0.53	-0.632	1.9
3879	84	0.51	-0.677	2.0
4380	88	0.48	-0.724	2.1
4665	89.5	0.48	-0.742	2.1
5395	95	0.44	-0.812	2.3
8970	113	0.34	-1.084	3.0
13980	130.4	0.24	-1.442	4.2
16140	134.9	0.21	-1.560	4.8
20220	146.2	0.14	-1.938	6.9
21780	149.4	0.13	-2.077	8.0
26160	158.3	0.07	-2.615	13.7
86400	169.3	0.01	-4.735	113.9

Figure: ln fraction remaining for decomposition of 2mL 30wt% HP in 20mL 3wt% NaOH at 40°C

Figure: 1/fraction remaining for decomposition of 2mL 30wt% HP in 20mL 3wt% NaOH at 40°C

Table D34: 20mL 2.1M NaOH, 2mL 30wt% HP, 40°C

time (sec)	Total evolved gas (mL)	fraction remaining	ln fraction remaining	1/fraction remaining
192	0.5	1.00	-0.003	1.0
389	1.5	0.99	-0.009	1.0
621	3	0.98	-0.018	1.0
860	4.5	0.97	-0.028	1.0
3316	19.5	0.88	-0.125	1.1
4152	24.5	0.85	-0.160	1.2
5569	32.5	0.80	-0.219	1.2
6701	38.5	0.77	-0.265	1.3
7836	44.5	0.73	-0.313	1.4
7960	45.1	0.73	-0.318	1.4
10980	59.1	0.64	-0.442	1.6
12456	65.6	0.60	-0.505	1.7
14265	73.1	0.56	-0.583	1.8
15000	76.1	0.54	-0.616	1.9
15827	79.1	0.52	-0.650	1.9
16975	83.1	0.50	-0.697	2.0
19500	91.6	0.45	-0.806	2.2
21000	96.6	0.42	-0.876	2.4
22560	102.1	0.38	-0.960	2.6
26000	111.1	0.33	-1.113	3.0
81960	132.1	0.20	-1.600	5.0
96720	136.9	0.17	-1.756	5.8
100500	139.2	0.16	-1.839	6.3
105720	142.9	0.14	-1.991	7.3
109920	146.6	0.11	-2.170	8.8

Figure: ln fraction remaining for decomposition of 2mL 30wt% HP in 20mL 2.1M NaOH at 40°C

Table D35: 20mL 2.1M NaOH, 2mL 67wt% HP, 40°C

time (sec)	Total evolved gas (mL)	fraction remaining	ln fraction remaining	1/fraction remaining	time (sec)	Total evolved gas (mL)	fraction remaining	ln fraction remaining	1/fraction remaining
22	1	1.00	-0.002	1.0	1226	130	0.77	-0.267	1.3
41	2.5	1.00	-0.005	1.0	1277	134	0.76	-0.277	1.3
58	4	0.99	-0.007	1.0	1303	136	0.75	-0.282	1.3
72	5.5	0.99	-0.010	1.0	1330	138	0.75	-0.286	1.3
88	7.5	0.99	-0.014	1.0	1369	141	0.75	-0.294	1.3
114	11	0.98	-0.020	1.0	1423	145	0.74	-0.303	1.4
127	13	0.98	-0.024	1.0	1490	150	0.73	-0.316	1.4
141	15	0.97	-0.027	1.0	1525	152	0.73	-0.321	1.4
154	17	0.97	-0.031	1.0	1554	154	0.72	-0.326	1.4
173	20	0.96	-0.037	1.0	1582	156	0.72	-0.331	1.4
200	24	0.96	-0.044	1.0	1610	158	0.71	-0.336	1.4
214	26	0.95	-0.048	1.0	1640	160	0.71	-0.341	1.4
227	28	0.95	-0.052	1.1	1714	165	0.70	-0.354	1.4
262	33	0.94	-0.061	1.1	1777	169	0.69	-0.364	1.4
283	36	0.94	-0.067	1.1	1840	173	0.69	-0.374	1.5
316	40.5	0.93	-0.076	1.1	1890	176	0.68	-0.382	1.5
334	43	0.92	-0.081	1.1	1978	181	0.67	-0.396	1.5
357	46	0.92	-0.087	1.1	2072	186	0.66	-0.409	1.5
390	50	0.91	-0.095	1.1	2165	191	0.66	-0.423	1.5
419	53	0.90	-0.101	1.1	2243	195	0.65	-0.434	1.5
443	56	0.90	-0.107	1.1	2303	198	0.64	-0.442	1.6
458	58	0.90	-0.111	1.1	2324	199	0.64	-0.445	1.6
474	60	0.89	-0.115	1.1	2364	201	0.64	-0.451	1.6
500	63	0.89	-0.121	1.1	2465	206	0.63	-0.465	1.6
517	65	0.88	-0.125	1.1	2648	214.5	0.61	-0.490	1.6
534	67	0.88	-0.129	1.1	2940	226.5	0.59	-0.526	1.7
551	69	0.88	-0.133	1.1	3115	233.5	0.58	-0.547	1.7
573	71.5	0.87	-0.138	1.1	3284	240	0.57	-0.568	1.8
597	74	0.87	-0.143	1.2	3366	243	0.56	-0.577	1.8
615	76	0.86	-0.148	1.2	3430	245.5	0.56	-0.585	1.8
647	79.5	0.86	-0.155	1.2	3472	247	0.55	-0.590	1.8
672	82	0.85	-0.160	1.2	3900	261	0.53	-0.637	1.9
710	86	0.84	-0.169	1.2	4200	270	0.51	-0.668	2.0
752	90	0.84	-0.177	1.2	4478	278	0.50	-0.697	2.0
782	93	0.83	-0.184	1.2	4930	290	0.48	-0.741	2.1
820	96.5	0.83	-0.191	1.2	5049	293	0.47	-0.753	2.1
855	100	0.82	-0.199	1.2	5291	299	0.46	-0.776	2.2
884	102	0.82	-0.203	1.2	5574	305.5	0.45	-0.802	2.2
907	104	0.81	-0.208	1.2	5777	310	0.44	-0.820	2.3
930	106	0.81	-0.212	1.2	6050	316	0.43	-0.845	2.3
949	107.5	0.81	-0.216	1.2	6443	324	0.42	-0.879	2.4
978	110	0.80	-0.221	1.2	6553	326	0.41	-0.888	2.4
1003	112	0.80	-0.226	1.3	6600	327	0.41	-0.892	2.4
1039	115	0.79	-0.233	1.3	7690	346	0.38	-0.980	2.7
1075	118	0.79	-0.240	1.3	8760	375.5	0.32	-1.133	3.1
1100	120	0.78	-0.244	1.3	12765	408	0.26	-1.334	3.8
1125	122	0.78	-0.249	1.3	17790	449.5	0.19	-1.668	5.3
1150	124	0.78	-0.253	1.3	23160	482.5	0.13	-2.047	7.7
1181	126.5	0.77	-0.259	1.3	48600	523.5	0.06	-2.899	18.2
1201	128	0.77	-0.263	1.3

Figure: ln fraction remaining for decomposition of 2mL 67wt% HP in 20mL 2.1M NaOH at 40°C

Figure: 1/fraction remaining for decomposition of 2mL 67wt% HP in 20mL 2.1M NaOH at 40°C

Table D36: 10mL 5.6M NaOH, 1mL 67wt% HP, 40°C

time (sec)	Total evolved gas (mL)	fraction remaining	ln fraction remaining	1/fraction remaining
511	1.5	0.99	-0.007	1.0
1262	4.5	0.98	-0.021	1.0
2745	11.5	0.95	-0.055	1.1
4820	21	0.90	-0.103	1.1
5604	26	0.88	-0.129	1.1
6278	31.5	0.85	-0.159	1.2
7045	38.5	0.82	-0.198	1.2
7843	45.5	0.79	-0.238	1.3
10430	66.5	0.69	-0.371	1.4
13410	86.5	0.60	-0.516	1.7
14291	92.5	0.57	-0.564	1.8
16366	105.5	0.51	-0.677	2.0
17370	111	0.48	-0.729	2.1
17550	112	0.48	-0.738	2.1
21660	131	0.39	-0.943	2.6
27120	151.5	0.29	-1.225	3.4
30240	161.5	0.25	-1.398	4.0
31860	166.5	0.22	-1.497	4.5

Figure: ln fraction remaining for decomposition of 1mL 67wt% HP in 10mL 5.6M NaOH at 40°C

Fig. D1: Arrhenius plot for sodium borohydride hydrolysis by hydrogen peroxide in NaOH

Fig. D2: Arrhenius plot for sodium borohydride hydrolysis by hydrogen peroxide without NaOH