

Synthetic and
spectroscopic studies
of triacetone
triperoxide biology
essay



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TATP belongs to the organic peroxide class of molecules with a structure containing three oxygen-oxygen bonds as part of a C-O-O-C linkage (Figure 1). The nine-membered, trimer is classified more specifically as a ketone peroxide and is formed through reaction of acetone and hydrogen peroxide in the presence of an acid catalyst.

The low bond energy of the oxygen-oxygen bond renders organic peroxides thermochemically unstable with trimeric ketone peroxides such as TATP the most dangerous. The high oxygen content of TATP makes it extremely sensitive to heat and shock and explosive decomposition is easily initiated.

Unlike most common nitro-group containing explosives, the explosion of TATP is entropic and not a thermochemically highly favoured event. The decomposition pathway of the trimer molecule was studied by Dubnikova et al. confirming the reaction as the formation of several small gas phase molecules from one trimer molecule without the generation of heat. The rate determining step of the decomposition reaction was identified as the cleavage of a peroxide bond. The breaking of the peroxide bond then triggers a chain reaction and the cleavage of other C-O and O-O bonds in the molecule. The two main products of TATP decomposition are acetone and ozone accompanied by the formation of dioxygen, methyl acetate, ethane and carbon dioxide.

2. 2 Physical Properties of TATP

TATP is a white solid with a vapour pressure of approximately 7 Pascal at room temperature. This high vapour pressure enables the solid to sublime readily, losing approximately 66% of its weight within two weeks at room

temperature. The melting point of TATP is reported in the range of 93-98°C. The solid is insoluble in water, but can be dissolved readily in numerous organic solvents. When dissolved in an organic solvent TATP remains relatively stable and it is only when air dried that the full explosive capabilities are enabled.

As a result of its high instability and sensitivity to mechanical shock as well as difficulties in storage and handling due to the high vapour pressure and sublimation of the molecule, TATP is not used in any industrial or military applications. Therefore despite being discovered as far back as 1895, TATP has been the subject of very few scientific publications until recent years when terrorist groups started using it.

3. TATP Synthesis

3. 1 History

TATP was first prepared in 1895 by Richard Wolffenstein, when his reaction of acetone and hydrogen peroxide (50%) yielded an unexpected white powder precipitate after being left at room temperature for four weeks. The precipitate was collected through filtration with further recrystallization from ether. The explosive nature of the product was shown through heating and was wrongly ascribed by Wolffenstein to the ether used in the workup. The trimeric structure proposed by Wolffenstein was later confirmed by Groth through crystal structure analysis as part of his study into the stereochemical features of cyclic organic peroxides. The nine-membered ring structure was described as a 'twisted boat chair' with D₃ symmetry (Figure 2).

Figure TATP stable conformer: Twisted boat chair (D3) structure.

In a continuation of Wolffenstein's work, Adolf Baeyer and Victor Villiger later developed a more rapid method of synthesis, with the addition of hydrochloric acid to a mixture of equal amounts of acetone and hydrogen peroxide. This was the first example of TATP synthesis utilising an acid catalyst and enabled the production of TATP from a simple method in a relatively short period of time and hence is the basis for all methods of synthesis devised since. As well as TATP the reaction was shown to yield the cyclic dimer diacetone diperoxide (DADP) (Figure 3).

Figure Molecular structure of diacetone diperoxide (DADP).

DADP is now a well-known side product of the trimer synthesis and is most commonly observed through use of a sulphuric acid catalyst. 4Bellamy Like its trimeric form, DADP is a highly volatile white solid which explodes violently on heating, impact or friction. The dimer has a higher melting point than TATP in the range of 131.5-133°C and lower solubility in organic solvents.

The acid catalysed synthesis of TATP was further developed by Nicholas Milas in 1959 who produced the peroxide trimer through the addition of acetone to a mixture of hydrogen peroxide (50%) and sulphuric acid with cooling.

Numerous examples of TATP syntheses now exist in scientific literature with various adaptations of the acid catalysed reaction of acetone and hydrogen

peroxide. Lower hydrogen peroxide concentrations are now used along with catalytic amounts of acid reduced to a few drops.

As well as the previously mentioned DADP dimer, the acetone tetramer, tertaacetone tetraperoxide (TrATrP) has been observed as a potential TATP synthesis by-product (Figure 4). Jiang and co-workers produced the tetramer in an 8.9% yield from reaction of hydrogen peroxide (30%), acetone and a hydrochloric acid catalyst at room temperature.

Figure Molecular structure of tetrameric acetone peroxide (TrATrP).

3.2 Mechanism of TATP Formation

Through the isolation of the organic peroxide reaction intermediates and their analysis by paper chromatography, Milas proposed the formation of the TATP trimer involved the conversion of 2, 2-bis(hydroperoxy)propane via the open chain oligoperoxide intermediate, 2, 2'-bis(hydroperoxy)-2, 2'-diisopropyl peroxide (Figure) (n= 1 and n= 2 oligomer in tandem esi paper).

A more complete reaction scheme later suggested by Hiatt, proposed the formation of TATP, like Milas, with the formation of a number of peroxide oligomer reaction intermediates and by products. The mechanism of formation of the peroxide dimer by product DADP was also shown. The reaction begins with the nucleophilic addition of hydrogen peroxide to the carbonyl group of the acetone molecule, forming the unstable 2-hydroxy-2-hydroperoxypropane.

The reaction proceeds through further nucleophilic addition of the 2-hydroxy-2-hydroperoxypropane to another acetone molecule leading to the formation of the double hemiacetal.

Reaction of hydrogen peroxide with the double hemiacetal forms 1-hydroxy-1'-hydroperoxydiisopropyl peroxide and 2, 2'-bis(hydroperoxy)-2, 2'-diisopropyl peroxide.

The conversion of the hydroxyl (-OH) group to the peroxide (-OOH) group occurs readily in the presence of an acid catalyst via the resonance stabilised oxo-carbonium ion.

The further addition of another 2-hydroxy-2-hydroperoxypropane molecule increases the oligoperoxide to the required length for the cyclisation to the TATP trimer. The acid initiated cyclisation is a condensation reaction with the loss of a water molecule from the open chain oligomer.

4. Clandestine TATP Manufacture and its Use in Terrorism

After its synthetic and structural analyses, TATP was subject of few publications until it found popularity amongst clandestine explosive manufacturers. In 1986, a case report by Hiram Evans and co-workers sought the identity of an unknown explosive accidentally detonated in the California desert, injuring its creator. The white solid was identified as the 'unusual explosive triacetone triperoxide' through infrared spectroscopy, and chemical ionization (CI) and electron impact (EI) mass spectrometry and comparison with previously published spectra. The same analytical

techniques were used to identify TATP found during a search as part of a

murder investigation reported by Gerald White in 1992. The 16g white
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powder was initially thought to be an illegal drug but was later characterised as the peroxide explosive. It is extremely fortunate that no one was harmed when handling this quantity of TATP and emphasised the need for more rapid and accurate TATP identification methods.

At the turn of the 21st century a number of high profile terrorist incidents used TATP as one of the main weapons of attack. In the attempted attack on American Airlines Flight AA63 in 2001, Richard Reid attempted to cause significant damage to the aircraft, whilst in flight with home-made explosives hidden in the hollowed soles of his shoes. The explosives were a mix of TATP and pentaerythritol tetranitrate (PETN), a powerful high explosive made from the reaction of pentaerythritol with concentrated nitric acid. TATP was planned to be used as the detonator. Reid was overpowered by passengers and crew on the flight after trying to set light to a fuse connected to the explosives. In the 2005 bombings of the London transport system, suicide bombers carrying rucksacks containing home-made organic peroxide explosives killed 52 people whilst injuring more than 700. Explosive devices were detonated simultaneously at three different locations on the underground subway system during the morning rush hour with a fourth device detonated on a double-decker bus an hour later. The explosives used contained a combination of TATP and hexamethylene triperoxide diamine (HMTD), a high explosive formed by reaction of hydrogen peroxide and hexamine in the presence of an acid catalyst.

With the significant increase of its use by terrorist groups, TATP was described in 2005 as the suicide bomber's weapon of choice, and its

detection has become a major challenge for global security in the war on <https://assignbuster.com/synthetic-and-spectroscopic-studies-of-triacetone-triperoxide-biology-essay/>

terror. Known by some terrorist groups as the 'Mother of Satan', TATP can be easily made from cheap and readily obtainable materials. The base ingredients of the reaction are both uncontrolled and commercially available meaning they can be readily obtained without attracting suspicion. Acetone can be obtained as a solvent, hydrogen peroxide as a bleach and sulfuric acid is found in certain drain cleaning products. The invention of the internet has significantly increased the availability of methods of synthesis and has enabled the worldwide sharing of information about home-made explosive production. Another major contributing factor to the popularity of TATP amongst terrorist organisations is its explosive power, which has been reported as 88% of that of trinitrotoluene (TNT) as measured through the Trauzl test. 14white

5. Spectroscopic Studies of TATP and its Detection

Uninitiated and initiated pre and post-blast and due to its volatility and instability only available commercially as dilute solutions (0.1 mg/mL) for use as analytical standards.

Unlike most conventional explosives such as TNT, TATP does not contain nitro groups or any metallic elements, making its detection via traditional methods such as standard airport security screening difficult. The unsuspecting white powder appearance does not draw attention to the solid which produces no significant absorption in the UV spectrum and does not fluoresce as there are no chromophoric groups in the molecule. The thermal instability of the compound also makes rapid detection by traditional analytical techniques difficult.

The sublimation and high vapour pressure of TATP at room temperature, as previously discussed, was determined as 7 Pa by Oxley and co-workers through application of gas chromatography with electron capture detection (GC/ECD). This translates to a factor of 104 more molecules of TATP in the air than TNT and suggests that analytical vapour sampling techniques may find success in detecting TATP samples from a greater distance. A disadvantage of the high vapour pressure of TATP is that its detection in post-blast residues is difficult and therefore analytical techniques with low limits of detection (LOD) are required.

Although insoluble in water, TATP can be dissolved in numerous organic solvents.

Solvent

g/100mL Solvent3Bellamy

wt% value3Bellamy

wt% value7Federoff

Chloroform

111

42. 7

42. 5

Toluene

34. 7

28. 6

Benzene

18. 0

Acetone

16. 5

17. 2

9. 15

Hexane

11. 1

14. 4

Petroleum ether

7. 35

Diethyl ether

5. 5

Methanol

3. 8

4. 5

Ethanol

3. 5

4. 2

0. 15

Investigations by Bellamy into a solvent which would enable the handling of TATP without the risk of accidental initiation showed toluene to be most appropriate. Through investigation of solutions, toluene was shown to offer high solubility along with low volatility. The detonation of saturated TATP toluene solutions could not be initiated and it was concluded dissolution in toluene renders TATP benign.

5. 1 Infrared and Raman Spectroscopy

Infra-red (IR) and Raman spectroscopy was first used in the investigation of organic peroxides by Minkoff in 1953. The vibrational spectra of over thirty organic peroxides including TATP was performed, with the aim of developing of a series of general rules which would enable the identification of a peroxide compound from its IR and Raman spectra. Due to the variation in peroxide spectra however, no general rules were able to be applied with the exception of the O-O band present for most organic peroxides within the 800-1000 cm^{-1} region.

The identification of organic peroxides through IR and Raman spectroscopy has more recently focussed on application to screening of explosives,

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primarily TATP. The success vibrational spectroscopy as a method of security screening is dependent on TATP producing a unique spectroscopic signature with large intensity in spectral regions that do not contain other common atmospheric species. It is also essential for the technique to be able to distinguish different peroxide groups from each other, for example peroxide explosives from other peroxides found in laundry detergents.

Oxley and co-workers recently assigned the Raman and IR spectra of TATP through comparison of spectra obtained in two different locations with theoretical spectra. There was a reasonable agreement between the measured and calculated spectra. (Figure).

Spectral Region (cm⁻¹)

Bond Assignment

1460

C-C stretching mode

1200-1300

C-O ring stretches

900-1000

O-O and C-O stretching modes

200-600

Ring deformations

TATP was shown to exhibit a unique splitting pattern of vibrational modes enabling the potential for its detection via high resolution methods. However, the main bands of the spectra (C-O and O-O) are part of a larger ring structure with additional vibrations resulting in the strong mixing of modes and a highly congested spectrum. These difficulties are unique to peroxide based explosives as most common explosives are detectable through the nitro and amine groups vibrations.

Standoff infrared and Raman spectroscopy (SIRS and SRS) systems enable the detection of explosive gasses and vapours present in air without the difficulties associated with other techniques that come with the handling and close range analysis of potentially explosive samples. For successful detection the explosive must have a high sublimation rate, which makes TATP a suitable candidate for detection. The main objective in the development of standoff systems is to enable the long range detection of explosives and therefore reducing the potential for severe damage.

In their development of a standoff detector system, Pacheco and co-workers investigated the gas phase vibrational spectra of TATP through Fourier Transform Infra-red (FTIR) spectroscopy. At high concentrations the TATP spectra was clearly observed over background levels with the vibrational signature of the molecule identified easily. When the concentrations of TATP were reduced to trace levels however, the characteristic spectra was less clear and could not be easily distinguished from background vibrations. The calculation of Partial Least Squares (PLS) was used to determine the perturbation produced by TATP on the normal air background spectrum. The

PLS results were used for Discriminative Analysis (DA) and determination of whether TATP was present or not in a two position switch type function.

More recently, Pacheco and co-workers reported the Raman detection of TATP at 514nm from a standoff distance of 7m with a limit of detection (LOD) of 10nm in a 10s acquisition time.

5. 2 Electrochemical Sensors

An electrochemical method for sensing TATP was reported by Munoz et al. based on the acid treatment of the peroxide. The hydrogen peroxide degradation product generated in the 0. 5M HCl solution containing 0. 1M KCl acidic medium is measured at a Prussian-blue (PB) modified electrode. PB is known also as artificial peroxidase and is a highly effective hydrogen peroxide electrocatalyst. Unlike the enzymes used for other peroxidase assays, PB is not deactivated under the strong acidic conditions used in the decomposition of TATP and therefore eliminates the need for an additional neutralization step. The technique was optimised to sensitivity down to 50ng levels within 60s of analysis.

PB modified electrodes had previously been used by Lu and co-workers to detect the hydrogen peroxide produced through photochemical degradation of TATP. However, the TATP current response produced following a 5min UV irradiation was six times lower than that produced following 15s of acid treatment. The fast, simple and sensitive detection of TATP enabled by the acid detection method has the potential for development of a low cost, low power, portable field screening device for all peroxide-based explosives.

5. 3 Colorimetric Spot Test Kits

The acid decomposition products of TATP were again utilised by Lin and Suslick in the production of a colorimetric sensor array for the detection of TATP vapour. The acidic, solid, polymer-based catalyst, Amberlyst-15 was used to decompose TATP and its vapour decomposition products were detected by a colorimetric sensor array of sixteen redox sensitive dyes (Figure enzyme coupled reaction). The method was shown to be highly sensitive with a LOD below 2ppb, or less than 0.02% of the saturation vapour pressure of TATP. The dyes are highly specific for TATP with common potential interferences such as personal hygiene products, laundry detergents and volatile organic compounds (VOCs) not generating an array response. TATP can also be differentiated from other chemical oxidants such as bleach, hydrogen peroxide and peracetic acid. The device is also portable and disposable which are highly advantageous in the screening of explosives.

5. 4 Mass Spectrometry

5. 4. 1 Gas Chromatography/Mass Spectrometry GC/MS

The first reported GC/MS analysis of TATP was reported by Evans and co-workers in 1986 and was used in the identification of an unknown home-made explosive. 13EVANS An electron ionization (EI) spectrum and a methane positive ion chemical ionization (PICI) spectrum were reported, both using a solid probe to introduce the sample into the ion source. The EI spectrum contained a base peak at m/z 43 with less abundant ions observed at m/z 59, 75 and 222. The PICI spectrum displayed a base peak of m/z 74 with less abundant ions at m/z 103, 117, 133 and 223 among others. The

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m/z 223 ion was of approximately 10% relative abundance and was assigned as the protonated TATP molecular ion, [TATP+H]⁺. The detection limits and source temperatures used in the analysis were not reported.

A later investigation by White¹⁴WHITE again utilised EI and PICI GC/MS spectra to identify an unknown white powder as TATP. The report did not include total ion chromatograms for either method with the PICI and EI spectrum reported in the mass range m/z 100-230 and m/z 10-130 respectively. The methane PICI spectrum displayed a base peak at m/z 223 and ions previously observed by the Evans group at m/z 103, 117 and 133 were present with similar relative abundances. The EI spectrum produced a base peak at m/z 43 with less abundant ions shown at m/z 59 and 75. The report did not include the LOD, or conditions for the quadrupole MS analysis.

A more pronounced TATP molecular ion peak at m/z 222 in the EI spectrum was reported by Fialkov and Amirav, through analysis in a supersonic expansion of helium. A supersonic molecular beam (SMB) is used as a medium for the ionization of the sample molecules and enables relatively low collision energies of sample compounds and carrier gas species during the supersonic expansion by a process called intramolecular vibrational supercooling. This method of EI with a SMB is termed 'Cold EI' and is used to enhance the molecular ion abundance and increase confidence in comparison with the standard 70eV EI. The cold EI TATP is shown (Figure).

A detection limit of 0.1 ng was reported for TATP by Stambouli and co-workers in their GC/EIMS analysis of headspace samples. Samples of post explosion debris, including soil, metal and glass were placed into an 850 ml

glass container and heated at 90°C for 30 min. A 1000µL sample of headspace gas was collected using a gas syringe and injected on the ion trap GC/MS. helium gas carrier. The GC oven program is held at 40 C for 1 min, ramped at 5degrees/min to 100 C, and held 6 min at final temperature. Splitless injections are done The heating zone temperatures on the GC/MS instrumentation were optimized to achieve the best sensitivity whilst avoiding the thermal degradation of TATP. An injector port temperature of 100°C was used with a transfer line and source temperature of 150°C. The TATP peak was shown at 13. 17min on the chromatogram with the ion trap spectrum containing ions at m/z 221 [TATP-1]+, 75 [C3H7O2]+, 59 [C3H7O]+ and 43 [C2H3O]+. The spectrum was considered to confirm the molecular structure of TATP despite the m/z 221 ion peak having less than 1% abundance of the base peak. Traces of the DADP not seen in any LCMS analysis were also shown to appear at 5. 80min in the chromatogram with a corresponding ion trap spectrum similar to that of TATP but with more intense fragments (Figure).

Figure Mass spectrum of triperoxide triacetone (TATP) and diperoxide diacetone (DADP) produced by Stambouli et al. through the GC/EIMS analysis of headspace samples.

An investigation of different GC/MS ionization methods and their use in the analysis of TATP was reported by Sigman et al., utilising instrumentation available in most forensic laboratories. Spectra were reported through liquid sample injection using electron ionization (EI) and methane and ammonia positive ion chemical ionization (PICI) and negative ion chemical ionization (NICI) on linear quadrupole and ion trap instruments.

PICI

NICI

EI

NH3

CH4

NH3

CH4

Ion trap

0. 10a

0. 5b

2d

1e

0. 5f

Quadrupole

0. 05a

0. 1c

1d

1e

0.5f

Key

Extracted ions (m/z)

in order of abundance

Assigned fragment

a

43

[C₂H₃O]⁺

59

[C₃H₇O]⁺

75

[C₃H₇O₂]⁺

b

58

Not assigned

240

[TATP+NH₄]⁺

c

240

[TATP+NH₄]⁺

223

[TATP+H]⁺

d

43

[C₂H₃O]⁺

59

[C₃H₇O]⁺

75

[C₃H₇O₂]⁺

91

[C₃H₇O₃]⁺

e

56

Not assigned

57

[C₃H₅O]-

59

Not assigned

f

57

[C₃H₅O]-

56

Not assigned

59

Not assigned

41

[C₃H₅]-

Instrument Setting

Sigman

Stambouli

Carrier gas

Helium

Helium

Injector port temperature (°C)

110

100

Initial GC oven temperature (°C)

50

40

Time held for (min)

3

1

Ramped (°C/min)

8

5

Final GC oven temperature

180

100

Source operating temperature (°C)

100

150

Transfer line temperature

100

150

The preferred technique for GC/MS analysis of TATP was assigned as PICI with an ammonia reagent gas. This method produced spectra containing the m/z 240 [TATP+NH₄]⁺ diagnostic ion observed as the base peak in the quadrupole mass spectrum and as a strong ion with greater than 60% abundance of the m/z 58 base peak in the ion trap spectrum. Low detection limits were also observed 0.5 ng and 0.1 ng ion trap and quadrupole respectively.

CID?

Unlike in previous methane PICI and EI analysis 223 and 222 peaks were not seen.

5. 4. 2 Liquid Chromatography/Mass Spectrometry (LC/MS)

A method for the LC/MS analysis of TATP using an atmospheric pressure chemical ionisation (APCI) interface operating in positive ion mode was

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reported by Widmer et al. in 2002. The analysis of TATP by LC/MS was investigated as a solution to the reported degradation of TATP in the injector port of previous GC/MS analyses. Both positive and negative mode APCI was investigated as well as positive and negative mode using an electrospray ionisation (ESI) interface. Negative mode analysis yielded little information through both ionisation techniques. A good response was observed through positive ESI, however APCI was the preferred technique returning a superior response.

Instrumentation setting and conditions were optimised (Table) and method developed enabling trace analysis of TATP at detection levels as low as 0.1 ng μl^{-1} .

Column Oven ($^{\circ}\text{C}$)

20

Mobile Phase

70: 30 MeOH: Water with 50mM ammonium acetate

Nebuliser Temperature ($^{\circ}\text{C}$)

330

Source Temperature ($^{\circ}\text{C}$)

120

Drying gas flow (l \cdot h $^{-1}$)

200

Sample cone voltage (V)

10

LC Stationary phase

C18

The produced spectrum contained the m/z 240 ion, corresponding to the molecular adduct $[TATP+NH_4]^+$ and was deemed to have formed from the nitrogen drying gas used in analysis. This assignment was confirmed by the fragments increase in abundance when ammonium acetate buffer was used. The expected molecular ions of m/z 223 $[TATP+H]^+$ and m/z 221 $[TATP-H]^-$ were not detected and their absence was ascribed to the high fragility of the TATP molecule.

Conditions In a later study, Xu and co-workers reported detection of the m/z 240 TATP ammonium adduct peak with a LOD of 3.3 ng through LC/MS analysis using an APCI interface. A fragment ion of m/z 89 was also observed at an abundance of 7% of the m/z 240 base peak, this was not assigned to a TATP fragment. Through further tandem MS analysis (MS/MS) and fragmentation of the m/z 240 precursor new fragment ions were observed at m/z 223, 132, 91 and 74 (Figure).

The fragment ions of m/z 223 and 74 were assigned as the protonated TATP molecular ion $[TATP+H]^+$ and $[TATP/3]^+$ or monoacetone monoperoxide

respectively. This was the first reported observation of the protonated TATP molecular through LC/MS analysis.

The main disadvantages of the APCI and ESI analysis of TATP is the excessive fragmentation in the mass spectra, the time taken for chromatographic separation and that they require the direct handling of samples. Desorption electrospray ionisation (DESI) enables the in-situ detection of TATP without the need for any sample pre-treatment with high sensitivity and selectivity, in a short amount of time, with limited fragmentation of the TATP molecule. The technique operates by directing an electrospray onto a surface and collecting the secondary ions generated through interaction of charged microdroplets with the analyte molecules on the surface. Cotte-Rodriquez and co-workers reported the formation of sodium, lithium and potassium TATP complexes using a spray solvent of methanol and water doped with ammonium acetate, sodium chloride, lithium chloride and potassium chloride. Detection limits were reported as low as 1ng for TATP deposited on a paper or metal matrix and 2ng on a brick surface. The positive DESI spectrum shown (Figure) was recorded using a 10ng TATP sample deposited on paper and sprayed using sodium acetate and sodium chloride in a methanol and water solvent. The most significant ions in the spectrum were observed at m/z 245 $[TATP+Na]^+$, m/z 240 $[TATP+NH_4]^+$ and m/z 223 $[TATP+H]^+$. Confirmation of the identity of the ions was achieved through tandem MS (MS/MS). The precursor m/z 240 $[TATP+NH_4]^+$ ion produces the m/z 223 $[TATP+H]^+$ fragment through loss of an NH_3 group. The fragmentation mechanism of the alkali metal complexes was different from the ammonium adduct with the major product ion at m/z 215 $[C_7H_{12}O_6]^+$

formed through loss of an ethane molecule (Figure). Other fragments as m/z 172 and m/z 81 were reported and assigned as $[C_5H_9O_5+Na]^+$ and $[C_3H_6O+Na]^+$ respectively.

Both potassium and lithium TATP complexes were reported also to exhibit similar fragmentation behaviour.

Through density functional theory (DFT) calculations the TATP- Na^+ binding energy was found to be 47kcal/mol which is approximately 11kcal/mol higher than the value for the weak O-O bond, reported by Oxley et al. as 36.3 kcal/mol. This accounted for the apparent retention of the sodium ion by the TATP molecule during fragmentation and cleavage of the peroxide (O-O) bond. The sodium ion was shown to be held centred and slightly above the binding cavity (Figure), most likely due to steric effects relating to size of the Na^+ ion and the cavity.

5.5 Ion Mobility Spectrometry

Ion Mobility Spectrometry (IMS) is an electrophoretic technique that allows the separation of ionised analyte molecules according to their relative mobilities in the gas phase. Ion mobility is determined by the limiting velocity of an ion through an electric field in the presence of a drift gas and is related to experimental conditions and analyte characteristics through the Mason-Schamp equation. At a specific drift gas pressure and temperature the mobility of an ion is therefore determined by the charge, reduced mass and collision cross section (size and shape) of the ion.

The sample ions are moved towards the drift region with a combination of gas flow and electric fields. An ion shutter or gate introduces the ions into <https://assignbuster.com/synthetic-and-spectroscopic-studies-of-triacetone-triperoxide-biology-essay/>

the drift tube in pulses. The ions are accelerated towards a detector situated at the end of the drift tube and their drift times recorded. The drift region also contains a drift gas at a constant pressure which enables the separation of ions of differing shape and size. Whilst passing through the drift gas, an ion will experience collisions which will reduce its velocity and therefore increasing its drift time. The ions with larger collision cross sections will experience more collisions whilst passing through the drift tube and therefore have a longer drift time.

IMS is already the method of choice for the screening of traces of explosives and narcotics in high risk areas. The use of IMS for such purposes enables the fast, simple and sensitive detection of substances which pose a security risk.

The application of IMS to the detection of TATP was first reported by McGann and co-workers in 2001. They described how an IMS instrument used for security screening is set for positive mode or negative mode whether detecting narcotics or explosives respectively. Through use of the IonTrack Instruments' (ITI) Ion Trap Mobility Spectrometry (ITMS) technique however, the simultaneous measurement of both positive and negative ion spectra in a single drift tube is achieved. The analysis of TATP yielded two peaks at 5.3 ms and 6.8 ms and assigned as the positive and