Adventures in Analysis of Peroxide Explosives

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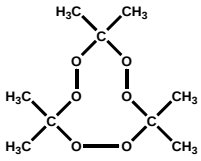
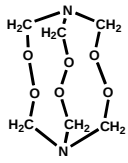
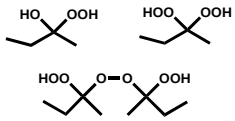


TATP



HMTD



Methyl Ethyl Ketone Peroxides

Professors: Jimmie Oxley & Jim Smith

PhD Students: Kevin Colizza Lindsay McLennan Alex Yeudakimau

This work is supported by the U.S. Department of Homeland Security but views & conclusions are those of the authors alone.

Studies with Peroxide Explosives

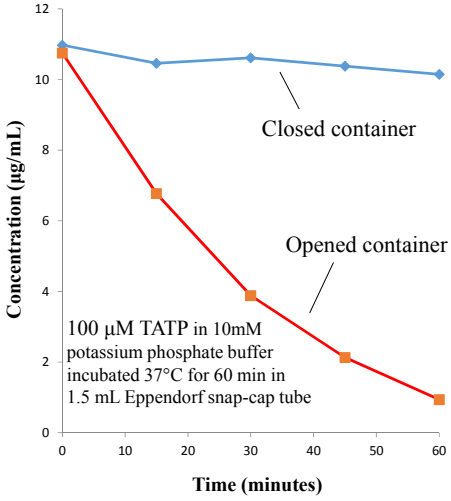
Hair as forensic evidence

Safe Scent Canine
Training Aids

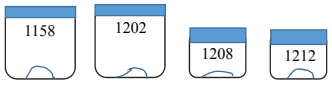
Methods: Gentle Destruction of Peroxides

450 g TATP digested in 25 min

TATP volatility is a problem!



~100 mg TATP in each container



1. Draw 2.5 mL vapor into a gas-tight syringe
2. Bubble gas through 0.5 mL of 50/50 ACN/water in a glass GC vial with PTFE septa
3. Perform this 3 times for each vessel
4. Directly inject solutions onto LC-MS system (N=2)

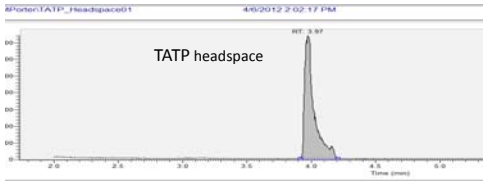
TATP Vapor by direct syringe of headspace

Sample	Mean (ng TATP/mL vapor)	SD (+/- ng/mL vap)
1158	354	34
1202	388	54
1208	384	1.6
1212	379	64
Mean	376 ⇒ $P_{vap} = 4.1 \pm 0.1$ Pa	
Standard Error	8	

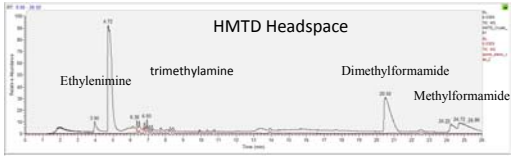
Vapor concentration independent of container size. Vapor pressure predicted for 25°C is 1.8 Pa by rising temp TGA & 6.95 Pa by headspace GC

Oxley, Smith, Moran, Shinde *PEP*, **2005**, *30*, 127-130
Oxley, Smith, Brady,, PEP, 2012, 37, 215-222

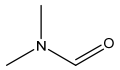
To make safe scent aids, headspace signature must be determined



- The headspace of TATP contains only TATP. The scent aid must be TATP
- The headspace of HMTD contains mainly decomposition products. These non-explosives make up the odor.



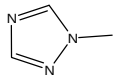
hexamine $N(CH_3)_3$ $HN(CH_2)_2$



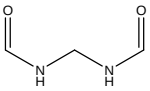
dimethylformamide

methylformamide

ethylenimine

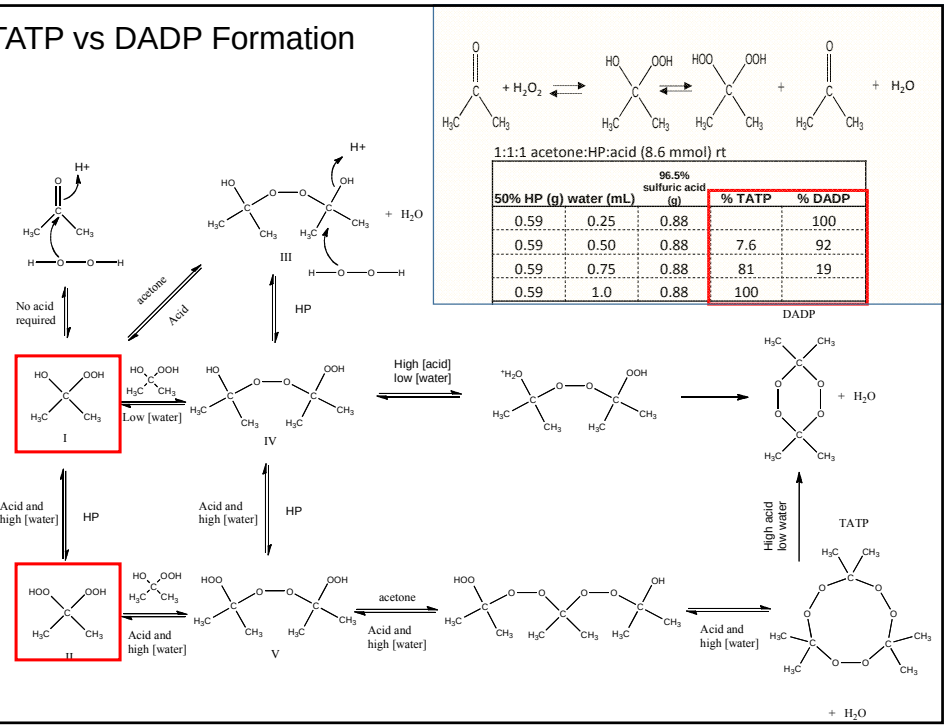


1-methyl-1H-1,2,4-triazole



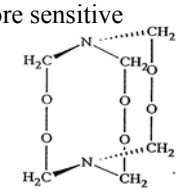
N,N'-methylenebis(formamide)

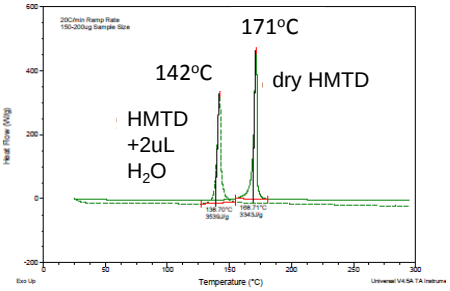
TATP vs DADP Formation



HMTD has little vapor pressure; its odor is decomposition products

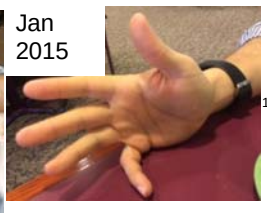
May 2013 HMTD (250mg in glass vial) exploded as chemist picked it up. As explosives start to decompose, they become more sensitive because porosity increases, & density decreases. Pores introduce heterogeneity which increases sensitivity.

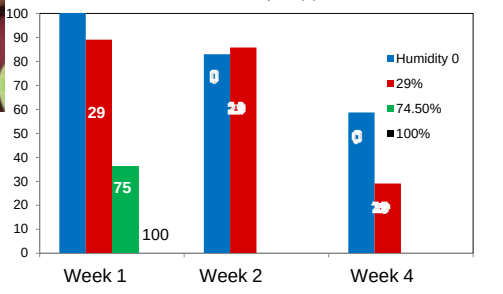




May 2013

Jan 2015

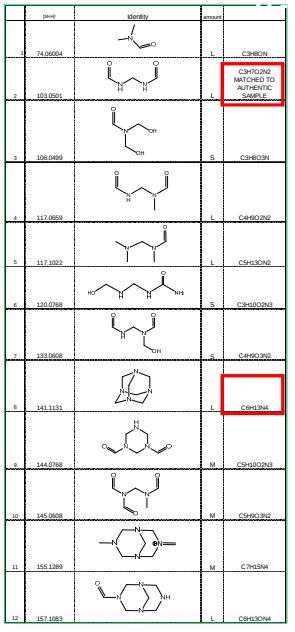




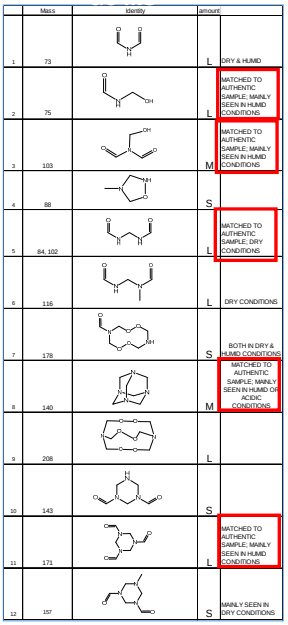
HMTD already has lower thermal stability than any military explosive (DSC_{exo} 200-300°C) & even most HME. Friction & ESD sensitivities are high.

HMTD Decomposition Products

LC-MS



GC-MS

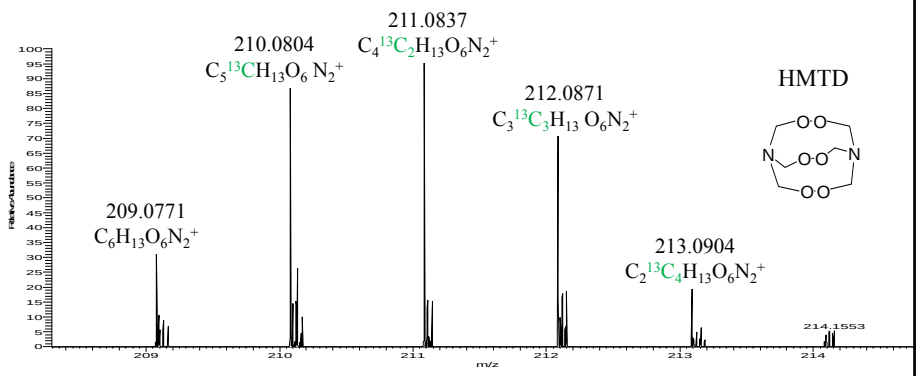


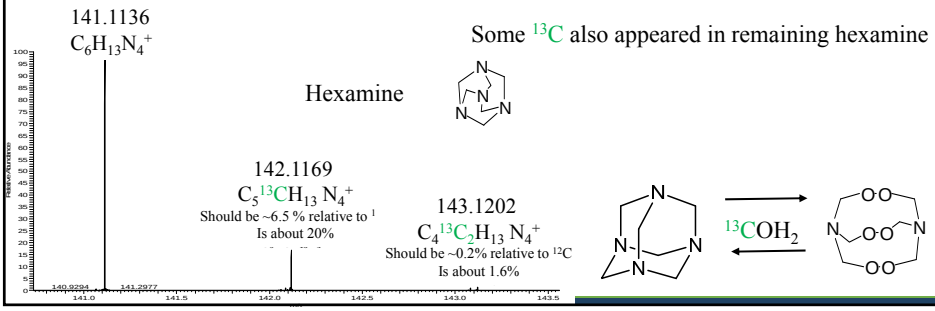
With added formaldhyde reaction is faster
Yield 130% based on 1 HMTD : 1 hexamine;
70% based on 2 HMTD : 1 hexamine

~~$C_6N_4H_{12} + 3\ H_2O_2 \rightarrow 1\ C_6N_2H_{12}O_6 + 2\ NH_3$~~

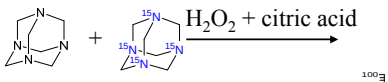
$$C_6N_4H_{12} + 6\ H_2O_2 + 6\ OCH_2 \rightarrow 2\ C_6N_2H_{12}O_6 + 6\ H_2O$$

^{13}C is incorporated in HMTD with added $^{13}COH_2$ under formation conditions.

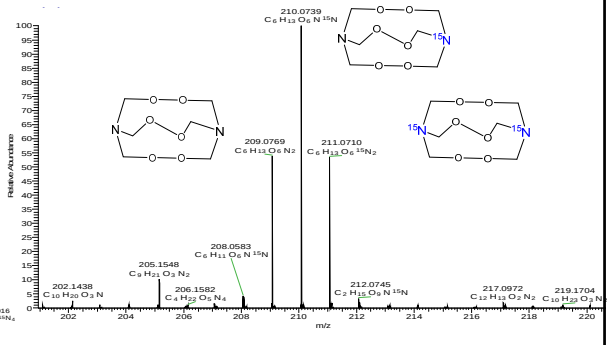


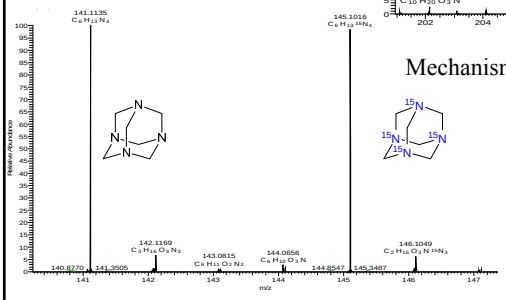


Formation Mechanism Evidence



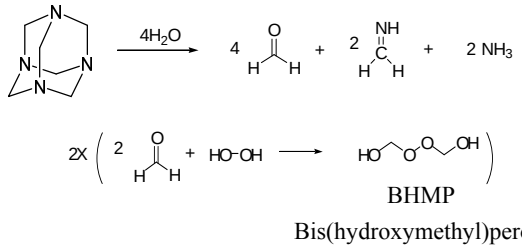
^{15}N label scrambled during HMTD formation, but no scrambling in starting materials observed.

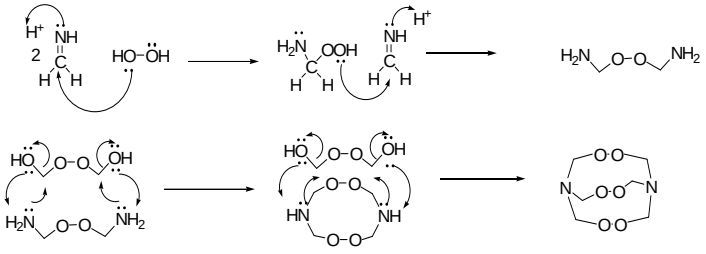




Mechanism where hexamine breaks down is supported

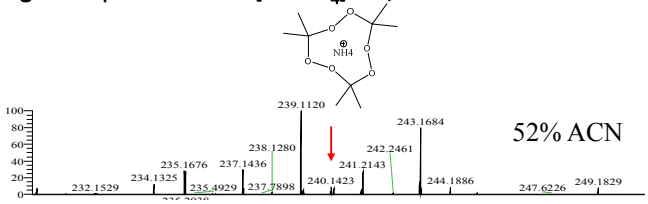
Mechanism for HMTD Formation involves C & N scrambling





Detecting Peroxide at low concentration

Signal response of TATP $[M+NH_4]^+$ m/z 240.1442 with & without acetonitrile (ACN)



52% ACN

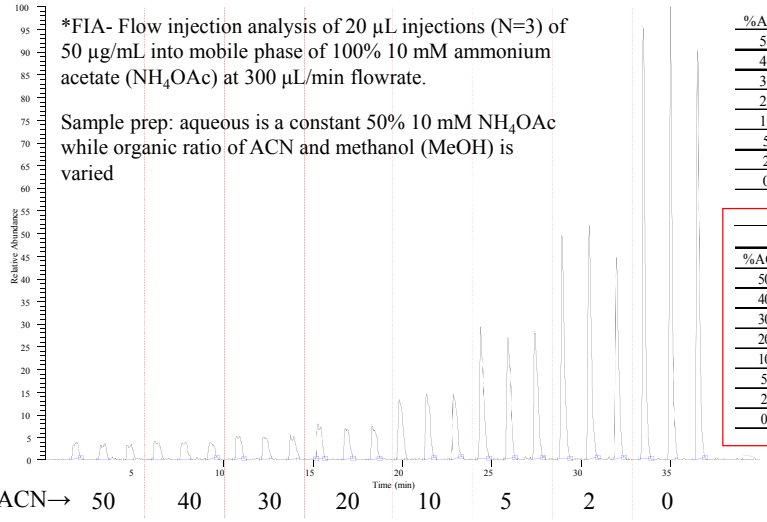
Response 240.1442

2.69×10^5

FIA* depicting TATP $[M+NH_4]^+$ response in ESI with decreasing concentration of ACN

*FIA- Flow injection analysis of 20 µL injections (N=3) of 50 µg/mL into mobile phase of 100% 10 mM ammonium acetate (NH_4OAc) at 300 µL/min flowrate.

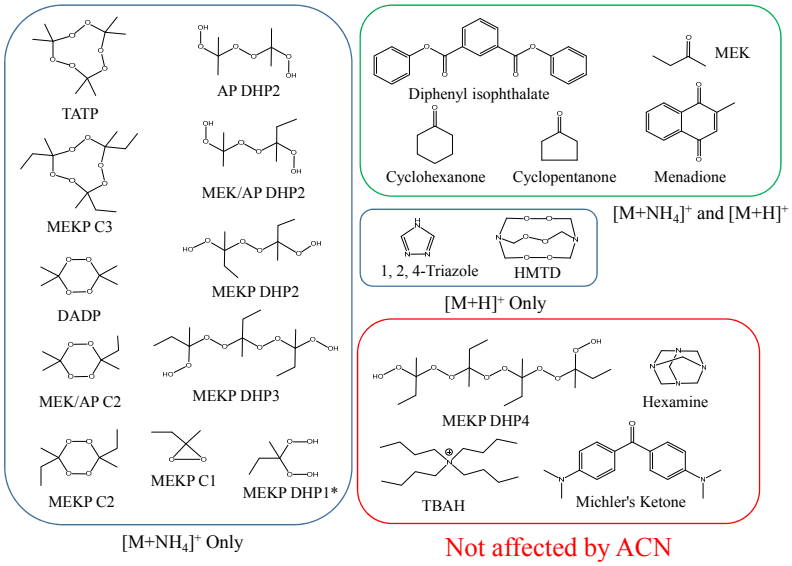
Sample prep: aqueous is a constant 50% 10 mM NH_4OAc while organic ratio of ACN and methanol (MeOH) is varied



	Average Area
%ACN	TATP response
50	1926146
40	2175977
30	2766516
20	3437664
10	6109970
5	10171818
2	15202570
0	24112311

	Normalized %
%ACN	TATP response
50	8
40	9
30	11
20	14
10	25
5	42
2	63
0	100

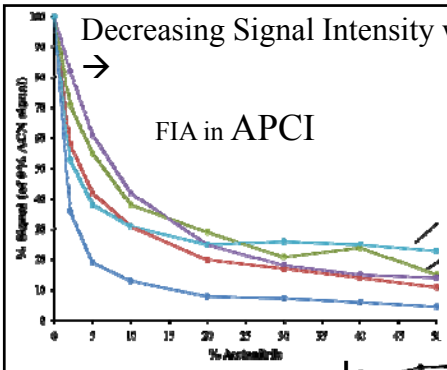
Compounds tested--ions formed & ACN effect on ionization



*Also produced sodium adduct equally affected

Decreasing Signal Intensity with Increasing ACN →

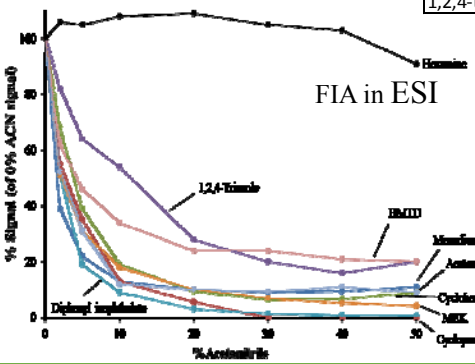
FIA in APCI



HMTD
cyclohexanone
1,2,4-triazole
menadione
MEK

	H^+ affinity
water	691
MeOH	754
ACN	779
cyanamide	806
pivalonitrile	811
acetone	812
cyclopentanone	824
MEK	827
cyclohexanone	841
ammonia	854
1,2,4-triazole	886

FIA in ESI

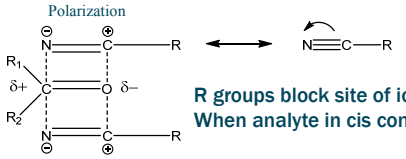


Hexamine
HMTD
1,2,4-triazole
menadione
acetone
cyclohexanone
MEK
diphenyl isophtha
cyclopentanone

This is curious since ACN has a lower proton affinity than most of the analytes.

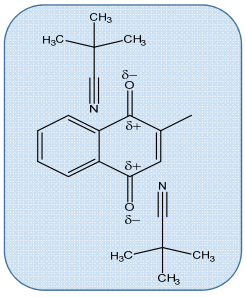
Proposed Mechanism for Ion Suppression by ACN

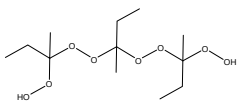
Polar interaction between nitrile and analyte causes formation of neutral aggregate



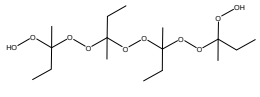
R groups block site of ionization
When analyte in cis configuration

Analysis with electron donating (-NH_2), electron withdrawing (-Br) and steric (trimethyl) nitriles support this mechanism.





MEKP DHP3



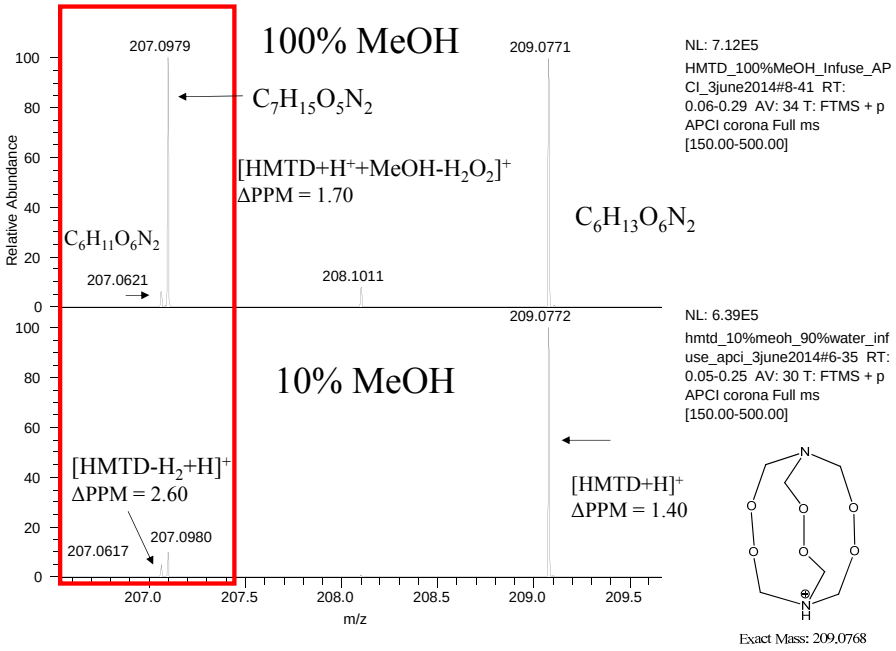
MEKP DHP4

Peroxide Detection

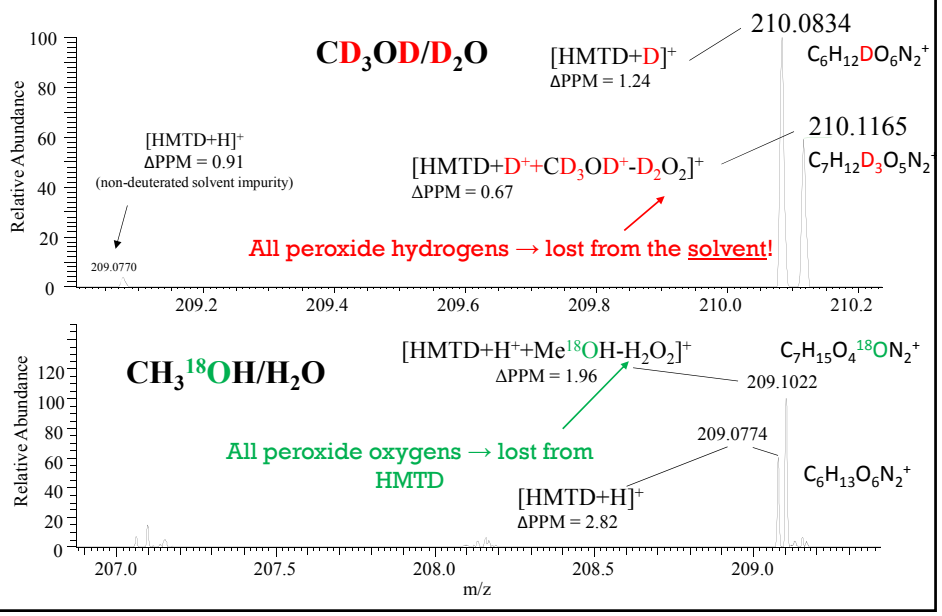
- Peroxides in cis formation have large dipole.
- TATP and HMTD are forced into cis configuration
- Large, linear peroxides cannot form cis isomer without self-steric interaction
- DHP3 and DHP4 were not affected by ACN
- Addition of heat (HESI) showed significant effect for DHP3 not DHP4!

Rapid Communications in Mass Spectrometry **2016**, 27(1), 1796-1804.

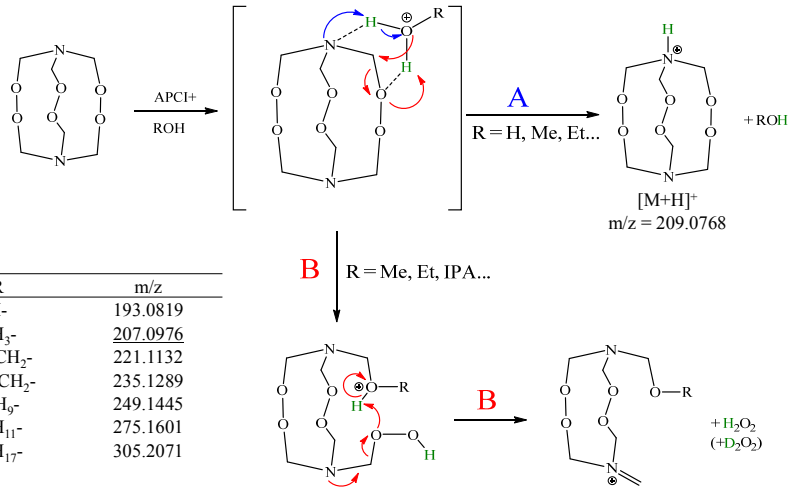
Full Scan of **HMTD** in MeOH/H_2O—why two 207 peaks?



HMTD infused in CD_3OD/D_2O or $CH_3{}^{18}OH/H_2O$



Proposed Mechanism for Formation of (A) Protonated HMTD or (B) Alcohol-Bonded Species



R	m/z
H-	193.0819
CH_3-	207.0976
CH_3CH_2-	221.1132
$C_2H_6CH_2$-	235.1289
C_4H_9-	249.1445
C_6H_{11}-	275.1601
C_8H_{17}-	305.2071

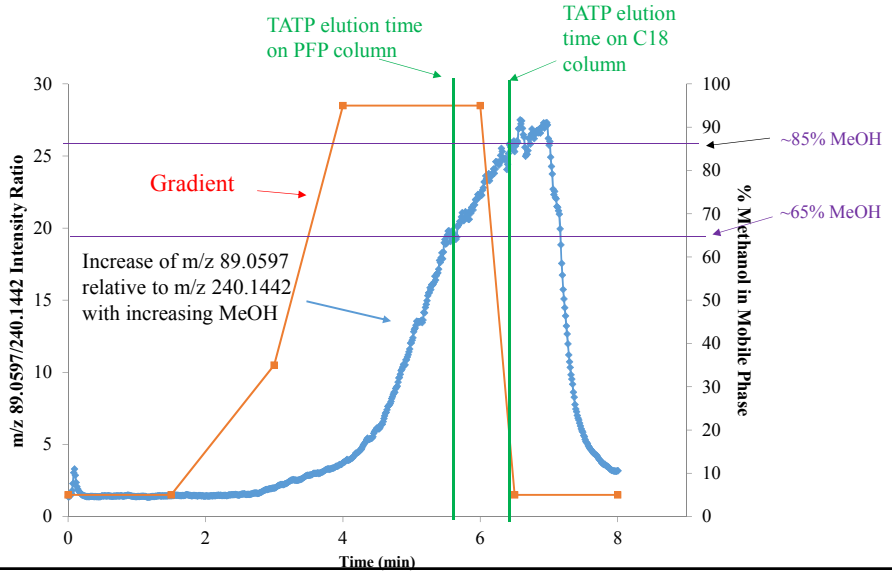
Rapid Comm Mass Spectrometry **2015**, 29(1), 74-80.

Hydrogens lost from solvent Oxygens lost from HMTD

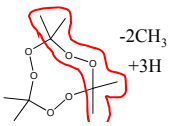
Which mass & column for best detection limits?

With ammonium modifier present → 240.1442 (TATP-NH_4^+) or 89.0597 ($C_4H_9O_2^+$)?

Post-column addition **TATP** in MeOH/water into LC flow of std gradient (10 mM NH_4OAc/MeOH) monitoring ratio of m/z 89.0597 to m/z 240.1442 with increasing methanol.



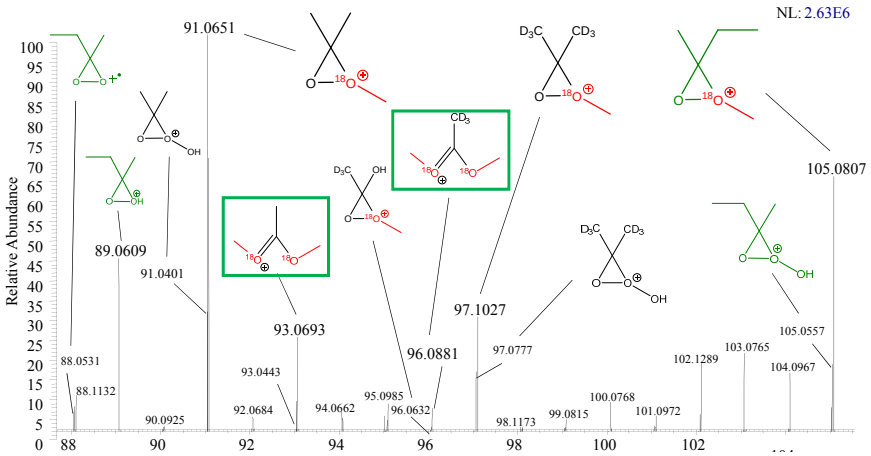
What is Mass 89.0597? $C_4H_9O_2^+$ is unlikely fragment!



Infusion of TATP, d_{18}-TATP & **MEKP** in CH_3OH in to APCI Source

Infusion of TATP, d_{18}-TATP & MEKP in $CH_3{}^{18}OH$ into the APCI source

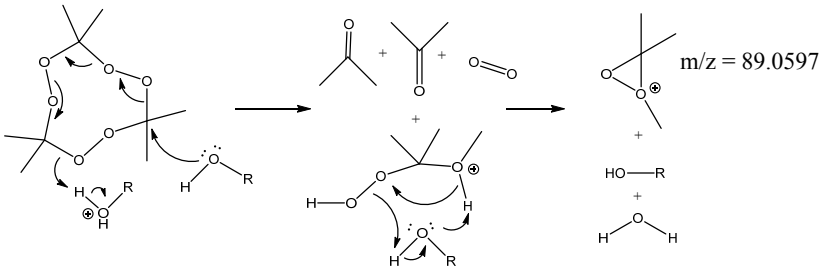
Direct Infusion (20 µL/min) of TATP (5 µg/mL), d_{18}-TATP (5 µg/mL) and MEKP (10 µg/mL) in 90% $Me^{18}OH$/10% 10 mM NH_4OAc. Only m/z 88-105 are shown for resolution purposes.



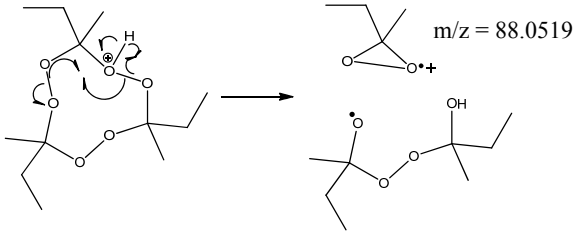
Lower gas flow promoted the formation of 95 and 92. Higher flow favored $[M+NH_4]^+$ and 97 formation. Lower gas flow may mean more time to react with MeOH in the discharge region or more time in the heated region of ceramic tube.

Proposed mechanism of gas phase formation of
m/z 89 for TATP or 103 for MEKP & m/z 88 for MEKP or m/z 74 for TATP

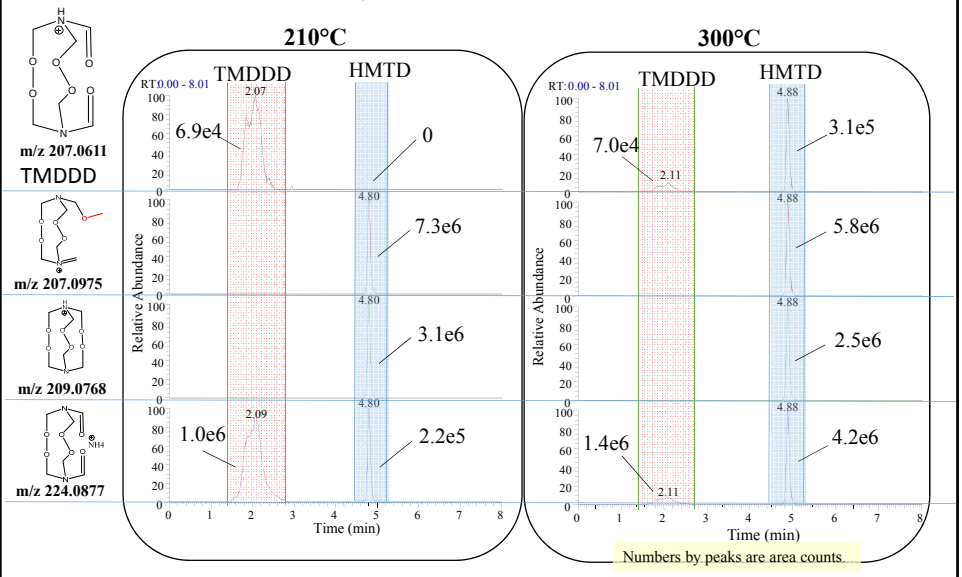
TATP formation of m/z 89.0597 (corresponds to MEKP m/z 103.0754)



MEKP formation of m/z 88.0519 (corresponds to TATP m/z 74.0362)



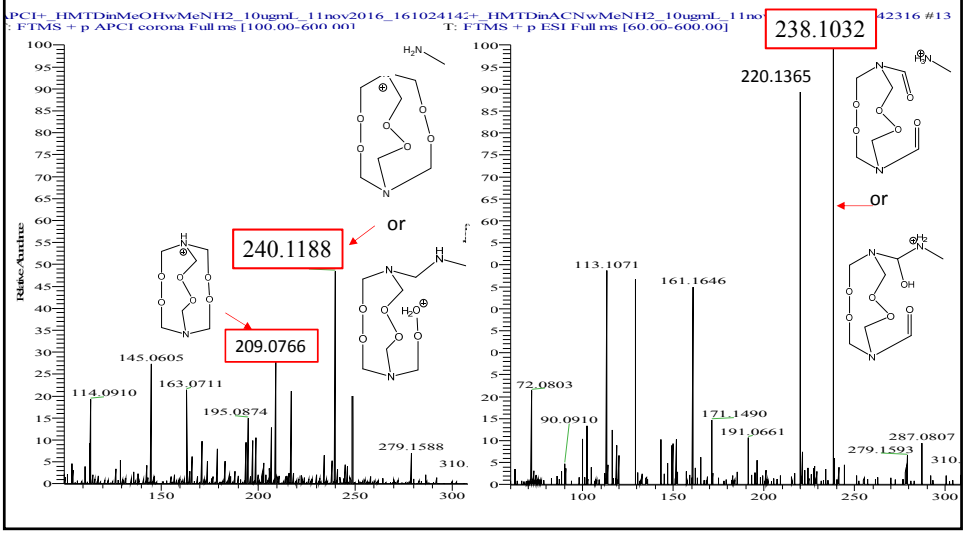
Krawczyk suggested converting HMTD to TMDDD would improve detectable, but….
We attempted to form in-situ by injecting HMTD (100 ng) onto 5cm PFP column with **APCI** source & raising temperature 210°C → 300°C. More TMDDD formed, but not enough.
We observed HMTD always had TMDDD contamination.



TMDDD unaffected by temperature rise. HMTD formation of TMDDD is affected by temperature

Could an amine replace ammonium in aiding detection of HMTD?
HMTD infused with $MeNH_2$ produced different peaks in APCI & ESI.

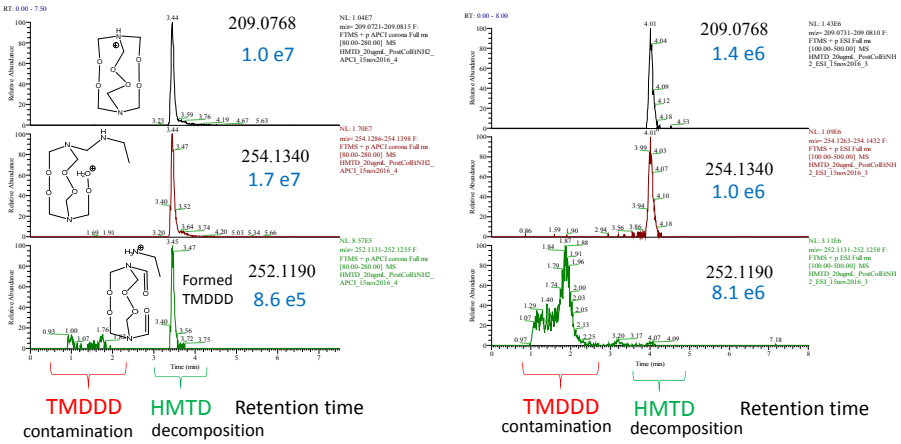
APCI **ESI**



Could detection of HMTD be improved by in-situ formation of TMDDD & interaction with amine? Thus, HMTD with post-column addition of $EtNH_2$

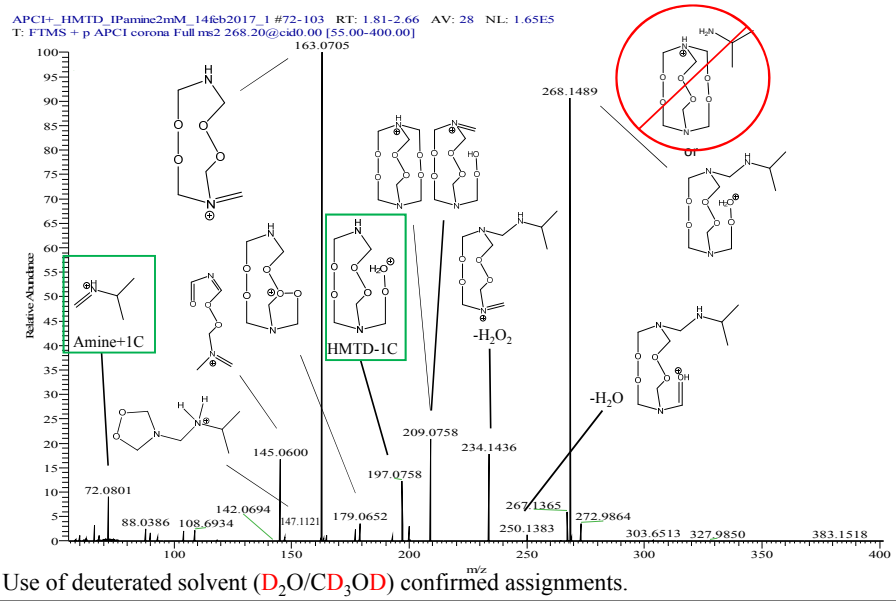
Note: HMTD is best observed by APCI, and TMDDD in ESI.

APCI Numbers in blue are peak area counts. **ESI**



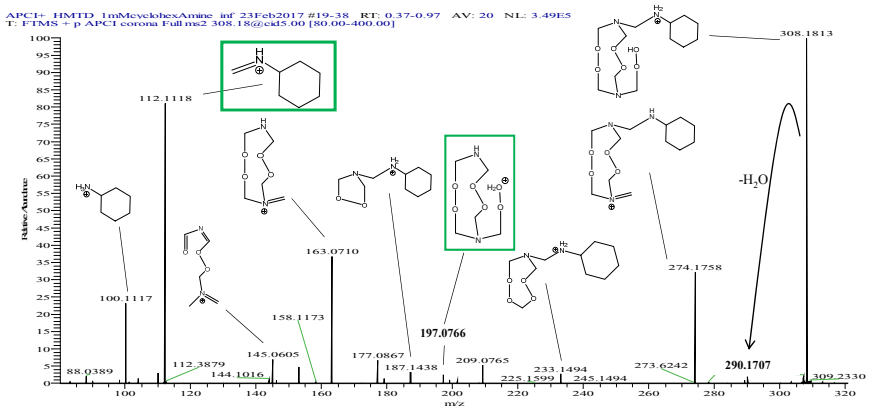
MS/MS fragmentation of HMTD-i-propylamine product formed in APCI

Result is a product not an adduct Amine removes 1 C from HMTD



Use of deuterated solvent (D_2O/CD_3OD) confirmed assignments.

HMTD with Cyclohexylamine in APCI+



Reaction of HMTD and TMDDD with Amines

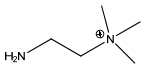
Amines infused with HMTD into APCI source

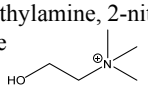
Organic Amine	Expected mass	Observed mass	ΔPPM	pKa
Methylamine	240.1190	240.1185	-2.1	10.62
Ethylamine	254.1347	254.1342	-2.0	10.87
Dimethylamine	254.1347	254.1341	-2.4	10.73
Triethylamine*	310.1973	310.1963	-3.2	10.78
Isopropylamine	268.1503	268.1489	-5.2	10.63
Cyclohexlyamine	308.1816	308.1813	-1.0	10.63
Aniline	302.1347	302.1338	-3.0	4.6
2-nitroaniline	347.1197	NR		-0.28
(2-aminoethyl)trimethylammonium	311.1925	NR		na

* Triethylamine forms an adduct to HMTD with no observable chemical reaction

NR-no reaction, na-not available

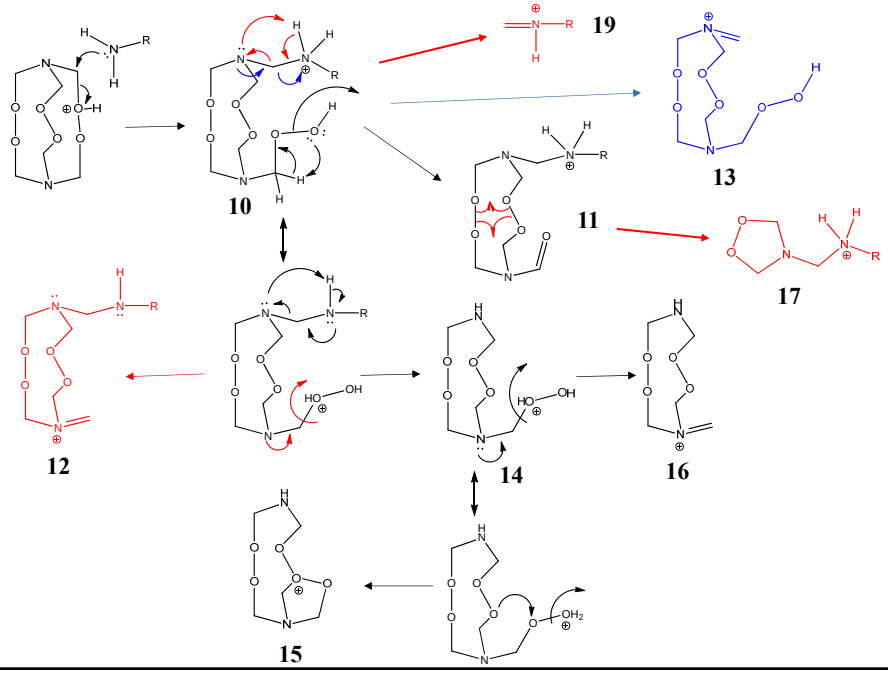
- TMDDD forms intense adducts with amines in ESI source
  - Adduct formation was confirmed since no fragments were detected for TMDDD + amine
  - When mass of amine was > 50 amu → detected fragment was only the ionized amine
- HMTD formed products with basic amines; these gave abundant MS fragments
  - Fragments suggest incorporation of the amine into the HMTD structure
  - Intensity of the product is related to the amine basicity
  - Triethylamine only forms an adduct with HMTD.
- Trimethylamine, 2-nitroaniline, (2-aminoethyl)trimethyl ammonium, & choline did not form covalent products with HMTD.





If amine reacted with HMTD, the quaternary amine would make a charged product

Thoughts on Mechanism for the Fragmentation of the HMTD/amine Product in CID



Summary of Lessons Learned

1. TATP is extremely volatile, even in solution, but in headspace TATP is intact, unlike HMTD where the headspace is decomposition products.
2. ACN in MP of LC-MS suppresses charge for some peroxides & ketones.
3. TATP and HMTD react with MeOH in gas phase
   for TATP this results in LC-MS peak at 89 indicating addition of 1 or 2 MeOH
   for HMTD this results in 207
4. Reactions of TATP or HMTD with ROH can be used to lower detection limits but variable results will be obtained if LC-MS analytical conditions are changed.
   Analytical conditions include
   - column
   - ionization source –TATP & HMTD prefer APCI (linear peroxides ESI)
   - solvent gradient
   - temperature
   - sheath & auxiliary gas flow rates
5. HMTD is generally contaminated with oxidation product TMDDD.
6. HMTD reacts with amines in gas phase. As with ROH, R_2NH or RNH_2 attack is at C
   unfortunately, unlike with ROH, addition of amines did not improve detection limits. TATP did not react with amines under the same conditions.
7. TMDDD tends to form adducts rather than products with amines