



Reducing the Threat from TATP & Other Peroxide Explosives



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Abstract

We have attempted to reduce the threat of TATP by attacking the problem from multiple directions. First we have sought an experimental and theoretical understanding of its preparation and destruction. Second, since the precursors - acetone and hydrogen peroxide (HP) - are widely available and cannot be removed from commerce, we have identified ways to denature these precursors to prevent illicit use without adverse effect on their legitimate use. Third we have sought a way to gently destroy TATP.

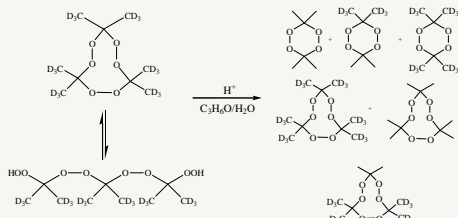
Relevance

Recent Peroxide Explosive Incidents:
Shoe Bomber, 2001 - TATP
London 2005, 2006 - TATP, HMTD, HP/fuel
Univ. of Oklahoma 2005 - TATP
Texas City 2006 - TATP
Clairexide 2009 - Concentration of HP
Escondido 2010 - HMTD

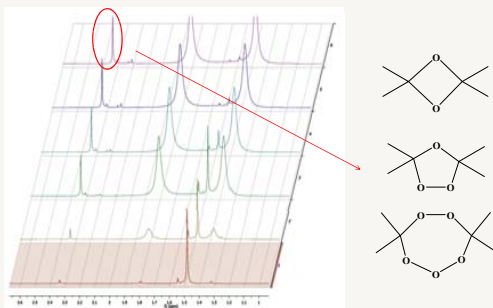
Peroxide-based explosives have emerged as terrorist threats. H₂O₂ (HP) maybe directly used, mixed with fuels, or chemical reactions may incorporate the peroxide group into unstable molecules: TATP, HMTD, DADP, MEKP. HP is most widely available as a 3% solution, but up to 27% in available to the public. To achieve better yield or to use HP as a liquid explosive, criminals boil the HP solution to evaporate water. We have identified non-toxic chemicals that, added to HP at ppm levels, promote HP decomposition at elevated temperatures. However, since low concentrations of HP can be used to synthesize TATP, we also seek materials that, added to acetone, reduce the yield and purity of TATP. Further, there are situations where the common render-safe procedure, blow-in-place, is not safe. We have found chemical methods that gently destroy TATP.

Mechanistic Investigation

To understand the decomposition of TATP & its conversion to DADP, we use theoretical (see poster) & experimental studies. We employ labeled compounds, mass spectroscopy & advanced NMR to elucidate the chemistry.



TATP decomposition kinetics: ¹H NMR taken every 5 min. after adding trifluoroacetic acid. Time interval between spectra is 200 min.



Technical Approach

Precursor Control: Acetone

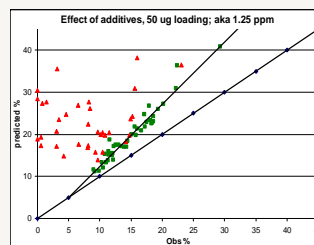
We have identified materials that interfere with acetone/HP reaction. Addition of these chemicals to acetone, reduce the amount and purity of the TATP produced.

Additivent	10% wt Additivent	
	Yield	melting point (° C)
No Additive	33-37%	90-95
Water	39%	82-94
Diethyl Ether	39%	85-95
Ethyl Acetate	37%	78-94
Methanol	41%	78-94
Ethylene Glycol	38%	86-93
2-Pentanol	44%	73-82
3-Pentanol	38%	72-86
Cyclopentanol	41%	68-87
2-Butanol	44%	68-80
2,3-Butanediol	42%	80-95
2,4-Pentanedione	41%	80-96
1,4-Cyclohexanedione	52%	75-95
Benzol	51%	69-82
Styrene	39%	72-80
Isobutylene (5% wt)	51%	78-88

Additivent	5% wt Additivent		10% wt Additivent	
	% Yield	HP:Acet Ratio 1:1	% Yield	HP:Acet Ratio 1:1
Metal Salts				
Clal	86%	77.90		
Ca(OAc) ₂ ·H ₂ O	48%	75.89		
ZnSO ₄	45%	79.65		
CuSO ₄	44%	74.84		
SnCl ₂ ·2H ₂ O	40%	74.89		
Ca(OAc) ₂ ·2H ₂ O	39%	75.80		
Clal·2H ₂ O	18%	73.81		
CuCl ₂ ·2H ₂ O	0%	—		
Salt Mixtures				
SnCl ₂ ·2H ₂ O/ZnCl ₂	62%	83.96	10%	1%
ZnCl ₂ ·SnCl ₂ ·2H ₂ O	62%	87.96	57%	84.90
Cu(OAc) ₂ ·H ₂ O/Et ₃ N	53%	81.96		
CaCl ₂ /Et ₃ N	26%	86.95		
SnCl ₂ ·2H ₂ O/Et ₃ N	15%	85.95		
ZnSO ₄ /Et ₃ N	11%	80.94		
PbCl ₂ ·H ₂ O/Et ₃ N	2%	90.95		
Amines				
Et ₃ N (triethylamine) (solid)			21%	91.94
NH ₃ (aq)			2%	85.92
DMTA (dimethylene triamine) (fresh)	22%	90.94	2%	94.96
DAP (diaminopropane) (old)			1%	91.97
Et ₃ N (triethylamine) (fresh)			4.97%	

Precursor Control: Hydrogen Peroxide (HP)

To prevent HP concentration for the making of liquid or solid peroxide explosives, we add GRAS* compounds at ppm levels to HP. Heating to drive off water promotes HP decomposition. We have identified additives which are safe for their HP market, catalysts for HP destruction at elevated temperature but do not affect storage stability of HP at 25-30° C.



GRAS = generally regarded as safe

Additive (1 mg/L)	Amount HP destroyed %		
	3% HP	12% HP	30% HP
I	33	21	18
II	90	27	25
III	27	16	20
IV	98	56	32
V	47	18	16
VI	38	20	20
VII	30	14	19
VIII	29	21	20
IX	36	19	21
X	99	55	31
X	27	25	17

Destruction



3 g TATP failure
100 g TATP success
Acid catalyzes TATP formation; it also destroys TATP. Strong acid reacts so quickly with TATP that it can detonate. A combination of weaker acid strength and slightly solvated TATP reduces rate of heat release & makes gentle destruct possible. Variables such as acid concentration, type & amount of solvent made the difference between success & failure. In December we gently destroyed 100 g TATP by moistening it with ethanol-water & adding concentrated HCl.

Accomplishments Through Current Year

A set of additives preventing HP concentration have been identified & tested & patent is in preparation. TATP destruction has been studied and a procedure to gently destroy TATP has been tested on 100 g TATP.

Future Work

Mechanistic studies continue as do those in precursor control. Prevention of TATP synthesis requires 10 wt% additive, probably too much. Adulteration of KNO₃ to reduce explosivity will continue.

Opportunities for Transition to Customer

Potential customers:
Beauty product manufacturers
3% HP suppliers
HP manufacturers
Acetone manufacturers

Patent Submissions

Security Safe Hydrogen Peroxide (in preparation)

Publications Acknowledging DHS Support

"Destruction of TATP – Theoretical Considerations"
Dubnikova, F; Kosloff, R; Oxley, J; Smith, J; Zeiri, Y, submitted *J Phys. Chem.*

"Gentle Destruction of TATP" Oxley, J.; Smith, J.; Brady, J. submitted *J Forensic. Sci.*

"Mechanism of the Acidic Decomposition of TATP"
Oxley, J.; Smith, J.; Zhang, G.; Brady, J manuscript in preparation.