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Destruction of Peroxide Explosives

ABSTRACT: Chemicals containing multiple peroxide functionalities, such as triacetone triperoxide (TATP), diacetone diperoxide (DADP), or hexamethylene triperoxide diamine (HMTD), can be explosive. They are impractical and are not used by legitimate military groups because they are shock and heat sensitive compared to military explosives. They are attractive to terrorists because synthesis is straightforward, requiring only a few easily obtained ingredients. Physical removal of these synthesis products is highly hazardous. This paper discusses methods to degrade peroxide explosives chemically, at room temperature. A number of mixtures containing metals (e.g., zinc, copper) and metal salts (e.g., zinc sulfate, copper chloride) were found effective, some capable of destroying TATP solutions in a few hours. Strong acids proved useful against solid peroxide materials; however, on a 1 g scale, addition of concentrated sulfuric acid caused TATP to detonate. Thus, this technique should only be used to destroy small-laboratory quantities.

KEYWORDS: forensic science, peroxides, destruction, TATP, DADP, HMTD, hydrogen peroxide, explosives

Improvised explosive devices (IEDs) may use conventional military explosives configured or reconfigured for a particular application, or they can be homemade devices powered by explosives which are relatively easy to make. Device construction is based on material availability and the creator's knowledge and imagination. In the U.S., most bombings use small, smokeless or black powder devices because the bombs are being used as murder weapons and because these powders are not heavily regulated. In Iraq, bombs are larger because they are the weapons of guerilla warfare and military explosives in the form of mortars, artillery shells, and landmines are ubiquitous. In the past, one of the major difficulties in bomb design was acquisition of initiating explosives. These are essential to the bomb function but not readily made. Typically, they required theft or illegal purchase. The ready knowledge of how to prepare peroxide explosives has been a major boon to the would-be bomber. While explosive performance of peroxide explosives is poorer than TNT, the Internet provides recipes and bulletin boards of advice on how to prepare initiating explosives such as triacetone triperoxide (TATP), diacetone diperoxide (DADP), or hexamethylene triperoxide diamine (HMTD), from readily acquired ingredients (Fig. 1). For law enforcement this has magnified the problems of detection and destruction.

Currently, the safest way to dispose of illegal explosives is to blow-in-place. This procedure keeps law enforcement from handling and transporting these highly sensitive materials. However, because relatively small quantities of peroxide explosives are usually discovered and they are frequently found in apartments and other high-population density areas, blow-in-place protocols are impractical. One of the goals of this work was to find a safe, effective, field-usable destruction method. A few publications have addressed this issue; two have suggested copper and tin salts to effect destruction at elevated temperature (1,2); one used mineral acids and elevated temperature (3). These articles were used as the starting point in a search for a room-temperature, chemical destruction method for peroxides.

Materials and Methods

Destruction of Peroxide Explosives

DADP, TATP, and HMTD were prepared in our laboratory (4,5). For initial destruction testing, a stock solution of TATP was made by dissolving it in tetrahydrofuran (THF) or ethanol (EtOH) to create a 200 mg/mL solution; typically, 5 mL of this solution was used. DADP and HMTD solutions were made in the same manner. The destruction reagents, such as a metal and metal chloride or sulfate salts were added to 20 mL flat-bottom vials. Distilled water (5 mL) was added and stirred until the salts dissolved. In some cases, sulfuric acid was added to adjust the pH of the aqueous solution. Five milliliters of the TATP, DADP or HMTD stock solution in THF or EtOH was added to the vial, and the mixture was stirred for 24 h and then analyze for remaining peroxide. If particulate was still visible, the slurry was allowed to settle. A 100 μ L syringe was used to transfer 0.100 mL reaction slurry/solution into a 2 mL volumetric flask, and the flask was filled with acetonitrile. Na₂SO₄ (anhydrous) was added to the volumetric flask to removed traces of water. If the solution had been acidified, a bit of NaHCO₃ (anhydrous) was added to neutralize the solution. It should be noted that combinations listed as "ambient" were subject to no pH adjustment. Solutions were filtered (Millex-FG syringe filters) into 2 mL, amber screw-cap gas chromatography (GC) vials, which were sealed with PTFE-septa screw-caps to await GC/ μ ECD analysis.

To determine whether solution destruction techniques would work on solid samples, 5 or 25 mg samples of DADP, TATP, or

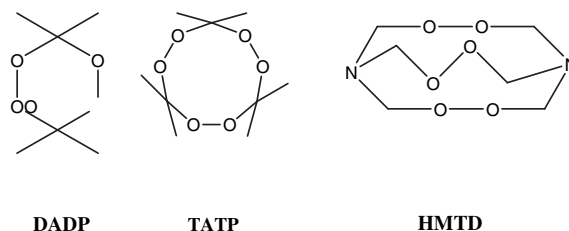


FIG. 1—Structures of DADP, TATP, and HMTD.

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TABLE 1—Metal/metal salts effectiveness in destroying TATP in THF solution (10 mg/15 mL).

Metal Salt	Metal	Equivalents Salt:TATP	Equivalents Metal:TATP	Added Acid	Solvent	TATP remaining after 24 h r.t. (%)
FeSO ₄		1 to 9 salt to 1 TATP		None or HCl	THF	100
FeCl ₂		1 to 3 salt to 1 TATP		None or HCl	THF	100*
CuSO ₄		2		None or HCl	THF	100
CuCl ₂		2 to 3 salt to 1 TATP		None or HCl	THF	100
ZnSO ₄		1		H ₂ SO ₄	THF	32
ZnCl ₂		3		H ₂ SO ₄	THF	60
CoCl ₂		1			THF	100
10%Pd(C)		1			THF	100
MgCl ₂		1			THF	100
FeCl ₃				pH = 1	EtOH	34
Co(NO ₃) ₂				1	EtOH	8
CrCl ₃ 6H ₂ O				1.3	EtOH	15
CrCl ₃ 6H ₂ O				1	EtOH	0
Cr ₂ O ₃				1.5	EtOH insoluble	0
Cr ₂ O ₃				1	EtOH insoluble	0
FeSO ₄	Fe	3	3		THF	100
FeCl ₂	Fe	3	3		THF	100
ZnSO ₄	Zn	3	3		THF	0
ZnCl ₂	Zn	3	3		THF	25
CuCl ₂	Cu	3	3		THF	5
CuSO ₄	Cu	3	3		THF	35
None	Cu	0	6		THF	100
None	Zn	0	6		THF	100
ZnSO ₄	Cu	3	3		THF	0
CuSO ₄	Zn	3	3		THF	100
M ₂ SO ₄	M = Mg,Al,Fe	3	3		THF	100
M(Cl) _n	M = Mg,Al,Fe	3	3		THF	100

*44% remains if rx in EtOH.

HMTD were placed in test tubes and treated with various reagents, typically 20 drops. Peroxide to reagent mole ratio was generally 1 to 5. The mixtures sat at room temperature without stirring for up to 12 h. After the soak time, 5 mL pentane or acetonitrile was added to the test tube to dissolve the remaining peroxide, and a 100 μ L aliquot of that solution was transferred into a 1 mL volumetric flask which was then filled to the mark with either pentane or acetonitrile. If acetonitrile was used, MgSO₄ (anhydrous) was added to the volumetric flask to remove traces of water, and, when necessary, a small amount of anhydrous NaHCO₃ was added to neutralize the solution. GC/ μ ECD was used to quantify the peroxide compound.

Gas Chromatography Analyses

GC- μ ECD was used to determine the amount of peroxide compound in the solution. An Agilent 6890 GC with μ -ECD and a

J&W DB-5 column (30 m \times 0.25 mm \times 0.25 μ m [film]) was employed. The inlet was set at 170°C with a 5:1 split ratio. The oven temperature started at 60°C; after a 1 min hold at 60°C, it was increased to 250°C at a ramp of 20°/min. The flow rate of helium in the column was constant at 4.0 mL/min. The μ -ECD detector was held at 300°C. Under these conditions, TATP retention time was 4.0 min and DADP retention, 2.1 min. For HMTD all the GC conditions were the same as above except that the inlet was set at 250°C with a 5:1 split ratio. The oven temperature started at 70°C; it was increased to 250°C at a ramp of 20°/min. The flow rate of helium in the column was constant at 8.0 mL/min. Under these conditions, HMTD retention time was 5.2 min. In all cases, untreated peroxide sample controls were analyzed alongside those treated for chemical destruction. This allowed direct determination of percent destruction.

TABLE 2—Metal/metal salt ratio effect on TATP destruction in THF (10 mg/15 mL).

Metal Salt	Metal	Equivalents Salt:TATP	Equivalents Metal:TATP	TATP Remaining After 24 h r.t. (%)
ZnSO ₄	Zn	0.3	3	77
ZnSO ₄	Zn	3	0.3	0
ZnSO ₄	Zn	3	0	100
ZnSO ₄	Zn	0	6	100
CuCl ₂	Cu	0.3	3	44
CuCl ₂	Cu	3	0.3	5
CuCl ₂	Cu	3	0	100
CuCl ₂	Cu	0	6	100
ZnSO ₄	Zn	3	3	0
CuCl ₂	Cu	3	3	5
ZnSO ₄	Cu	3	3	0

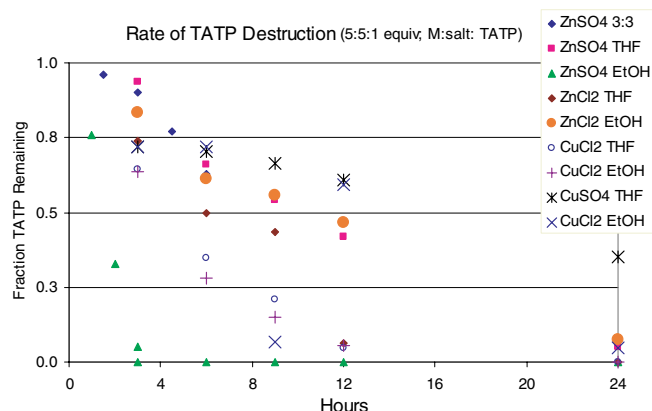


FIG. 2—Destruction of TATP over 24 h using various M/MX aqueous mixtures.

TABLE 3—Effects of SnCl₂ and SnSO₄ on the destruction of TATP.

Metal Salts (I)	Metal	Metal Salts (II)	pH	Solvent	TATP Remaining After 24 h r.t. (%)
SnCl ₂	Zn or Cu		1 or ambient	EtOH or THF	100
SnSO ₄	Zn or Cu		1 or ambient	EtOH or THF	100
SnCl ₂		ZnSO ₄	Ambient	EtOH or THF	<10
SnSO ₄		CuCl ₂	Ambient	EtOH or THF	<1

Results and Discussion

Destruction of THF Solutions of TATP

Previous work reported that TATP could be destroyed by reaction with tin (II) chloride or copper compounds at elevated temperatures (1–3). In this study, a number of metal salts were used to attempt the destruction of TATP. When it was observed that they did not function alone, metal or acid was added to enhance reactivity. The protocol involved dissolving TATP in THF or other solvent and adding an aqueous solution of the metal salt, with or without metal or acid. After a period of stirring at room temperature, usually 24 h, 100 µL of the peroxide-containing solution was diluted in acetonitrile and analyzed by GC/µECD to determine the amount of peroxide compound remaining. Table 1 shows the percentage of TATP remaining after 24 h exposure to various metal/metal salts; 0% indicates complete destruction of TATP, while 100% indicates essentially no destruction. Zinc and copper salts appear effective, but only when combined with metal. Neither was effective alone. The metal was required only in catalytic amounts. In contrast, more than an equivalent of the metal salt was required. In general, three equivalents were as effective as five (Table 2).

As would be expected, peroxide destruction was most effective if all the species were in solution. In most studies, THF was used to predissolve TATP and the metal salt. However, methanol or

TABLE 4—The effect of other salts on the destruction of TATP.

Metal Salts (I)	Metal Salts (II)	pH	Solvent	TATP Remaining After 24 h r.t. (%)
KI		1/0.6	EtOH	60/0
KI	CuCl ₂ or ZnSO ₄	1	EtOH	<5
NaBr	CuCl ₂ or ZnSO ₄	1	EtOH	<8
KI	CuCl ₂ or ZnSO ₄	Ambient	EtOH	<80
NaBr	CuCl ₂ or ZnSO ₄	Ambient	EtOH	100
KSCN	CuCl ₂ or ZnSO ₄	1 or ambient	EtOH or THF	100
Na ₂ SO ₃		1/ambient	EtOH or THF	60/100
Na ₂ S ₂ O ₃	CuCl ₂ or ZnSO ₄	1 or ambient	EtOH or THF	100
KMnO ₄		1	EtOH	50
KMnO ₄	MnSO ₄	1	EtOH	29
KMnO ₄	ZnSO ₄	1	EtOH	8
KMnO ₄	CuCl ₂	1	EtOH	60
KMnO ₄	Zn	1	EtOH insoluble	39
NH ₂ NH ₂		Ambient	EtOH	100
NH ₂ NH ₂	ZnSO ₄	Ambient	EtOH	100
NH ₂ NH ₂	CuCl ₂	Ambient	EtOH	48
NH ₂ NH ₂	ZnSO ₄	1	EtOH	100
NH ₂ NH ₂	CuCl ₂	1	EtOH	100
NH ₂ NH ₂	CuCl ₂	10	EtOH	46
NH ₂ NH ₂	KI	10	EtOH	42
NH ₂ NH ₂	Fe	10	EtOH insoluble	39
NH ₂ NH ₂	Cu	10	EtOH insoluble	35
P(OEt) ₃		Ambient	EtOH	100
PPh ₃	Alone or ZSO ₄	Ambient	EtOH	100
SMe ₂	Alone or ZSO ₄	Ambient	EtOH	100

EtOH was also effective in dissolving the metal salts. Under these circumstances after 24 h all the TATP had disappeared. However, in chloroform and hexane, in which the metal salts were not soluble, no loss of TATP was observed. These results illustrate the importance of dissolving both the metal salt and the TATP. Slight differences in the performance of the chloride and sulfate salts are

TABLE 5—Best candidates for destruction of TATP, DADP, and HMTD solutions (1 peroxide : 5 reactant1 : 5 reactant2).

Salt System	Solubility in Organic	TATP (20 mg) Remaining		DADP (10mg) Remaining		HMTD (10mg) Remaining	
		pH	THF (%)	EtOH (%)	THF (%)	THF (%)	
5 eq reagent in 5 mL organic + 5 mL water after 24 h							
Zn	ZnSO ₄	Insoluble	Ambient	0	0	3	31
Zn	ZnCl ₂	Insoluble	Ambient	0	7	7	76
Zn	ZnSO ₄	Insoluble	1	0			0
Zn	ZnCl ₂	Insoluble	1	0			0
Cu	CuCl ₂	Insoluble	Ambient	5	0	0	1
Cu	CuSO ₄	Insoluble	Ambient	35	5	20	15
SnCl ₂	ZnSO ₄	Insoluble	Ambient	1	0	7	1
SnCl ₂	CuCl ₂	Insoluble	Ambient	0	0	5	0
SnSO ₄	ZnSO ₄	Insoluble	Ambient	19	8	18	0
SnSO ₄	CuCl ₂	Insoluble	Ambient	0	1	5	0
KMnO ₄	ZnSO ₄	Soluble	Ambient	–	63	1	81
KMnO ₄	ZnSO ₄	Soluble	1	–	13	1	1
KMn ₄		Soluble	1		0	23	1
NH ₂ NH ₂	CuCl ₂	Soluble	Ambient		4	0	0
NH ₂ NH ₂	ZnSO ₄	Soluble	Ambient		58	–	–
KI	None	Soluble	1		11	86	0
KI	CuCl ₂	Soluble	1		5	41	0
KI	ZnSO ₄	Soluble	1		3	51	0
NaBr	None	Soluble	1		8		0
NaBr	CuCl ₂	Soluble	1		2	67	0
NaBr	ZnSO ₄	Soluble	1		3	37	0

attributed to solubility differences. For example, CuSO_4 was ineffective in destroying TATP if the THF solution of TATP was added to the water before the copper salt was fully dissolved.

It was found that combinations ZnSO_4 and CuCl_2 with Zn and Cu destroyed TATP within 24 h at room temperature. To determine whether a full 24 h was required, several zinc and copper combinations at a 5:5:1 ratios were tested. The results, shown in Fig. 2, show the destruction could be complete in as little as 3 h.

Tin salts have been reported effective in rapidly destroying TATP, but only at elevated temperatures (1,2). An attempt was made to promote room temperature reactivity with tin salts by adding metal and metal salts. While zinc or copper did not aid the action of the tin salts, zinc sulfate and copper chloride did (Table 3). Similarly, zinc sulfate or copper chloride added to KI and NaBr were found to be effective if acid were added to the solution (Table 4). Table 4 examines the effect on TATP solution of a number of oxidizing and reducing agents.

The combinations successful in destroying TATP were tested against DADP and HMTD. Since HMTD was not soluble in EtOH, studies of that peroxide were conducted in THF only. At the ratio of 5:5:1 equivalents of metals to equivalents metal salt to equivalent peroxide, complete destruction of TATP, DADP, and HMTD was accomplished in 24 h with most of the acidified combinations reported in Table 5.

Having found a number of combinations that destroy TATP when that species was dissolved in THF, we looked for a solvent more readily available to law enforcement. The first data column in Table 5 shows the loss of TATP after 24 h when aqueous EtOH solutions of it and the reagents were used. In cases where the reaction had been incomplete in THF, it went further to completion in EtOH, presumably due to the greater miscibility of the reactants. Unfortunately, HMTD is not soluble in EtOH; therefore, in determining reactivity of DADP and HMTD with the same reagents, the peroxides were dissolved in THF. Table 5 shows there are a number of soluble and insoluble chemical combinations that destroy all three peroxides.

Destruction of Solid Peroxides

Generally, HMTD was destroyed more readily than TATP; and DADP was the most difficult to decompose (Table 5). This is in line with their thermal stabilities. In some cases, GC-ECD analysis showed that TATP had been consumed, but DADP was present; it may be formed during TATP decomposition (6). The ordering roughly follows their thermal stabilities. Since HMTD was the most easily destroyed in solution, it was the first candidate for solid peroxide destruction studies. In a vial, one of the following salts (NaBr, KMnO_4 , CuCl_2 , ZnCl_2 , ZnSO_4 , SnSO_4 , sulfuric acid only) was placed on top of 5 mg of HMTD; four drops of an aqueous sulfuric acid solution were added; and the mixture was allowed to stand overnight. The mole ratio of salt to HMTD was 5 to 1; the neat acid was diluted 1 to 1 with water or 1 to 5 with water; nevertheless, in all cases consumption of HMTD was complete after 14 h. Using the same protocol the destruction of TATP was attempted, and the reaction was monitored over a 12-h interval. None of the acids which had been diluted 1 to 5 with water destroyed TATP completely within that time, nor did battery acid (labeled "battery" in Table 6). A number of combinations of chemicals resulted in complete TATP destruction within 5 to 8 h, but the goal was complete destruction in under 2 h. Meeting that criteria, were only the concentrated mineral acids—methyl sulfonic acid

(99%), sulfuric acid (98%), nitric acid (70%), and hydrochloric acid (36%) (Table 6). This is in line with the report (3) that hydrobromic acid destroys HMTD and hydroiodic acid destroys TATP within 2 h. **Warning:** *The destruction of 1 g of TATP confined in a plastic vial was attempted remotely using less than 10 mL concentrated sulfuric acid. The sample detonated.*

Conclusions

The goal was to find a chemical "cocktail" that when sprayed on any of the sensitive solid peroxides, would cause quiescent decomposition without further handling. Destruction of TATP, DADP, and HMTD solutions could be affected in 24 h at room temperature by the application of ZnSO_4 , or CuCl_2 if these salts were used in combination with (a) zinc or copper metal; (b) tin chloride or sulfate salts; (c) KMnO_4 , NH_2NH_2 , KI, or NaBr. Reagents (a) or (b) are effective but yield slurries rather than solutions. Any of the reagents listed in (c) when combined with zinc sulfate or copper chloride are water soluble. Most of these systems affect destruction more rapidly when acidified; this may be due to increased solubility.

This study demonstrated that strong acids, methyl sulfonic acid (99%), sulfuric acid (98%), and nitric acid (70%), when applied directly to solid (5 mg) TATP, DADP, and HMTD, even without stirring, accomplished destruction in 15 min. *However, this destruction technique is unsuitable for use in even gram quantities of TATP. We believe the reaction with acid is exothermic. While this is not noticeable on the milligram-scale, it provides sufficient energy to initiate the TATP on the gram-scale. Gram-scale tests have not been performed on DADP or HMTD.* Thus, further safety tests are required. Nevertheless, it can readily be used by canine trainers to simply dispose of the small quantities of these peroxides found on canine training aids.

Acknowledgments

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