TECHNICAL NOTE

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Triacetone Triperoxide: Its Chemical Destruction

ABSTRACT: Due to the known use of triacetone triperoxide (TATP) as an improvized explosive by terrorist organizations, it is essential that those involved in dealing with suspect materials should be aware of the characteristic properties of TATP, and have a means for disposing of it. This paper evaluates possible methods for disposing of TATP and describes in detail a convenient chemical reduction method. The risks involved in handling this sensitive explosive are shown to be considerably reduced by dissolving it in toluene.

KEYWORDS: forensic science, triacetone triperoxide (TATP), improvized explosives, chemical destruction

Triacetone triperoxide (TATP, I) is prepared by reacting acetone and hydrogen peroxide in the presence of an acid catalyst (1,2), and has been used as an improvized explosive by terrorist organizations in, for example, Israel (3), USA (4,5) and the UK (6). We have investigated reactions that might provide a means of destruction of TATP samples and identified one which allows convenient disposal.

(I)   (II)

Results and Discussion

As an explosive TATP is reported (2) to be almost as powerful as TNT, but is 'extremely sensitive' to friction and is 'one of the most sensitive explosives known' in impact sensitivity tests. It is also reported (2) to detonate even when it contains up to 25% wa-

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ter. The sublimation of TATP, even at room temperature (weight loss 6.5% at 14–18°C during 24 h, 68.6% during 14 days (2)), can also contribute to the hazards associated with handling the material.

The purity of a TATP sample was found to be dependant upon the acid used to catalyze the condenzation, HCl giving a much purer product than H_2SO_4 as judged by TLC, GC, FTIR and DSC. The TATP from a H_2SO_4 catalyzed reaction is usually contaminated (TLC, GC, FTIR) with diacetone diperoxide (DADP, II).

While TATP is insoluble in water, it is very soluble in both chloroform and toluene (see Table 1 for solubility measurements made at room temperature for various common solvents; the results agree reasonably well with those reported (2)). In seeking a solvent that would enable TATP to be handled with reduced risk of accidental initiation, toluene appeared to offer both high solubility and low volatility. By contrast, chloroform is very volatile. Toluene was therefore selected for closer study. In order to ascertain the hazards posed by handling toluene solutions of TATP, trials were performed in an attempt to detonate these solutions using a no. 8 detonator (see Experimental). It was observed that saturated solutions of TATP in toluene (~28 wt%) could not be initiated, and it is therefore concluded that TATP can be rendered relatively benign by dissolution in toluene. Such solutions are chemically stable and may be stored in a closed vessel provided the cap/stopper is leakproof; leakage would result in evaporation of the toluene leaving a dangerous residue of TATP on the outer surface of the vessel. However, should such a residue be formed, it may be allowed to sublime away in a well-ventilated area. It is recommended that a seal with an inert plastic disc insert be used in order to avoid solid TATP crystallizing within the threads of a screw cap.

Chemical Destruction of TATP

Destruction of unwanted samples of TATP could in principal be achieved in three ways (a) burning, preferably of a TATP solution, (b) thermal degradation, and (c) chemical destruction.

Destruction by burning of an acetone solution of TATP has been found to be somewhat hazardous, with localized detonations occurring periodically. This was probably due to evaporation of the solvent and might be more controlled if toluene or xylene solutions were used, but this method is not recommended. Destruction by thermal degradation is also not recommended as it is rather slow. Simple thermolysis of TATP in refluxing toluene (b.p. 111°C) was found to leave some TATP unchanged even after 12 days. In this respect, TATP resembles di-t-butyl peroxide; the half-life for thermal destruction of the latter at 111°C is about 105 h (calculated from data in ref. 7). The half-life for the decomposition of TATP in

TABLE 1—*Solubility of TATP in common solvents at room temperature.*

Solvent	g/100 mL Solvent	wt%	lit (2)*
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

  * Units unspecified; assumed to be wt%.

benzene at 100°C, in the presence of aqueous H_2SO_4, is reported to be 44 min; this is further reduced to 31 min and 27 min respectively when hydroquinone or triphenylthiophosphate are also present (8).

In searching for a chemical method of destruction for TATP, it was observed that TATP, like di-t-butyl peroxide (9), does not behave as a typical dialkyl peroxide. Little or no reaction was observed with many of the reducing agents commonly used to destroy peroxides viz. acidified KI (the iodine coloration took several days to develop in toluene and chloroform solutions; this was not noticeably affected by adding 18-Crown-6), $FeSO_4$, $(NH_4)_2SO_4 \cdot FeSO_4$, Ph_3P.

However TATP was found to be readily reduced by an excess of tin(II) chloride in ethanol (<1 h at reflux, 6 h at 65°C, no reaction at room temperature) to give water-soluble products. The reduction was also found to work satisfactorily with toluene as a co-solvent, and, since toluene solutions of TATP had already been shown to be insensitive to initiation, this gave a simple and convenient method for chemical destruction of TATP (see Experimental for details). Although pure TATP could be destroyed within 30 min by this method, it was observed that DADP reacted more slowly and required a longer reaction time (~2 h). DADP is invariably present to some extent in the TATP from a H_2SO_4 catalyzed preparation, and it is also formed during the reduction of such a sample, increasing the quantity of DADP requiring destruction. [DADP is not formed during reduction of TATP from a HCl catalyzed preparation.] Consequently, destruction of a sample of TATP of unknown origin and purity requires a minimum of 2 h to ensure that all of the DADP has been reduced.

Experimental

Warning—Triacetone triperoxide is an extremely sensitive explosive and should be treated with the utmost caution. Even small (<1 g) amounts should be handled with great care. Where possible use protective shielding. If the dry solid is encountered in quantities exceeding 1 g, it should be either dissolved in toluene immediately, with minimal handling, or soaked in water. Water-wet TATP may be subsequently dissolved in toluene and the aqueous layer separated. The chemical destruction of TATP described below is still effective if the toluene solution is saturated with water.

TATP and DADP were prepared as described (1,2). It was observed that TATP has a terpene-like smell and this could be a useful characteristic for preliminary identification at a crime scene.

TLC Conditions for Analysis of TATP and DADP

Plates—Merck precoated silica gel 60 F_{254}, 0.25 mm on glass (both sample spots are invisible under UV light); sample solvent-

ethyl acetate (1 mg/mL); development solvent—toluene; spray reagent—1% diphenylamine in conc. H_2SO_4; R_f values—TATP 0.57, DADP 0.66.

GC Conditions

Column—CO-SIL-8CB, 1 μm, 0.33 mm ID, 25 m; temperature programme 50°C (1 min) then increasing at 10 K min^{-1} to 250°C (10 min); on column injection of dichloromethane solutions; RT values—TATP 9.65, DADP 5.15 min.

DSC Conditions

1–2 mg in a sealed pan; $20 \rightarrow 120°C$ at 3 K min^{-1} for melting endotherm only, $20 \rightarrow 200°C$ at 10 K min^{-1} for decomposition. Pure TATP exhibits a sharp-melting endotherm at 97°C (Fig. 1) and exothermic decomposition above 160°C. The DSC characteristics of impure TATP are variable (depending upon the acid used to catalyze the condensation reaction), with both melting (broad endotherm) and decomposition occurring at lower temperatures.

FTIR Analysis

As KBr discs. Fig. 2: pure TATP; Fig. 3: TATP + DADP.

Sensitivity to Detonation of TATP Solutions in Toluene

An essentially saturated solution of TATP (60 mL) was placed in a cylindrical glass tube (diam. 35 mm, height 95 mm), the flat base of which was glued onto an aluminum witness plate. A no. 8 detonator was inserted to a depth of 15–20 mm into the solution and fired. After firing, the remains of the glass tube and the witness plate were examined. A control firing used water instead of the toluene solution.

No measurable dent was observed on the witness plate in 6 such firings. The base of the glass tube remained intact and was still glued to the witness plate. This mirrored the firing of a no. 8 detonator in water.
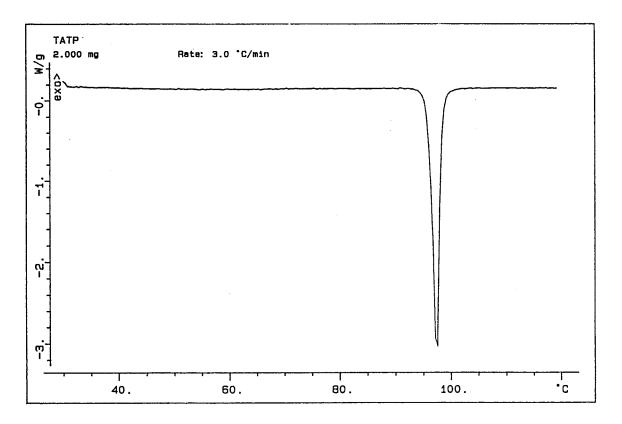
Destruction of TATP

Thermolysis of TATP in Toluene

TATP (30 mg) in toluene (30 mL) was heated under reflux during 280 h. After this time TLC analysis still indicated the presence of TATP. Analysis of the final solution by GC-MS indicated that the following were present: bibenzyl, benzyl alcohol, benzaldehyde, trimethylbenzene and TATP.

Chemical Destruction of TATP

(a) 1 g TATP scale - $SnCl_2 \cdot 2H_2O$ (6.0 g, 27 mmol, ~100% excess) was dissolved in ethanol or methylated spirit (10 or 30 mL) and heated to boiling. A solution of TATP (1.0 g, 4.5 mmol; endothermic dissolution) in toluene (4 or 6 mL respectively) was added to the boiling solution and the course of the reduction was monitored by TLC. When all of the TATP had been reduced (45 min for the larger solvent volumes, 10 min for the smaller solvent volumes), the hot, clear, yellow solution was poured into water (450 mL) to give a white suspension. Concentrated HCl (5 mL) was added and the mixture stirred briefly. A clear solution was obtained after standing overnight.

When the smaller quantities of solvent were used, boiling became more vigorous during and immediately after the addition, but with the larger quantities of solvent there was no noticeable
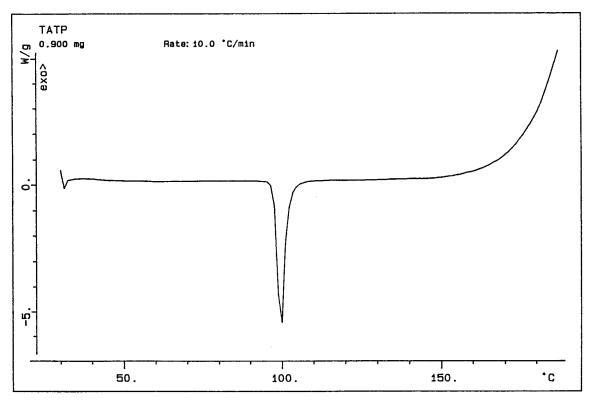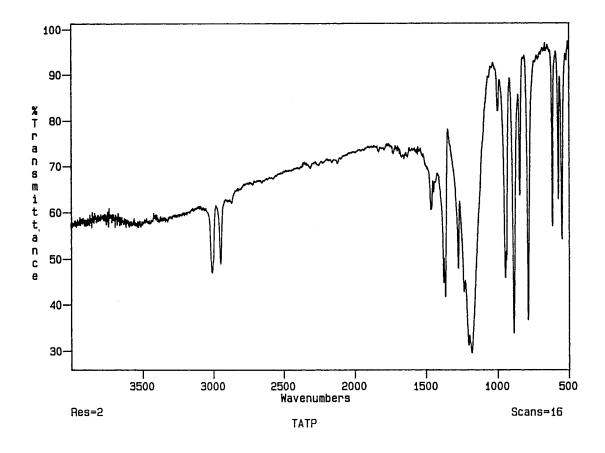
TATP
2.000 mg   Rate: 3.0 °C/min
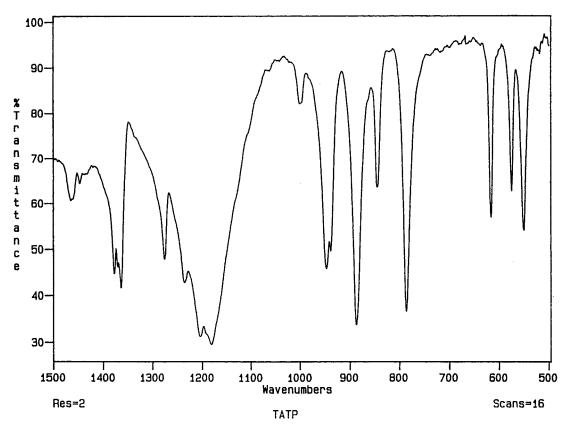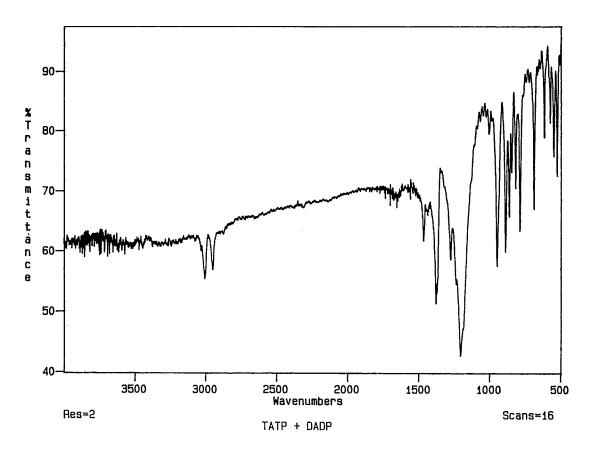
FIG. 1—*DSC of pure TATP.*
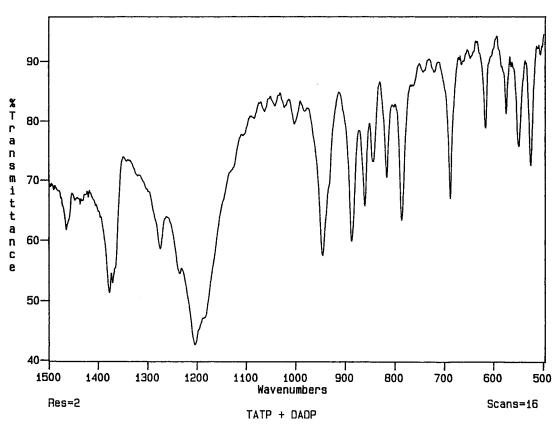
FIG. 2—*FTIR of pure TATP.*

FIG. 3—*FTIR of TATP + DADP.*

exotherm. During the course of the reduction the boiling temperature of the solution decreased, presumably due to the release of acetone. For TATP prepared by the H_2SO_4 method, there appeared to be competition between reduction of the TATP and its conversion to DADP. Pure DADP, added as a slurry in toluene due to its lower solubility compared to TATP ($<$5 wt% vs 28 wt%), required about 2 h for complete reduction under the same conditions. The presence of DADP as a contaminant in TATP prepared by the H_2SO_4 method became apparent during the preparation of the toluene solution prior to the addition, because the solution was always cloudy, presumably due to undissolved DADP.

(b) Larger scale destruction. $SnCl_2 \cdot 2H_2O$ (96 g, 0.425 mol, ~100% excess) was dissolved in methylated spirit (160 mL) and heated to boiling in a round-bottomed flask fitted with a reflux condenser. The flask was removed from the heat source and a solution of TATP (~16 g, 0.072 mol, containing some DADP) in toluene (50 mL) was added at such a rate as to maintain gentle boiling (10 min). [Should any solid TATP crystallize on the tip of the addition tube, it may be washed in with a little toluene, as can the solution residue in the addition vessel.] The flask was returned to the heat source and refluxing was continued for 2 h. (TLC indicated that all TATP and DADP had disappeared after 15 and 60 min respectively. However, the absence of TATP/DADP should always be checked by TLC before discontinuing heating.) The final, pale yellow solution was poured into water (4), acidified with concentrated HCl (80 mL), and left until clear before discarding.

While the author has not destroyed TATP on a scale larger than 16 g, it is anticipated that larger scale destruction could use the same procedure, provided that the rate of addition of the TATP/toluene solution is controlled in order to allow time for the heat liberated to be dissipated by gentle boiling of the solvent.

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