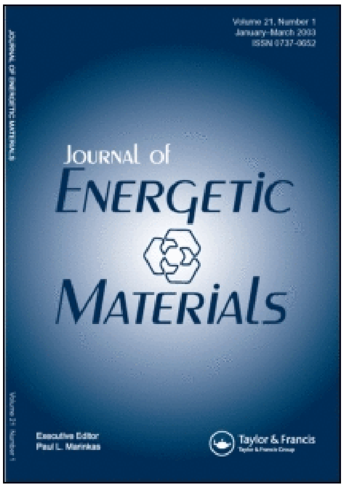

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TATB—Strong basic reactions provide soluble derivatives for a simple, qualitative high explosive spot test

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TATB — STRONG BASIC REACTIONS PROVIDE SOLUBLE DERIVATIVES FOR A SIMPLE, QUALITATIVE HIGH EXPLOSIVE SPOT TEST

by

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ABSTRACT

Reactions of TATB in aqueous, strongly basic solutions gave metal salts of 1,3,5-trihydroxy-2,4,6-trinitrobenzene (THTNB) also called trinitrophloroglucinol. Thus, we prepared potassium, sodium, and barium salts. The mono- and diammonium salts were prepared by treating THTNB with ammonia and ammonium hydroxide, respectively. Some explosive properties of the salts were evaluated. From the physical characteristics of the salts in various solvents, a spot test was developed for known high explosives (HE) containing TATB.

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I. INTRODUCTION

High explosives (HE) may become scattered among fragmented materials during field testing of weapons. It would obviously be desirable to identify the HE promptly so it can be removed before it burns or detonates. 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB), in particular, is difficult to distinguish from colored inert materials; it is insoluble in most solvents and does not respond to known identification tests. This is attributable to the fact that it is a symmetrical, strongly hydrogen-bonded compound. We have developed a test for TATB based upon its reaction with strong bases. However, the products from these reactions are energetic compounds.

II. PROCEDURES

A. Spot Test for Explosives

Milligram quantities of selected explosives were placed on Whatman No. 2, 9-mm filter paper. Test solutions (n-butylamines, KOH, diethylamine, ethylenediamine or BW_H reagent) were thoroughly shaken and a few drops added to the explosive. Characteristic colors were observed for positive reaction. The amine solutions were 20% amine and 80% solvent. The composition of BW_H reagent was 90Ml DMSO, 5Ml H_2O, and 5 g of potassium hyroxide.

B. Reaction of TATB with Strong Bases, NaOH, KOH, $Ba(OH)_2$

Six and one-half grams (0.025M) of TATB were dissolved in 100 ml of 3M $M(OH)_x$, where M = Na, K, Ba; X = 1, 2. The solution was heated on a hot plate at 83-85°C for 2.5 h, then cooled at room temperature overnight. During cooling large orange crystals precipitated, which were filtered through a medium-pore sintered-glass crucible and air dried. A 75:25 per cent mixture of water:ethanol was used to recrystallize the salts. The ratio of the solvent mixture was changed to 25:75 water:ethanol in some recrystallization processes. Samples of the respective salts were taken for elemental and DTA analyses. Then the remainder of the sample was oven-dried at 130°C for several hours.

Additional tests were run on the salts. Nuclear Magnetic Resonance (NMR) spectra were run for identification. Spark-gap, hammer, and impact-sensitivity tests were also performed.

C. Reaction of Ammonium Hydroxide with THTNB

Several batches of the sodium salt of trinitrophloroglucinol were combined and treated with 6N H_2SO_4. A quantitative yield of 1,3,5-trihydroxy-2,4,6-trinitrobenzene, THTNB, was obtained.

One hundred milliliters of concentrated ammonium hydroxide were used to dissolve 1.4882 g (0.006M) THTNB. The solution was heated just below boiling temperature, 80-85°C for 30 min. The water was removed on a Rota-Vac and orange crystals precipitated. The product was recrystallized from water. Elemental and DTA analyses were obtained. The compound was identified as the diammonium salt of 1,3,5-trinitrophloroglucinol.

Also, an attempt was made to prepare the diammonium salt by bubbling NH_3 through an aqueous solution of THTNB. The mono-ammonium salt was the final product.

III. RESULTS AND DISCUSSION

A. Chemistry of the Spot Test

The compounds tested are the more common DOE explosives (Table I). Only those with aromatic nuclei, TNT, tetryl, and TATB, react with BW_H reagent to give a positive color test. The color is attributed to the formation of resonance-stabilized anion. There are two possible and probably co-existing mechanisms that would explain the anion formation (Reactions 1-5). The Meisenheimer-type intermediate produced by the reaction of base with HE is responsible for the color.

The BW_H reagent (90 Ml DMSO, 5 g KOH, and 5 Ml H_2O) is shaken thoroughly before each use. One can vary the composition of the reagent. However, if the amount of water and KOH exceeds 20%, other explosives such as RDX may produce a faint color. Results would be similar to what one sees with very concentrated KOH solution, but could not be confused with the bright orange color produced from TATB. One would also notice a decrease in the solubility of TATB in the test reagent.

The reagent did not give positive results with TATB when other aprotic solvents were substituted for DMSO. The corresponding anions from N,N-dimethylformamide (DMF) and hexamethylphosphortriamide (HMPA) do not have low-energy resonance stabilized intermediates as does the DMSO anion (Reactions 1 and 2, Reaction 1 being the most likely of the two). We have eliminated the hydroxyl ion as the attacking species because 5M aqueous KOH did not react with TATB under our test conditions. However, we were able to hydrolyze TATB in strong base solution at elevated temperatures. Both the amine group

TABLE I

RESULTS FROM A SPOT TEST FOR POLYNUCLEAR COMPOUNDS USED IN THE MORE COMMON DOE HIGH EXPLOSIVES

Reagents[a]	Ethylenediamine		n-Butyl amine	Dimethyl amine		BW_H Reagent [b] 90 ml DMSO, 5 g KOH,
Compounds	H_2O	DMSO	DMSO	DMSO	5 M KOH	5 ml H_2O
KEl-F	NR	NR	NR	NR	NR	NR
HMX	NR	NR	NR	NR	NR	NR
PETN	NR	NR	NR	NR	NR	NR
TETRYL[c]	Red	Red	Red	Red	Red	Red
RDX	NR	NR	NR	NR	NR	NR
TNT	Wine	Wine	Purple	Wine	Purple	Purple
TATB[c]	NR	Yellow orange	NR	NR	NR	Bright orange

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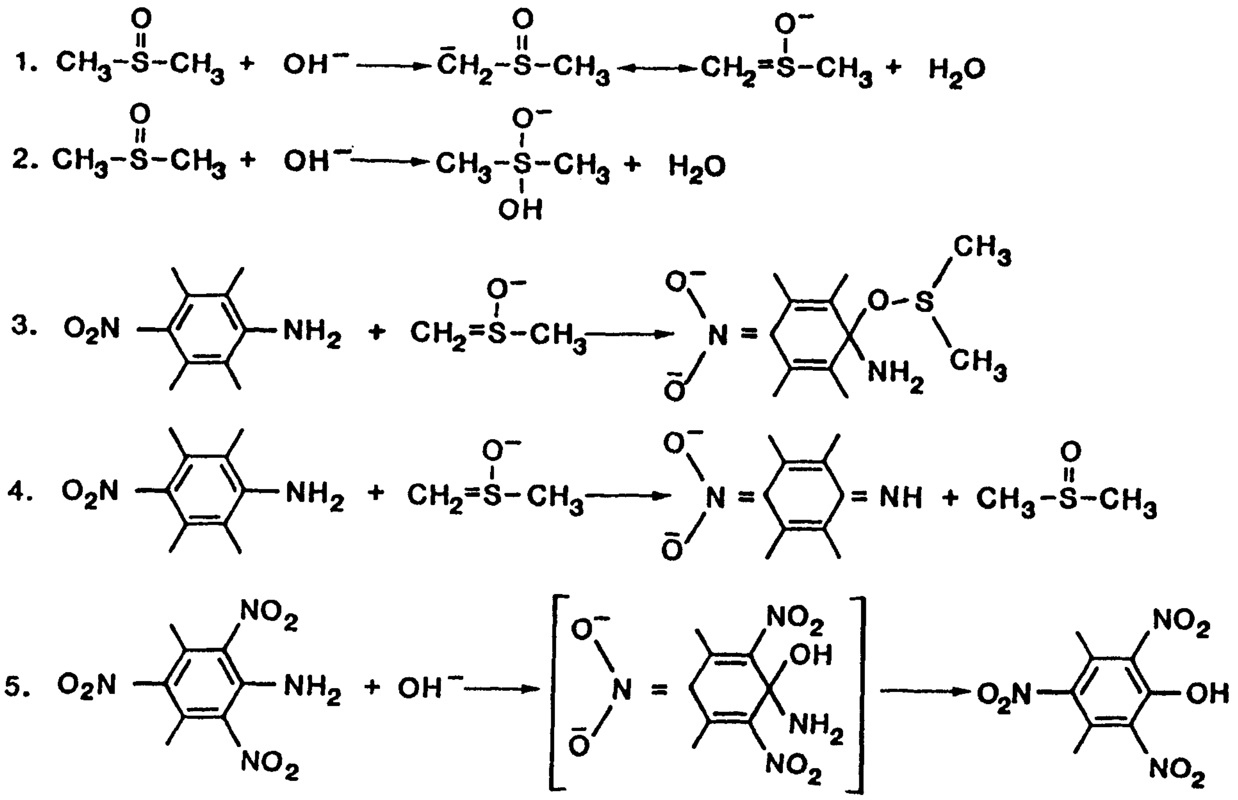
[a] The amines used as reagents were 20% by volume in a given solvent.

[b] Also tested with BW_H reagent were Cyclotol and Composition B, which gave a purple color. PBX 9404, PBX 9010, and PBX 9011 gave negative test results.

[c] These are yellow solids whereas the other compounds are colorless.

REACTIONS



$$1.\ CH_3-\overset{\overset{O}{\parallel}}{S}-CH_3 + OH^- \longrightarrow \bar{C}H_2-\overset{\overset{O}{\parallel}}{S}-CH_3 \longleftrightarrow CH_2=\overset{\overset{O^-}{|}}{S}-CH_3 + H_2O$$

$$2.\ CH_3-\overset{\overset{O}{\parallel}}{S}-CH_3 + OH^- \longrightarrow CH_3-\underset{\underset{OH}{|}}{\overset{\overset{O^-}{|}}{S}}-CH_3 + H_2O$$

and the ring are possible positions of attack. When less concentrated base was used to generate the colored intermediates, they reverted back to TATB when quenched. It was the color of the hydrolyzed products, trinitrophloroglucinol salts, that prompted the investigation for the spot test using this chemistry.

The bright orange color produced when TATB reacts with BW_H reagent is unique. It is easily distinguished from the bright red color produced with the test reagent and other explosives, such as dipicramide, or with TATB impurities. These compounds readily dissolve in the test reagent producing the intense red color whereas TATB is not extensively solubilized. In addition to dipicramide, the TATB impurities tested were 1-chloro-2,4-diamino-3,5-dinitrobenzene (ClDADNB), 1,3-diamino-2,4,6-trinitrobenze (DATNB), and 1,3,5-triamino-2,4-dinitrobenzene (TADNB).

B. Hydrolysis of TATB with Base

TATB was hydrolyzed to the salts of trihydroxytrinitrobenzene (THTNB), which were isolated as orange-yellow hydrates, that became yellow upon heating. Recrystallization from ethanol also gave a yellow precipitate. Sufficiently concentrated base solution, 3-5 M, gave tri-metal, sodium and potassium salts as the major product (Reaction 5). More dilute aqueous solution of base gave predominantly the mono- and di-sodium or -potassium salts. Our infrared analysis gave positive evidence that the amine group was still present in the mono- and di-metal salts. Elemental analyses were in agreement with those calculated.

A DTA endotherm at 140°C was accredited to the removal of water of crystallization (Table II). The endotherm shifted to higher temperatures (150-165°C) when ethanol was used as a recrystallization solvent. We did not determine whether this was caused by an entrapped solvent or by the production of THTNB as an impurity. Exotherms are also listed in Table II.

Elemental analyses and other data suggest that barium hydroxide reacts with TATB to form the diphenoxy barium salt. Again, the amine groups are detected by infrared spectroscopy. The half salt was prepared by heating the product from the first reaction in hot water.

Concentrated ammonium hydroxide was used to prepare the diammonium salt from THTNB, but we were not successful in forcing the reaction to go to the triammonium derivative. When ammonia gas was bubbled through the aqueous THTNB solution, only the mono-ammonium salt was produced. We attempted to confirm the presence of the two ammonium ions in the partially reacted molecules by ^{13}NMR, but were unsuccessful (Table III); exchange between the ammonium ions and the negative oxygen was too rapid. A typical structure of salts might be:

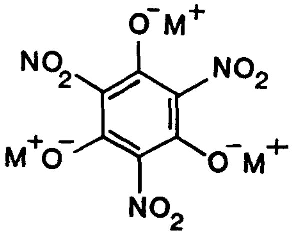


TABLE II

DTA ANALYSES OF PRODUCTS ISOLATED FROM THE REACTION OF TATB WITH STRONG BASES, NaOH, KOH, $Ba(OH)_2$. ALSO, DTAs OF THE AMMONIUM SALTS FROM THE REACTION OF CONCENTRATED NH_4OH WITH THTNB. HEATING RATE 20°C/MIN.

Compound	Molecular Formula	Hydration[a]	Endotherm (°C)	Exotherm(s) (°C)
THTNB	$C_6H_3N_3O_9$	$2H_2O$	155,168	178
Na_3THTNB	$C_6H_4N_3O_{11}Na_3$	$2H_2O$	140	245, 295, 345
Na_2ADHTNB	$C_6H_4N_3O_{11}Na_2$	$2H_2O$	140	245, 295, 345
K_2ADHTNB	$C_6H_6N_4O_{10}K_2$	$2H_2O$	150	265
K_3THTNB	$C_2H_2N_3O_{11}K_3$	$1H_2O$	140	275
NH_4 DAHTNB	$C_6H_8N_5O_7$	Dried	---	232
$(NH_4)_2$ ADNHTNB	$C_6H_{10}N_6O_8$	Dried	---	257
Ba $(DAHTNB)_2$	$C_{12}H_8N_{10}O_{14}Ba$		---	295, 355 (Doublet)

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[a] Recrystallization from 25:75 water:ethanol causes the endotherm to be shifted to higher temperatures (150-165°C range).

TABLE III

^{13}C-NMR OF THHTNB AND ITS SALTS IN D_2O

Compounds	Chemical Shifts (ppm)	
THTNB	145.88	114.97
K_3THTNB	150.70	118.67
Na_3THTNB	149.30	117.60
$(NH_4)_2$ ADHTNB	152.60	116.62

Determination of the explosive properties of these salts showed that the potassium and sodium salts are insensitive in the hydrated form; however, the dry salts are sensitive to both spark and impact (Table IV). The hydrated salts have an impact sensitivity comparable to that of granular TNT, whereas, that of the dried salt more closely parallels the sensitivity of Composition A-3. Some recrystallized forms of the barium salts detonated during elemental analyses but these salts would not be produced in significant quantities in the spot test. Therefore, special anti-explosive precautions are unnecessary.

IV. CONCLUSIONS

Solutions of the DMSO anion react with TATB to give a bright orange resonance-stabilized anion that is easily distinguished from the bright red solution produced with other explosives or with the TATB impurities. This is the

TABLE IV

EXPLOSIVE PROPERTIES OF TRINITROPHLOROGLUCINOL SALTS FROM THE HYDROLYSIS OF TATB WITH BASE AT ELEVATED TEMPERATURES

	Sensitivity 50% Height (cm)		Mean Energy	
Compounds	Type 12	Type 12B	3-mil Foil (J)	10-mil Foil (J)
K_3THTNB (dried)	85	—	0.17	0.19
K_3THTNB (hydrated)	148	—	—	—
Na_3THTNB (dried)	1 go at 320 cm	1 go at 320 cm	0.50	0.53
Na_3THTNB (hydrated)	166	119	—	—
$Ba(DAHTNB)_2$	1 go at 320 cm	191	0.36	0.87
RDX	22	41	0.22	0.55
PETN	12	37	0.19	0.36
TNT	80	>177	0.46	2.75

basis for the spot test for TATB using BW_H reagent. This reagent is stable, easy to use, and chemically safe. Ethylenediamine/DMSO, diethyl amine/DMSO and strong bases are known test reagents for polynitro compounds.[1-6] However, they were inadequate for TATB primarily because of its insolubility in the reagent. BW_H reagent dissolves enough TATB to be a valuable tool for identifying the compound in the field, on contaminated equipment, or in the work places.

V. GLOSSARY

ADHTNB	Aminodihydroxytrinitrobenzene
ClDADNB	Chlorodiaminodinitrobenzene
DAHTNB	Diaminohydroxytrinitrobenzene
DATNB	Diaminotrinitrobenzene
HMX	1,2,5,7-Tetranitro-1,3,5,7-tetrazacyclooctane
Kel-F	Chlorotrifluoroethylene/Vinylindine Fluoride Copolymer 3:1
PETN	Pentaerythritol tetranitrate
TATB	1,3,5-Triamino-2,4,6-trinitrobenzene
TETRYL	Trinitrophenylmethylnitramine
THTNB	Trihydroxtrinitrobenzene
TNT	1,3,5-Trinitrotoluene

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REFERENCES

1. D. J. Glover and E. G. Kayser, Anal. Chem. 40, p. 2055 (1968).
2. J. P. Hoetis and J. W. Cavett, Anal. Chem., 31, p. 1977 (1959).
3. J. W. Wilbrand, Ann. 128 p. 18 (1863).
4. P. Hepp, Ann. 215 pp. 316, 344 (1882).
5. J. Urbanski, S. Kwiatkowska, and W. Kutkiewicz, Bull. Acad. Polon. Sci., Ser. Chim., 7 p. 397 (1959).
6. E. F. Reese, "Color Reactions and Color Reagents," in "Encyclopedia of Explosives and Related Items," 3 p. C 405 (1966), edited by B. T. Fedoroff and D. E. Sheffield, PA-TR-2700, Picatinny Arsenal, Dover, NJ.

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