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TEX, by AXT

1 Background

1.1 TEX (4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane) (4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diaza-tetracyclododecane)

TEX is a recently synthesized explosive that may comply to the very strict property requirements needed for a commercial or military explosive. As an explosive, TEX is notable for its very high density. Having a measured crystal density of 1.99, TEX has one of the highest known densities of all CHNO based explosives. This high density is due to its isowurtzitane structure having a close-packed crystal lattice, with the nitro groups occupying the free space between the cages[1].

TEX is very energetic, combining a high velocity of detonation with low sensitivity to mechanical stimuli and good thermal stability. The seven-membered rings of the isowurtzitane structure put a strain on the cage and thus increase the energy content of the molecule. A part of the explosive power of TEX is derived from this cage strain[1]. The insensitive nature of TEX suggests that it may be a suitable high performance alternative to such explosives as TATB and NTO, thus giving RDX class performance to insensitive compositions[3]. Comparative performance figures for these explosives is shown in Table 1.

The original synthesis of TEX reported by Joseph Boyer and colleagues[5] involved the nitration of a mixture of 1,4-diformyl-2,3,5,6-tetrahydroxypiperazine (DFTHP) and trimeric glyoxal with mixed 100% nitric and sulphuric acids, a process that required over two days to complete. This method was found by Highsmith and coworkers to only provide low yields of impure products. It was later discovered and patented by Highsmith that the nitration of DFTHP to TEX could be done in the absence of trimeric glyoxal, and even in very mild nitrating conditions[10].

The exact mechanism by which TEX is formed from DFTHP is not known, but its believed that strong acids serve to catalyse the formation of the isowurtzitane structure [10]. The crude TEX is usually accompanied by some reaction by-products, both lower and higher nitrated derivatives, up to HNIW. These compounds do not significantly affect the sensitivity or performance of compositions containing TEX[3]. Crude TEX of 97% purity is described as a pale yellow solid[10].

The precursor, DFTHP, is formed by the condensation of two molecules of glyoxal with two of formamide at pH 9[6, 7, 9]. It is possible to substitute formamide with other

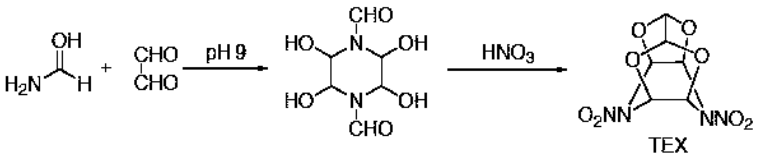
Figure 1: Properties of selected explosives. RDX: Cyclotrimethylenetrinitramine; HMX: Cyclotetramethylenetetranitramine; NTO: 3-nitro-1,2,4-triazol-5-one; NQ: Nitroguanidine

	Calculated			Measured				
Explosive	Density (g/cm^3)	VOD (m/s)	P_{CJ} (Kbar)	Density (g/cm^3)	VOD (m/s)	P_{CJ} (Kbar)	Impact (cm)	Impact (J)
TEX	1.99	8665	370.00	1.99			33	24.25
RDX	1.82	8802	359.58	1.77	8700	338	3.5	5.90
HMX	1.90	9046	392.56	1.905	9110	390	1.8	6.40
NTO	1.91	8120	306.99					71.71
NQ	1.710	8348	286.39	1.55	7650			43.45
References	[3]			[2]			[3]	[4]

suitable amines, such as sodium sulphamate, to form the analogous disodium-2,3,5,6-tetrahydroxypiperazine-1,4-disulphamate, which can be nitrated to TEX though reportedly with heavy contamination by reaction byproducts[10]. DFTHP is also the precursor to other highly energetic explosives such as HHTDD[9] and 1,4-diformyl-2,3,5,6-tetranitratopiperazine[7, 8].

2 Synthesis

Figure 2: TEX synthesis

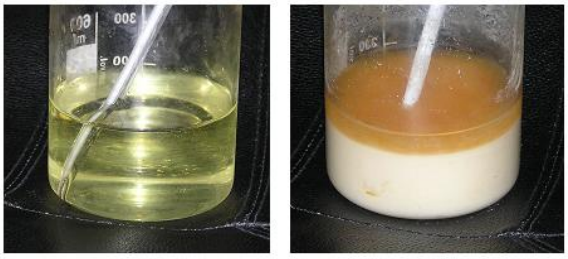


2.1 1,4-diformyl-2,3,5,6-tetrahydroxypiperazine (DFTHP)

145 g (1 mol) 40% glyoxal was combined with 45 g (1 mol) formamide at room temperature in a 600 mL beaker. No increase in temperature was observed. A dilute solution of sodium hydroxide was then dripped into the combined solution until a pH of 9 was

determined by litmus paper. A slow exothermic reaction increased the temperature from 20°C to 50°C over ~30 minutes. The solution turned yellow to orange and a large volume of small white crystals precipitated which solidified the solution (Figure 3). The solid solution was broken up by stirring and left to return to room temperature. The white precipitate was then filtered, flushed with 300 mL ethanol and dried to give 63 g (61%) of free flowing white crystals.

Figure 3: Condensation and precipitation of DFTHP



2.2 4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diaza-tetracyclododecane (TEX)

A mixed acid solution was made, comprised of 50 g potassium nitrate and 140 g 98% sulphuric acid. The mixed acids were then heated up to 60°C and placed under vigorous stirring via a drill press. 20 g DFTHP was then added in one portion. The solution foamed and gassed as an exothermic reaction raised the temperature to 75°C over ~20 minutes (Figure 4). Stirring was continued until the reaction subdsided and temperature dropped to 25°C. The solution was then dumped with vigorous stirring into 750 mL cold water which resulted in a very fine, fluffy precipitate (Figure 4). The precipitate was then filtered, rinsed with water, then with dilute sodium bicarbonate, finally with water again and dried. The very fine mud-like substance (Figure 5) was then powdered and extracted with 200 mL acetone. Evaporation of the acetone extract deposited 3.3 g of crude TEX as a fine pale yellow powder (Figure 5). The crude TEX deflagrated with a hissing flame leaving a small quantity of black residue and could not be initiated by striking with a hammer on steel.

Figure 4: Nitration of DFTHP (left); fluffy precipitate in water (right).

Figure 5: Drying crude precipitate (left); acetone extract of TEX (right).

References

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