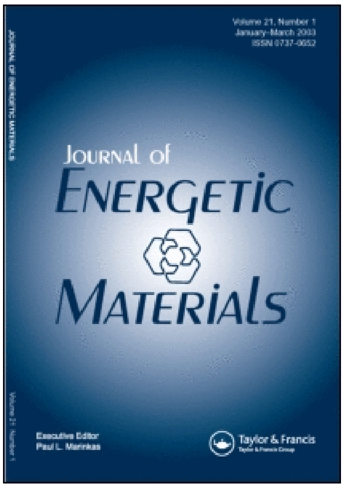

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3-Nitro-1,2,4-triazol-5-one, a less sensitive explosive

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3-NITRO-1,2,4-TRIAZOL-5-ONE, A LESS SENSITIVE EXPLOSIVE

by

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ABSTRACT

A new, less sensitive explosive has been prepared and subjected to preliminary characterization tests. The compound, 3-nitro-1,2,4-triazol-5-one (NTO) has a crystal density of 1.93 g/cm^3 and calculated detonation velocity and pressure equivalent to those of RDX. Results from initial small-scale sensitivity tests indicate that NTO is less sensitive than RDX and HMX in all respects. A 4.13-cm-diam, unconfined plate-dent test at 92% of crystal density gave the detonation pressure predicted for NTO by the BKW calculation. Finally, NTO can be prepared in high yield from inexpensive starting materials.

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INTRODUCTION

In the past, the common explosives RDX, HMX, and TNT were considered adequate for all weapons applications. Due to the many catastrophic explosions resulting from unintentional initiation of munitions by either impact or shock aboard ships, aircraft carriers, and ammunition trains, these explosives have become less attractive.

Triaminotrinitrobenzene (TATB) is noted for its insensitivity and is currently employed as an insensitive high explosive (IHE) in some applications. Unfortunately, TATB does not have the energetic performance of either RDX or HMX. Therefore, the need exists for explosives that are powerful yet resistant to accidental and sympathetic initiation.

This report describes a new candidate energetic explosive, 3-nitro-1,2,4-triazol-5-one (NTO). The chemical, physical, and explosive properties of NTO are reported together with the procedure for its preparation. Results from initial performance tests are also included.

PROPERTIES OF NTO

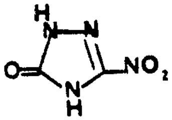
NTO is a white crystalline compound, moderately soluble in water to give yellow solutions. NTO is relatively acidic (pKa = 3.67)[1], and forms stable salts with mono or bivalent metals. The potassium, sodium, and lithium salts of NTO have been reported.[2] We have studied the formation of amine salts with NTO and have prepared the ammonium and ethylenediaminium salts of NTO in essentially the same way as reported for 5-nitrotetrazole.[3,4] The chemical properties of NTO are given in Table I. The CO-balanced explosive was found to have a crystal density of 1.93 g/cm^3 by x-ray crystallography.[5]

Results of small-scale screening tests of NTO are tabulated in Table II. For comparison, data from RDX are also listed. It can be seen that NTO is less sensitive and more stable than RDX in all the tests. In addition, the pyrolysis temperature for gas evolution from NTO is greater than 260°C while that for RDX is 160°C.

TABLE I

CHEMICAL PROPERTIES OF NTO

Structural Formula:



$C_2H_2N_4O_3$

Molecular Weight: 130

Acidity: pka = 3.67[1]

NMR Spectrum:

^1H NMR (DMSO-d_6): 12.7 ppm (>NH)

^{13}C NMR (DMSO-d_6)[a]: 148.0 ppm (>C-NO_2), 154.4 ppm (>C=O)

Elemental Analysis:

Calc: C, 18.46; H, 1.54; N, 43.08

Found: C, 18.81; H, 1.73; N, 43.03

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[a] The ^{13}C NMR chemical shifts were assigned unequivocally from the spectrum of 3-nitro-^{15}N-1,2,4-triazol-5-one, in which the signal at 148.0 ppm was split into a doublet, J = 29 Hz.

TABLE II

PHYSICAL AND EXPLOSIVE PROPERTIES

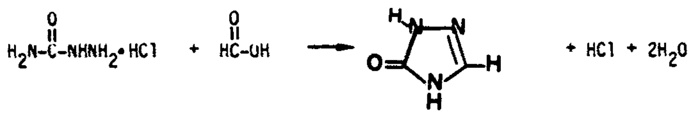
	NTO	RDX
Crystal Density (g/cm^3)	1.93	1.806
DTA Exotherm (°C)	>236	210
Heat of Formation (kcal/mole)	-14.30	+14.71
Henkin Critical Temp (°C) (0.64-mm size)	237	219.6
Impact Sensitivity (cm)		
Type 12	>280	22
Spark Sensitivity (J)		
3 mil	0.91	0.22
10 mil	3.40	0.55
Vacuum Stability		
(ml/g/48 h at 100°C)	0.2	
(ml/g/48 h at 120°C)	0.3	0.12-0.9

PREPARATION OF NTO

NTO is prepared by a modification of the procedure reported in the Russian literature.[2] It consists of preparing the intermediate 1,2,4-triazol-5-one (TO) followed by nitration with 70% nitric acid.

I. Preparation of TO (6 mol)

TO is obtained by condensing semicarbazide hydrochloride (SC) and formic acid with the evolution of hydrochloric acid, Eq. 1. Thus, to 690 ml formic acid (88%) in a large, three-necked round bottom flask is added 669 g SC and the mixture is heated with stirring until the SC is all dissolved. To remove excess formic acid, the mixture is concentrated by distillation until crystallization occurs. Water (~ 1 liter) is added and distillation is continued until the mixture is near dryness. Then it is cooled to temperature below 30°C, ready for nitration.



(1)

SC TO

II. Preparation of NTO

To the cooled flask containing the TO mixture as described above is carefully added 3.1 l 70% nitric acid. The mixture is then heated to boiling (55-60°C) with sufficient agitation. The reaction is exothermic and brown fumes are evolved. After the reaction is completed, the product is chilled to 5°C in an ice bath, the NTO solid is collected by filtration, and washed with ice water to remove excess nitric acid. Pure NTO is obtained by recrystallization from water followed by drying in an oven at 70°C for 16 hours. The purity of NTO was determined by both ^{1}H nmr and ^{13}C nmr spectroscopy. Inorganic ions, if any, were determined by ion chromatography.

PERFORMANCE TESTS OF NTO

We have evaluated the performance of NTO by conducting unconfined plate-dent tests at various charge diameters and pressed densities. NTO can be easily pressed to desired densities without binders. Results of these tests are compiled in Table III. For comparison, data from RDX and TATB are also listed.

TABLE III

DETONATION PROPERTIES

Explosive	Charge Density (g/cm^3)	Charge Diameter (cm)	P_{CJ} (kbar) Measured[6]	P_{CJ} (kbar) BKW[7]
NTO	1.93 (100% TMD)	--	--	349
	1.781 (92.2% TMD)	4.13	278	284
	1.853 (96% TMD)	4.13	260	316
	1.782 (92.3% TMD)	2.54	240	284
	1.855 (96.1% TMD)	2.54	Failed	316
	1.759 (91.1% TMD)	1.27	250	271
	1.824 (94.5% TMD)	1.27	Failed	
RDX	1.767 (97.8% TMD)	4.12	338	348
TATB	1.87 (96.5%)	4.12	277	313

SUMMARY

We have prepared an explosive compound that could be a candidate for future weapons applications. Initial small-scale sensitivity tests of NTO indicate that it is much less sensitive than RDX and TNT in all respects, but somewhat more sensitive than TATB. Results from a 4.13-cm-diam unconfined plate-dent test of NTO at 92.2% of crystal density gave the detonation pressure predicted for NTO by the BKW calculation, which is equal to that measured for TATB at 96.5% of crystal density. However, other small-scale tests at higher charge densities and/or smaller diameters gave less than the calculated performance. These are indications that the material may have a large failure diameter. In order for NTO to achieve its calculated potential, we must find ways to overcome its failure at high ensities and small diameters. Future work is being planned in these areas.

Our initial large-scale production of NTO demonstrated that NTO could be produced in high yield from inexpensive starting materials.

A full-scale gap test of NTO is now underway to determine its shock sensitivity.

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6. M-1 Development and Testing Section, L. A. Stretz, Section Leader.

7. Calculated by James P. Ritchie, T-14, Los Alamos National Laboratory.