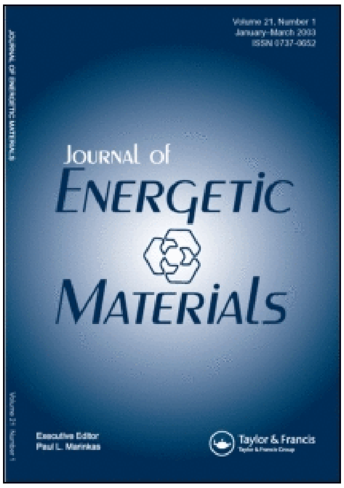

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Quantitative evidence for nitroso compound formation in drop-weight impacted RDX crystals

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QUANTITATIVE EVIDENCE FOR NITROSO COMPOUND FORMATION IN DROP-WEIGHT IMPACTED RDX CRYSTALS

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ABSTRACT

Quantitative results are presented for the formation of two nitroso compounds during the drop-weight impact of Holston production-grade Class D RDX explosive crystals. Gas chromatography, using a sensitive Ni-63 electron capture detector, was employed to analyze "RDX residues" recovered from impact tests involving a 5 kg mass dropped from 10, 12, and 14 cm heights. The compounds, 1,3,5-trinitroso-1,3,5-triazacyclohexane (R) and 1,3-dinitroso-5-nitro-1,3,5-triazacyclohexane (RO) were detected at levels of (0.80 to 9.3) X 10^{-5} percent and (1.3 to 560) X 10^{-5} percent, respectively. More RO than R was formed at the 14 cm drop height. This appears to be the first time that nitroso compounds structurally similar to RDX have been observed in impacted RDX crystals.

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INTRODUCTION

Some years ago, Bowden, Fox, and Soria-Ruiz[1] reported the detection, by mass spectrometry, of gaseous decomposition products resulting from the fracture of a variety of explosive and non-explosive compounds in a high vacuum. The amount of decomposition was suggested to be proportional qualitatively to the chemical reactivity of each material. Subsequently, the work was described in more detail, and the results were extended to obtain an estimate of the temperature at the tip of the crack during the fracture process.[2] Particularly noteworthy was the spectrometric observation for the relatively complex molecular solid, PETN, (1,1,1,1-tetra (nitroxymethyl)-methane), that on fracturing, the molecule cleaved at the four central C-C bonds primarly yielding $-CH_2-ONO_2$ fragments. It was further determined that these fragments were short-lived and ultimately decomposed to CO and NO.

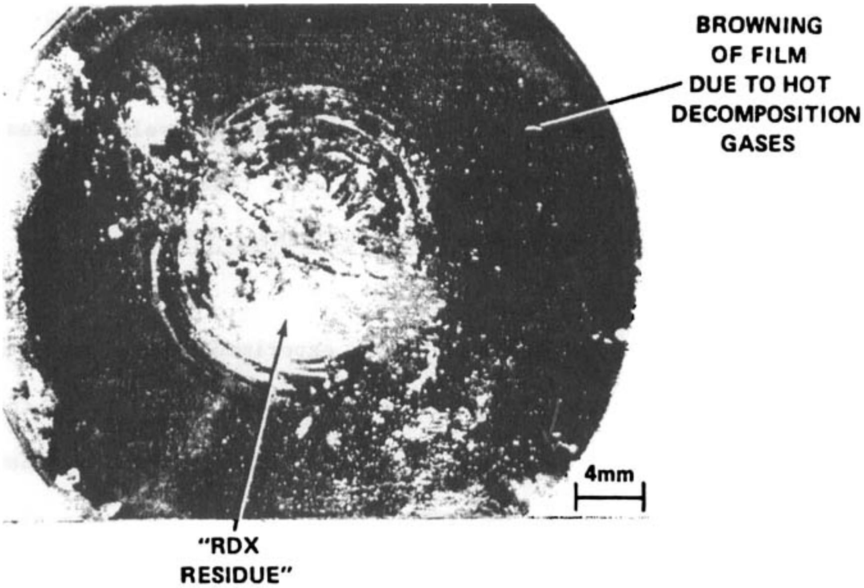
Recently, Hausner, Field, and Mohan[3] performed a more extensive mass spectrometric study of the fracture-induced decomposition of PETN. It was determined that the decomposition path was dependant upon the amount of energy transmitted to the crack. For the high energy case in which the fracture of a single PETN crystal was caused by an explosively driven chisel, C-C bond rupture occurred. In the less energetic case in which the chisel moved very much slower using a linear motion drive, the CH_2O-NO_2 bond was broken.

Somewhat related work has also been reported for RDX (1,3,5-trinitro-1,3,5-triazacyclohexane), a molecular solid that is structurally more complicated than PETN. Miles, DeVries, Britt, and Moniz[4] described efforts using electron spin resonance (ESR) to detect free radicals in RDX samples subjected to impact stresses up to 4 kbar. Although free radicals were not detected in the impacted samples, they were observed in samples exposed to gamma radiation. Owens and Sharma[5] used x-ray photoelectron spectroscopy (XPS) to study recovered RDX samples that had been exposed to shock pulses insufficient to cause detonation. It was determined that about 14 percent of the N-N bonds holding the nitro groups to the ring were broken. Recently, Dickinson, Miles, Elban, and Rosemeier[6] observed the emission of electrons and positive ions from production-grade Holston Class D and laboratory-grown RDX single crystals that had been fractured in compression. For laboratory-grown crystals fractured in a three-point bending arrangement, electron emissions of differing character resulted which were correlated to the nature of the fractures.

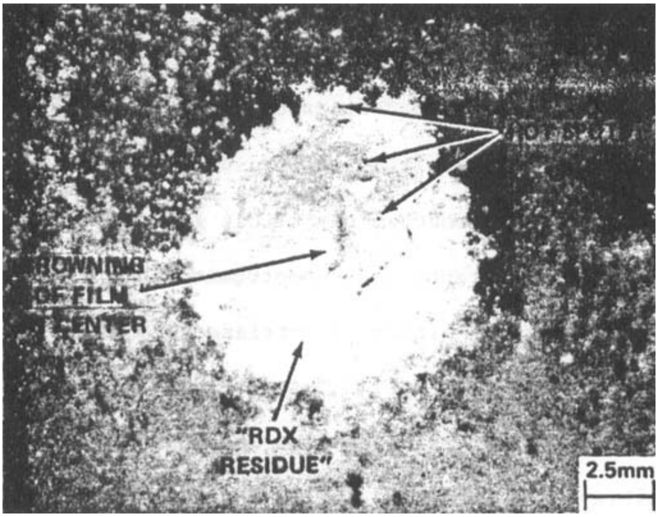
In addition, work has been reported using microhardness testing to understand the degree and nature of localized plastic deformation and fracture in RDX.[7-11] Plastic deformation was found to be highly inhomogeneous in RDX as evidenced by extremely localized strain fields surrounding hardness impressions that were also frequently accompanied by cracking. A large plastic anisotropy was observed[7-9,11] indicating that a limited number of slip systems are operative which would provide limited ways to relieve dislocation pile-up stress intensities. This relates to the proposal by Armstrong, Coffey, and Elban[12] that hot spots within deforming materials are microstructurally determined, resulting from the collapse of internal obstacles blocking dislocation pile-ups. Identifying chemical decomposition products that occur in deformed RDX might provide useful information for unraveling how the energy dissipation at dislocation pile-ups is coupled to the intramolecular bonding.

INITIAL WORK

In a limited study,[13] a series of drop-weight impact experiments were performed on Holston production-grade Class D (NSWC designation X924) RDX crystals (approximately 0.041 g granular samples). A heat sensitive film technique[14,15] was used to detect hot spots and the generation of hot gaseous decomposition products. Gas chromatographic analyses,[16] using a sensitive Ni-63 electron capture detector were performed on the recovered fractured samples. R-salt (referred to as R in this paper), the trinitroso analog of RDX, was conclusively identified as being formed in production-grade RDX that had been impacted. This occurred in samples that were impacted not only at energy levels sufficient to cause the evolution of hot decomposition gases (Figure 1 (a) as an example), but, also at lower energy levels that resulted only in hot spots (Figure 1 (b) as an example). The coloration of the heat sensitive film appearing in Figure 1(a) is actually brown. Prior to testing, the film color is uniformly light blue. Impacting the film



(a) EXPERIMENT #1 (10 cm DROP HEIGHT: GO)



(b) EXPERIMENT #2 (5 cm DROP HEIGHT: NO GO)

FIGURE 1. HEAT SENSITIVE FILM RECORDS OF DROP-WEIGHT IMPACTED HOLSTON CLASS D RDX (NSWC LOT X924)

without sample results in no discoloration of the film. For our purposes, the presence or absence of hot decomposition gases, as detected by the heat sensitive film, respectively delineates the so-called "go" and "no-go" descriptors (Table 1).

QUANTITATIVE EXPERIMENTAL STUDIES

Drop-Weight Impact Experiments

A number of repeated impact experiments were performed on production-grade Holston Class D RDX (NSWC X924) using the portable NSWC drop-weight machine[17] with a 5 kg mass. Samples weighing approximately 0.037 g were placed as a loose pile between two discs of heat-sensitive film[14,15] and tested at 10, 12, and 14 cm. For these samples, both liquid and gas chromatography were evaluated as analytical methods for determining the levels of nitroso compounds formed.

Standards

RO_3, 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) was recrystallized three times from acetone, dried, and checked for purity by thin-layer chromatography (TLC), gas chromatography (GC), and gas chromatography/mass spectrometry (GC/MS).

RO, 1,3-dinitroso-5-nitro-1,3,5-triazacyclohexane, was prepared in admixture with R, 1,3,5-trinitroso-1,3,5-triazacyclohexane, by the photo-oxidation of R in benzene under oxygen purge and ultraviolet (UV) irradiation (American Ultraviolet Co., germicidal lamp, G10T 5 1/2 H). Approximately 0.4 g of R in 100 ml of benzene was photolyzed for 180 min to yield a mixture of 27 percent RO and 73 percent R by liquid chromatographic (LC) analysis. Photo-oxidation beyond 180 min led to

TABLE 1

Summary of Preliminary Drop-Weight Impact Experiments on Class D RDX (0.041 g Sample: Loose Pile, NSWC Lot X924)

Experiment #	Drop Height,[a] cm	Go/No Go	Comments
1	10	Go[b]	--
2	5	No Go	Tiny Amount of Browning at Center[c]
3	8	No Go	Tiny Amount of Browning at Center[c]
4	9	No Go	Tiny Amount of Browning at Center[c]
5	9.5	No Go	Tiny Amount of Browning at Center[c]
6	9.8	Go[b]	--
7	9.7	No Go	Considerable Amount of Browning at Center[c]

(a) 5 kg mass
(b) As indicated by browning of film beyond the extent of the impacted sample [Figure 1 (a)].
(c) Visual observation of heat sensitive film discoloration.

a mixture of R, RO, RO_2 and RO_3. Enrichment of RO was accomplished by column chromatography with silica gel and benzene eluent and yielded 0.080 g which was 70 percent RO and 30 percent R by LC analysis. The structure of RO was established by GC/MS (Finnigan 4000) under chemical ionization (CI) conditions with a methane plasma.

R, 1,3,5-trinitroso-1,3,5-triazacyclohexane, was prepared by the low temperature nitration of hexamethylenetetramine at pH 1-2 as outlined by Urbanski.[18] The purity of R was ascertained by TLC, GC, and GC/MS.

LC Standard Solutions

0.003558 g of RDX were dissolved in 10 ml of methanol in one volumetric flask while 0.005311 g of a mixture containing 0.003724 g of RO and 0.001587 g of R were dissolved in 10 ml of methanol in a second volumetric flask. Two ml of each solution were diluted together to 10 ml in a third volumetric flask to yield the following solution: 3.21×10^{-4} M RO_3; 3.92×10^{-4} M RO; and 1.82×10^{-4} M R. A 5.0 µl injection produced the LC chromatogram shown in Figure 2.

GC Standard Solutions

A 100 µl aliquot of the LC standard solution was diluted to 10 ml with pesticide-grade benzene to give the following solution: 3.21×10^{-6} M RO_3; 3.92×10^{-6} M RO; and 1.82×10^{-6} M R. A 1.0 µl injection produced the GC chromatogram shown in Figure 3.

GC/LC Response Factors

GC response factors were determined by making several injections of the GC standard solution under the conditions specified under GC analysis. For a 1.0 µl injection, the following peak heights and retention times were obtained: RO_3 (24.0 mm, 14.8 min); RO (100 mm, 4.9 min); and R (64.7 mm, 2.4 min). From these data, the GC response factors shown in Table 2 were calculated.

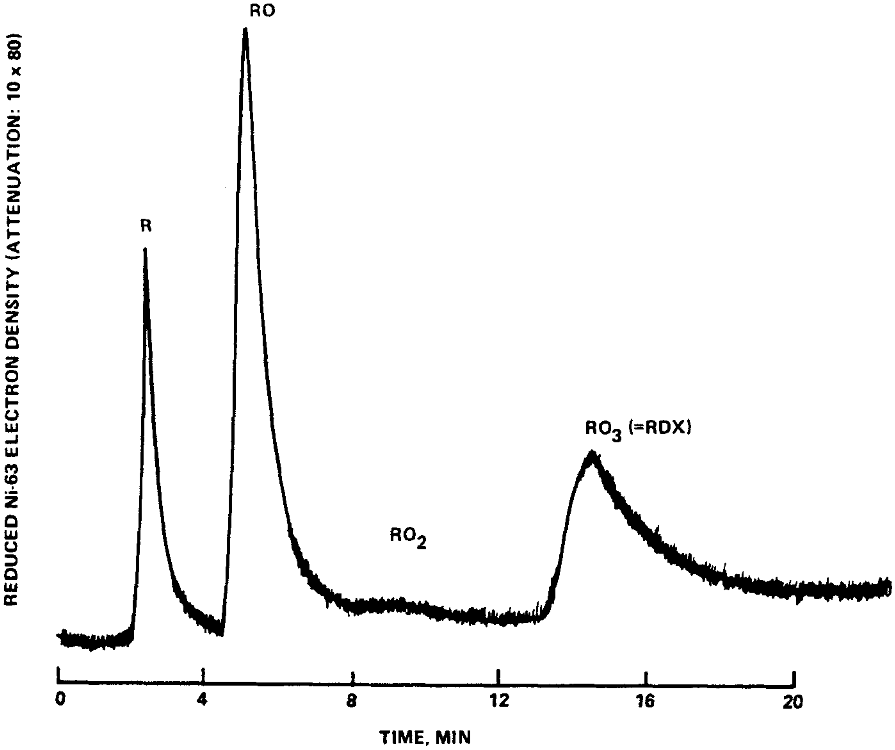


FIGURE 3. GAS CHROMATOGRAPHIC SEPARATION OF 1,3,5-TRINITRO-1,3,5-TRIAZACYCLOHEXANE (RO_3); 1-NITROSO-3,5-DINITRO-1,3,5-TRIAZACYCLOHEXANE (RO_2); 1,3-DINITROSO-5-NITRO-1,3,5-TRIAZACYCLOHEXANE (RO); AND, 1,3,5-TRINITROSO-1,3,5-TRIAZACYCLOHEXANE (R)

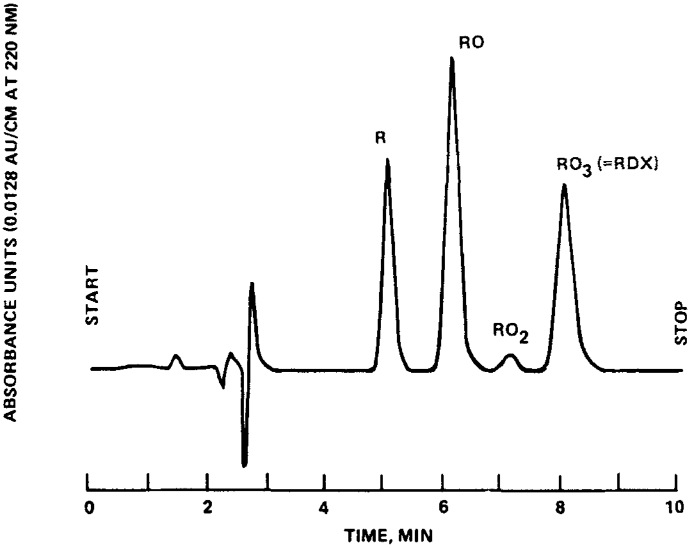


FIGURE 2. LC SEPARATION OF 1,3,5-TRINITRO-1,3,5-TRIAZACYCLOHEXANE (RO_3);1-NITROSO-3,5-DINITRO-1,3,5-TRIAZACYCLOHEXANE (RO_2); 1,3-DINITROSO-5-NITRO-1,3,5-TRIAZACYCLOHEXANE (RO); AND, 1,3,5-TRINITROSO-1,3,5-TRIAZACYCLOHEXANE (R)

LC response factors were determined in a similar manner. For a 5.0 µl injection, the following peak heights and retention times were obtained: RO_3 (35.0 mm, 8.0 min); RO (58.3 mm, 6.1 min); and R (38.3 mm, 5.0 min). These data were used to calculate the response factors shown in Table 3.

Extraction of Impacted "RDX Residues"

The impacted residues were scraped into tared 0.3 ml Micro "V" vials (Wheaton # 986213) and weighed. To these residues were added 200 µl of LC grade cyclohexane by means of a micropipet, and the mixtures were triturated with a small glass rod in order to extract the RDX decomposition products. Prior to GC analysis, the sample mixtures were filtered through a small glass-fiber plug held in a disposable Pasteur pipet (Fisher brand) into a 1.0 ml vial and capped. GC analyses were made directly on these filtered cyclohexane extracts.

GC Analysis

One µl aliquots of the filtered cyclohexane extracts were injected into a Hewlett-Packard research gas chromatograph (Model 5754A) equipped with a Model 5763A electron capture (ec) Ni-63 detector and pulser kit under the following conditions: 1.22 m X 6.35 mm glass column; 3.52 percent Dexsil GC 300 on 80/100 HP Chromosorb (Varian); column, 150°C; injection, 155°C; flow, 168 ml/min; carrier, Ar/CH_4: 95/5 (v/v); detector, 285°C; 150 µs pulse interval; and attenuation, 10 X 8.

TABLE 2

Gas Chromatographic Data: Retention Times and Response Factors with the Ni-63 Electron Capture Detector for RDX and Nitroso Compounds

Compound	Retention Time, min	Molar Response, mm/pmole[a]	Response Factor, pg/mm	Relative[b] Response
RO_3	14.8	8.33	26.6	1.00
RO_2	9.1[c]	(17.1)	(12.1)	(2.05)[d]
RO	4.9	28.1	6.75	3.38
R	2.4	40.2	4.33	4.83

(a) 10^{-12} mole.
(b) Mole basis.
(c) See Figure 3.
(d) Extrapolated from linear plot: log retention time versus relative response.

Weight Percentages of Nitroso Compounds

The weight percentages of R and RO in each residue were calculated from the expression, Wt % = $100(H)(RF)(W^{-1})(200)(10^{-12})$, where H is the height (mm per one µl injection) of the GC peak; RF is the response factor (pg/mm); W is the weight (g) of sample analyzed; and 200 is the µl volume of cyclohexane used in the extraction.

RESULTS AND DISCUSSION

The results of the GC analyses of the cyclohexane extracts of impacted Class D RDX are given in Table 4. The average weights of residue and the percentages of starting RDX were as follows: (a) 10 and 12 cm impact height (No Go), 0.028 g (75 percent); (b) 14 cm impact height (No Go), 0.032 g (86 percent); and (c) 14 cm impact height (Go), 0.0069 g (18 percent). A few hot spots were observed in the heat sensitive film at the 10 and 12 cm levels, while partial browning to deep browning with holes in the film were observed at the 14 cm level.

TABLE 3

Liquid Chromatographic Data: Retention Times And Response Factors for RDX and Nitroso Compounds

Compound	Retention Time, min	Molar Response, mm/nmole[a]	Response Factor, ng/mm[a]	Relative[b] Response
RO_3	8.0	21.8	10.2	1.00
RO_2	7.0[c]	--	--	--
RO	6.1	29.9	6.4	1.37
R	5.0	43.3	4.0	1.99

(a) 10^{-9} mole. Hewlett-Packard Model 1084A liquid chromatograph equipped with a variable wavelength detector (HP Model 1030) and a variable volume injector with a 10 µm RP-8 column, 25 cm X 4.6 mm ID at 40°C; eluent, 25% methanol-water (v/v); flow, 1.0 ml/min; wavelength, 220 nm; attenuation, 0.0128 AU/cm.

(b) Mole basis.

(c) See Figure 2.

Cyclohexane was chosen to extract the impacted RDX crystals because of the greater solubility of R in cyclohexane than RDX. The approximate solubilities of RDX and R in cyclohexane at room temperature were found to be 9.75×10^{-5} and 5.42×10^{-3} g/l, respectively, by GC analysis. The solubility of RO would be expected to be similar to R. Thus, for residue weights of 0.030 and 0.0069 g, the limiting amount of R that could be analyzed would be 3.6×10^{-3} and 15×10^{-3} percent, respectively. The values of R and RO given in Table 4 are all much lower than these limiting solubilities.

Although both R and RO may be determined by LC (Figure 2, Table 4), it is evident that the response factors are about 1/1000 the response factors observed by GC using the sensitive Ni-63 detector (Figure 3, Table 2). For the current work, the R and RO levels measured by GC analysis would not have been detected by LC analysis.

Considering the values of R and RO listed in Table 4, several observations can be made: (1) Both R and RO in the "no-go" impacted residues at all levels were found to be, on the average, 4×10^{-5} percent with the ratio of RO to R being about 7 to 1. (2) Both R and RO in the "go" impacted residues at the 14 cm height were found to be, on the average, 50×10^{-5} percent with the ratio of RO to R being about 18 to 1. (3) Individual values found for R and RO at all impact heights varied widely, reflecting the statistical nature of the impact testing of explosives.

TABLE 4

Nitroso Compound Content In Impacted RDX Crystals

Drop Height,[a] cm	Weight Percent X 10^{-5}					
	R[b]			RO[c]		
10 (No Go)	-[d]	-	-	-	-	-
	1.9	1.7	1.5	-	59	-
12 (No Go)	1.1	1.1	1.1	1.3	7.4	1.8
	0.8	1.1		1.3	1.8	
14 (No Go)	1.8	0.8	-	2.1	1.9	7.4
	1.6	2.7	2.3	51	1.7	2.9
	1.7			1.5		
14 (Go)	-	-	9.3	14	47	560
	3.9	6.2	8.5	14	130	6.5
	5.6	8.8		-	-	
0 (Not Impacted)	-	-	-	-	-	-
	-	-	-	-	-	-

(a) 5 kg mass.
(b) R = 1,3,5-trinitroso-1,3,5-triazacyclohexane.
(c) RO = 1,3-dinitroso-5-nitro-1,3,5-triazacyclohexane.
(d) -, not detected; detection limit = 0.2 X 10^{-5} Wt %.

It is important to note that nitroso analogs of RDX are known decomposition products of thermally degraded RDX. The thermal degradation of RDX has been observed[19] to follow, in part, the following sequence: RDX (= RO_3) $\rightarrow$ RO_2 $\rightarrow$ RO $\rightarrow$ R. Sealed capillary decomposition of RDX has been observed to form RO_2, and small amounts of RO; while open capillary decomposition of RDX formed RO_2, RO, as well as R. In addition, early unidentified peaks in the GC traces of thermally degraded RDX are similar to early peaks in the GC traces from the cyclohexane extracts of impacted RDX crystals.

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