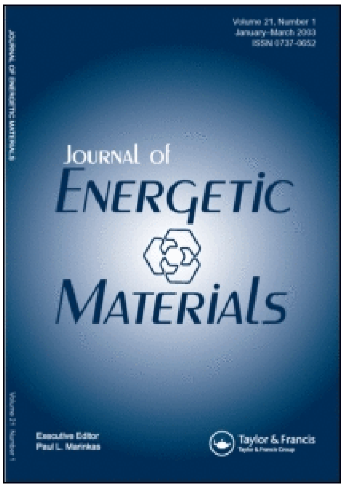

Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

EPR investigations of thermal decomposition of nitramines: I. primary nitroxide radicals from RDX

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To cite this Article Pace, M. D. , Britt, A. D. and Moniz, W. B.(1983) 'EPR investigations of thermal decomposition of nitramines: I. primary nitroxide radicals from RDX', Journal of Energetic Materials, 1: 2, 127 — 132
To link to this Article: DOI: 10.1080/07370658308010628
URL: http://dx.doi.org/10.1080/07370658308010628

EPR INVESTIGATIONS OF THERMAL DECOMPOSITION OF NITRAMINES:
I. PRIMARY NITROXIDE RADICALS FROM RDX

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ABSTRACT

We have observed that the free radical produced from solid RDX undergoing thermal decomposition can also be produced in RDX-sulfolane solutions. Under milder conditions, an earlier free radical is produced which is identified as the known nitroxide. Pronounced radical-cage effects are observed.

INTRODUCTION

The ultraviolet (UV) decomposition of RDX, HMX, and other cyclic nitramines was investigated more than a decade ago.[1,2] Either solid films or moderately concentrated solutions (10^{-3}-10^{-4} $\underline{M}$) were used, owing to quantum yields. The primary

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Journal of Energetic Materials Vol. 1, 141-175

Published in 1983 by Dowden, Brodman & Devine, Inc.

photolytic step involves cleavage of a single nitramine bond, which can occur in two ways: (a) loss of NO_2 to form an amino-radical; and (b) loss of NO to form a nitroxide radical. Both types of processes have been observed using Electron Paramagnetic Resonance (EPR) to detect the amino- and nitroxide radicals, respectively.[1-5]

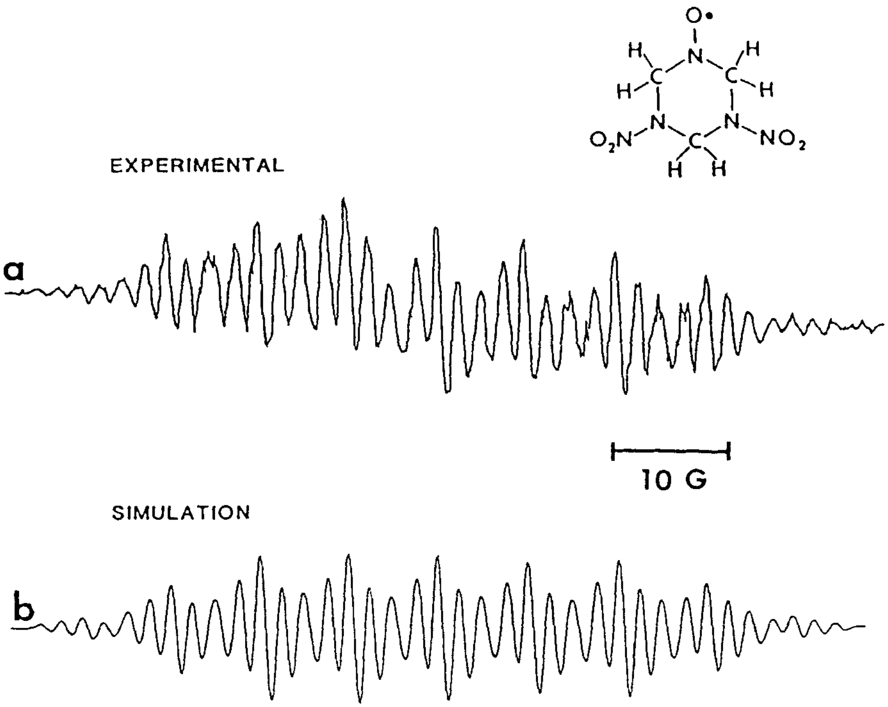
EPR studies have also shown free radicals in solid samples of RDX and HMX, near their melting temperatures.[3] The molecular structures of these free radicals were not identified. It was clear, however, that the free radicals produced thermally were not simply the same as either of the two radicals observed by photolysis.

In this present work, we describe EPR measurements on solutions of RDX which exhibit the same free radical spectrum as solid RDX. A two-step radical sequence is observed, and we identify the primary radical as the known nitroxide.[1,2]

EXPERIMENTAL

RDX was recrystallized from either ethanol or acetone before use. Analysis by NMR and MS showed 4-6% HMX as the only impurity. Solvents were A. R. grade, with the exception of sulfolane (b. p. 285°C), which was practical grade. RDX dissolves in sulfolane and forms a 1:1 complex at room temperature.[6] Above 70°C the complex dissociates into the constituent RDX and sulfolane molecules. Neat sulfolane at 160°C-180°C gave no EPR signals.

Samples were open to the air, and were heated to various temperatures in the cavity of a Bruker ER 200D spectrometer, equipped with a variable temperature accessory.



I	EQUIVALENT SPINS	HYPERFINE COUPLINGS	INTENSITY RATIOS
1	1	15.8 GAUSS	1:1:1
1/2	4	7.7	1:4:6:4:1
1	2	1.8	1:2:3:2:1

Fig. 1. (a) This first derivative EPR spectrum was recorded with an 0.1M sample of RDX in sulfolane at 170°C. (b) The spectrum was computer simulated. The simulation required three ^{14}N couplings and a coupling from four equivalent protons.

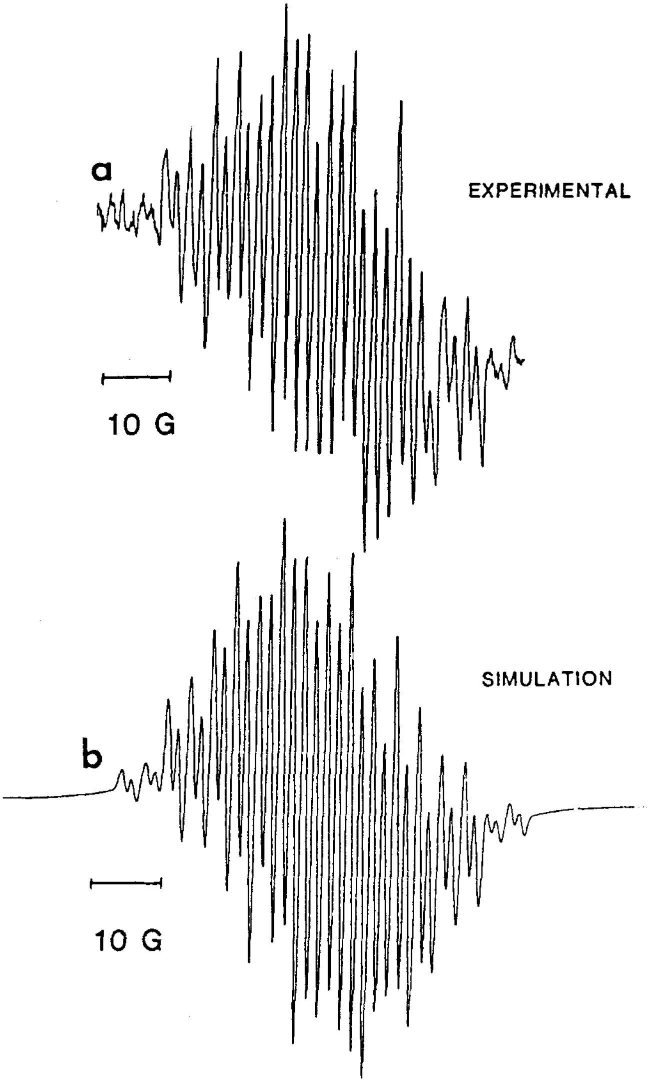


Fig. 2. (a) This first derivative EPR spectrum was recorded from a 1M sample of RDX in sulfolane at 170°C.

(b) The spectrum was computer simulated by using the following couplings:

1) 1xI=$^1/_2$ A=9.98 G
2) 1xI=1 A=8.21 G
3) 4xI=$^1/_2$ A=6.66 G
4) 1xI=$^1/_2$ A=3.4 G
5) 1xI=$^1/_2$ A=1.25 G

RESULTS AND DISCUSSION

We confirm previous results that free radicals are produced in solid RDX in the temperature range 190-195°C.[3] With longer heating times, radicals were observed as low as 180°C. We also observed water as a product of this thermal decomposition, which condensed in the colder, upper portion of the sample tubes.

Dilute solutions (ca. 0.1 M) of RDX in sulfolane at 150-160°C show EPR spectra of the known nitroxide.[1],[2] This is referred to as Radical I (see fig. 1). More concentrated solutions (ca. 1.0 M) at 160-179°C show EPR spectra identical to that observed from solid RDX at 190°C (see fig. 2). This is referred to as Radical II, which has not yet been identified, but which we suspect to be derived from Radical I by ring-opening. (The complex spectral pattern with 36 hyperfine lines suggests a radical with a structure more complicated than I.) A similar process has been observed photolytically.[1]

A curious feature of this reaction is that there is no obvious gas evolution, if the temperature does not exceed 170°C. Efforts to elucidate this point, and to identify Radical II, are in progess.

ACKNOWLEDGEMENTS

Drs. Wilkes and Pugh of the Frank J. Seiler Research Laboratory, USAF Academy, generously shared crucial details of their original work with us. We also want to thank Drs. Brenda Holmes and Joseph Campana of NRL for NMR and MS analyses, respectively.

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