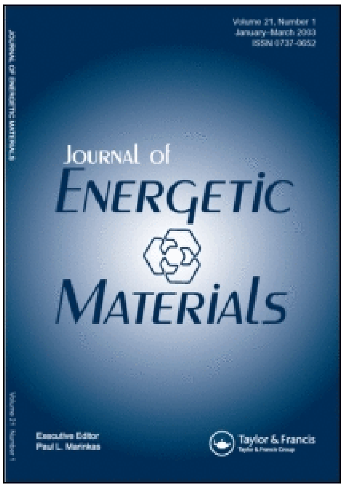

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THERMAL DECOMPOSITION OF RDX: EVIDENCE OF A NITRONYLNITROXYL FREE RADICAL INTERMEDIATE

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ABSTRACT

The thermal decomposition of RDX produces free radical intermediates which are detected by using ESR (electron spin resonance) spectroscopy. The assignment of certain ESR signals from thermally decomposed RDX and HMX to a nitroxyl radical (RNO•) has been discussed in earlier publications. Spectral data from isotopically labelled RDX (RDX-d_6 and RDX-$^{15}NO_2$) supports a nitronylnitroxyl radical ($R(N^+-O^-)NO\bullet$) assignment to the ESR signals detected during liquefaction of RDX at 200°C.

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INTRODUCTION

Free radical intermediates produced during the thermal decomposition of RDX and HMX were reported in two previous articles.[1,2] These free radicals were assigned to nitroxyl radicals having the unpaired electron localized in the N-O bond.[3] In reference 1 an ESR spectrum of another free radical was reported but not assigned. This complex spectrum is composed of many hyperfine lines and is produced during liquefaction of RDX at 200°C.[4] (The spectrum is also produced by prolonged thermal decomposition of unsubstituted RDX in sulfolane at 170°C). New spectral evidence from isotopically substituted RDX supports an assignment of this radical to a nitronylnitroxyl radical. A nitronylnitroxyl radical contains two functional groups, a nitrone ($-N^{+}-O^{-}$) and a nitroxyl ($-N-O\bullet$).[5] Resonance hybrids can be drawn in which the unpaired electron alternates between these groups.

EXPERIMENTAL

Isotopically labelled perdeutero-RDX (RDX-d_6) and ^{15}N nitro group labelled RDX (RDX-$^{15}NO_2$) were used (not ^{15}N labelled on the ring nitrogens). RDX-d_6 was prepared by a new synthetic route described by Boyer et.al.[6] The purity of this material was greater than 95 percent. RDX-$^{15}NO_2$ was synthesized by research scientists at the Naval Surface Weapons Center at Silver Spring, MD. This synthesis has been published.[7] The samples were prepared for study by dissolving either RDX-d_6 or RDX-$^{15}NO_2$ in a high boiling point solvent (sulfolane, bp. 285°C). Dissolving the energetic material into a chemically inert solvent was found to enhance the signal-to-noise ratio of the ESR spectral lines without introducing spectral artifacts. The sample concentration was 0.2M. Samples were heated in a TM_{110} ESR cavity by flowing hot N_2 gas through an insert dewar. The temperature was maintained in the range 160-170°C during the experiments. This temperature range gave ESR signals which persisted for several hours indicating a steady-state concentration of free radicals in solution. An IBM-Bruker ER200 X-band ESR spectrometer was used. The spectrometer settings were a sweep width of 50 Gauss (G), microwave power of 2 milliwatts, time constant of 1/10 sec, gain of 100,000 and a modulation amplitude of 1/2 G. Signal data were processed with a Nicolet 1275 Signal Averaging Computer.

RESULTS

In Fig. 1 is shown the previously reported radical structure and ESR spectrum of a nitroxyl radical derived from RDX by loss of NO. (This spectrum is recorded at 150°C from an 0.1M solution of RDX in sulfolane). The pattern arises from an electron-nuclear hyperfine coupling (hfc) of the ^{14}N (nitroxyl nitrogen) equal to 15.8 G, four equivalent beta protons with an hfc value of 7.7 G, and two symmetrical ^{14}N nuclei with an hfc value of 1.8 G. The diagram of these components (shown below

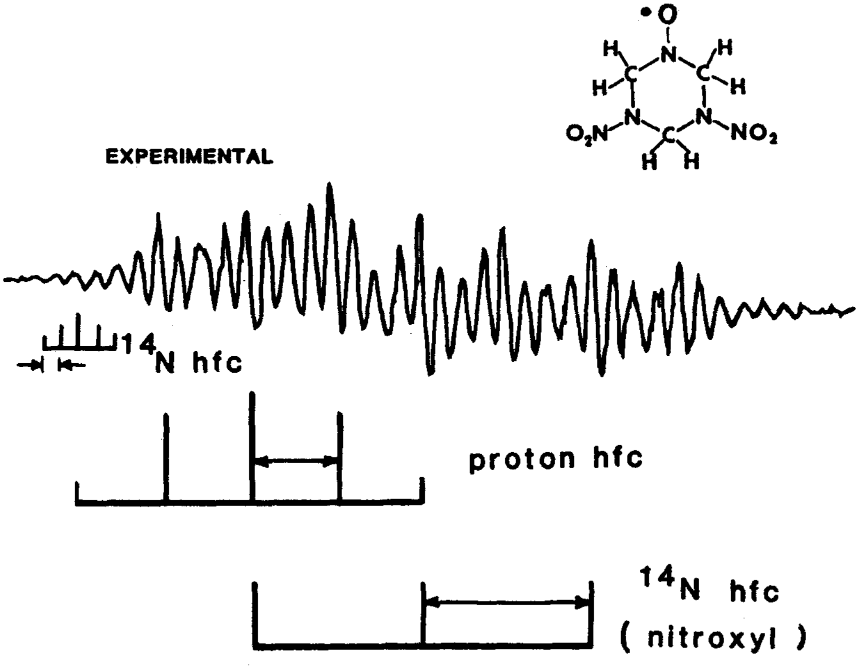
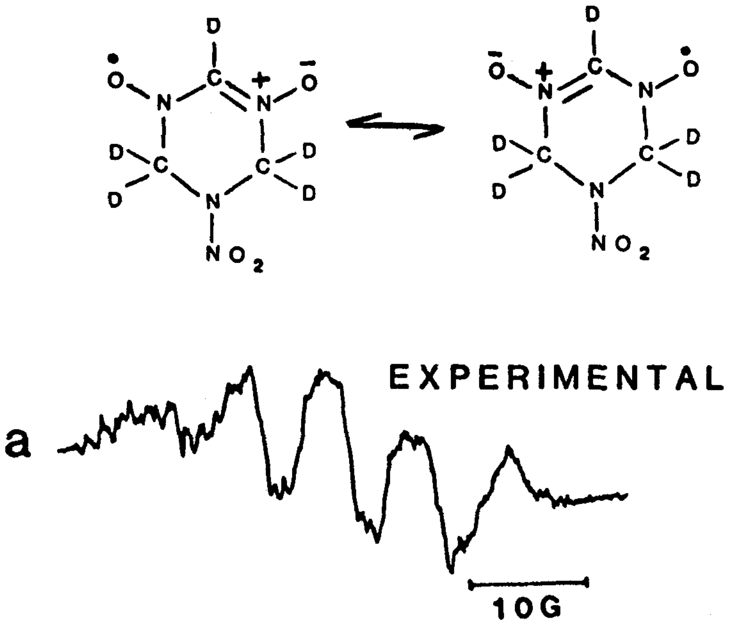


Fig.1) Nitroxyl radical spectrum reported in reference 1 for an RDX/sulfolane solution at 150°C. The diagram indicates the ^{14}N and proton spectral components. (Only one branch of the proton and minor ^{14}N components is shown).

the spectrum) indicates their relative signal intensities.

A nitronylnitroxyl radical is derived from the RDX nitroxyl radical by net loss of HNO. Two resonance hybrids of such a radical are shown in Fig. 2a. (Deuterated structures are shown). The deuterated nitronylnitroxyl radical has an hfc value of 7.9 G for two equivalent ^{14}N nuclei, (the unpaired electron alternates between the $N-\dot{O}$ and $\overset{+}{N}-\overset{-}{O}$ functional groups. In a simple model this means that the unpaired electron spends one-half of its time at each position. This reduces the effective hyperfine coupling by 1/2 that of the nitroxyl radical; 1/2 x 15.8 G = 7.9 G). The four beta deuterons are magnetically equivalent due to a resonance hybridization. The hfc value of these deuterons cannot be directly measured from the spectrum in Fig. 2a (due to unresolved spectral signals) but can be estimated based on the nitroxyl radical in Fig. 1. The hfc value of these deuterons is reduced (relative to the proton's coupling of the nitroxyl radical) by the ratio of nuclear g-factors ($g_D/g_H = 0.15$) and by a



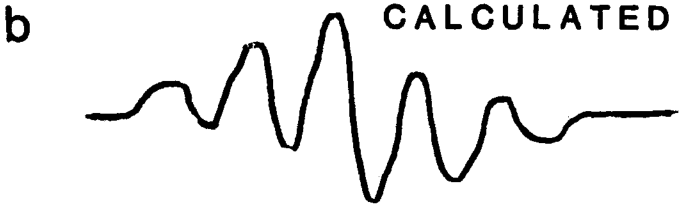


Fig. 2a) The experimental first-derivative ESR spectrum of RDX-d_6 in sulfolane at 170°C. Resonance hybrids of a nitronylnitroxyl radical derived from RDX-d_6 are shown.

Fig.2b) Computed spectrum using the hyperfine couplings (listed in the text) of a deuterated nitronylnitroxyl radical.

factor of 1/2 due to resonance hybridization. This gives 0.15 x 1/2 x 7.7 G or 0.58 G for this hfc value. The minor ^{14}N hfc value is ca 1.8 G (unchanged due to the symmetry of the radical). The alpha deuteron located between the N-O and $\overset{+}{N}$-$\overset{-}{O}$ functional groups has no analog in the nitroxyl radical. The hfc value of this deuteron was first thought to be small due to its proximity relative to the p-orbitals of the N-O• functional group. (See Discussion) The hfc value of the alpha deuteron is estimated to be ca 1.5 G (for a proton this value is 1.5 G/0.15 or 10 G). Based upon these couplings a five line pattern is predicted for the deuterated nitronylnitroxyl radical. The two equivalent ^{14}N nuclei create this pattern ($2x\sum m_I + 1 = 2(2) + 1$ or 5) with relative intensity ratios of 1:2:3:2:1. The proton couplings broaden these five spectral lines. A spectrum computed by using these couplings matches the experimental spectrum (Fig. 2b).

The $^{15}NO_2$ labelled RDX was heated in sulfolane at a constant temperature of 170°C. The ESR spectrum which was recorded matches the spectrum reported in reference 1 for unlabelled RDX. This is consistent with a nitronylnitroxyl free radical assignment. A single $^{15}NO_2$ group remains attached to the ring in the nitronylnitroxyl radical's structure. The distance of the $^{15}NO_2$ group from the unpaired electron site precludes a detectable influence on the spectral pattern. The ESR spectral pattern is not expected to change for the $^{15}NO_2$ labelled RDX in this experiment.

DISCUSSION

The unsolved free radical spectrum reported in reference 1 is assigned to a nitronylnitroxyl radical. This is supported by the ESR spectrum of RDX-d_6 shown in Fig. 2a. (The $^{15}NO_2$ labelled RDX ESR spectrum is consistent with this assignment). In an earlier publication a ring-opened structure was considered as a possible assignment. The nitronylnitroxyl structure excludes this possibility. The "ring-closed" nitronylnitroxyl radical is consistent with FTIR (Fourier Transform Infrared) spectroscopic studies which report intact molecules from thermally produced liquid phase RDX.[8] Alkylnitronylnitroxyl radicals and related free radicals are reported to be unusually stable.[9,10] The alpha proton in these radicals is approximately located in a plane defined by the ON--C--NO nuclei. The dipolar interaction of this proton with an unpaired electron in the p_z orbital of the N-O• group is expected to be small. However, the molecular orbital structure of the N-$\dot{O}$ group is not exactly known. Semiempirical calculations indicate that s orbital character is admixed to the unpaired electron causing a significant electron-nuclear contact interaction.[3] This means that the alpha proton has a measurable hfc value. In the RDX nitronylnitroxyl radical the proton is assigned a value of approximately 10 G. This is based upon a comparison of the spectral width of the unlabelled RDX spectrum (reference 1) with the spectral assignment of the deuterium labelled RDX spectrum in Fig. 2a.

A further test of the assignment was made by using the "predicted" hyperfine couplings of the unlabelled nitronylnitroxyl radical to compute a spectrum. The computed spectrum closely matches the experimental spectrum reported in reference 1. Differences are attributed to variation of the proton's hyperfine coupling (which cannot be precisely measured from the spectrum in Fig. 2a.)

ACKNOWLEDGEMENT

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REFERENCES

1. M.D. Pace, A.D. Britt, and W.B. Moniz, J. Energetic Materials, 1, 127 (1983).

2. A.D. Britt, M.D. Pace, and W.B. Moniz, J. Energetic Materials, 1, 367 (1983).

3. B. Delley, P. Becker, and B. Gillon, J. Chem. Phys. 80, 4286 (1984).

4. C. Dorey, J.S. Wilkes, L.P. Davis, H.L. Pugh, W.R. Carper, A.G. Turner, and K.E. Siegenthaler, F.J. Seiler Research Laboratory, Report no. FJSRL-TR-80-0026, (1980)

5. P.W. Kopf, R. Kreilick, D.G.B. Boocock and E.F. Ullmann, J. Am. Chem. Soc. 92, 4531 (1970).

6. J.H. Boyer and G. Kumar, J. Labelled Comp. and Radiopharm. 22, 1 (1985).

7. M.E. Sitzmann, J. Labelled Comp. Radiopharm., 22, 1165 (1985).

8. R.J. Karpowicz, and T.B. Brill, Combust. Flame, 56, 317 (1984).

9. D.G.B. Boocock, R. Darcy, and E.F. Ullmann, J. Am. Chem. Soc., 90, 5945 (1968).

10. E.F. Ullmann, L. Call, and J.H. Osiecki, J. Org. Chem. 35, 3623 (1970).