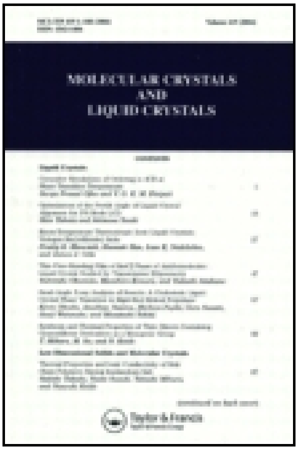

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ELECTRON PARAMAGNETIC RESONANCE OF ULTRAVIOLET IRRADIATED HMX SINGLE CRYSTALS

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The secondary explosive HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) undergoes thermal and photolytic decomposition to produce free radical products. This is firmly established by studies using electron paramagnetic resonance (EPR) spectroscopy. In this study paramagnetic $\bullet NO_2$ molecules are shown to form during ultraviolet photolysis of single crystals of HMX at 77K. The $\bullet NO_2$ molecules are highly ordered in the monoclinic crystal lattice of HMX. EPR spectra of different alignments of the HMX crystal relative to the applied magnetic field direction indicate $\bullet NO_2$ formation at the N(3)-N(4) bond location of the HMX molecule. This differs from our previous study of RDX (hexahydro-1,3,5-trinitro-s-triazine) which indicates $\bullet NO_2$ formation at the axial and equatorial N-N bond positions of the RDX molecule as a result of ultraviolet photolysis.

INTRODUCTION

Nitramines are well known for their application as explosives. The chemical reactions which precede the rapid change of state and exothermic release of heat and light during deflagration or detonation are not known with certainty. Insight into initial reactions can be gained by looking at what bonds are broken and what new products are formed while these materials retain their crystallographic order in the condensed phase. Electron paramagnetic resonance is ideal for this task when free radical products are involved. Recent studies have proven that free radicals occur during thermal and photolytic decomposition of solid state nitramines. These radicals have structures which resemble fragments of their parent nitramine molecules. Research on RDX has shown that in ultraviolet irradiated single crystals paramagnetic $\bullet NO_2$ free radicals are produced having asymmetrical conformations in the orthorhombic crystal lattice.(1) Ultraviolet photolysis of RDX and HMX in solution generates nitroxyl radicals and a paramagnetic reaction product of $\bullet NO_2$ with the solvent.(2) In thermal decomposition studies a nitroxyl radical and a proposed nitronyl nitroxyl radical have been detected using EPR.(3,4) This article reports the study of $\bullet NO_2$ free radicals formed by ultraviolet photolysis of β-HMX single crystals. The spatial locations of the $\bullet NO_2$ free radicals in the crystal lattice are determined and compared to the $\bullet NO_2$ formation in RDX.

EXPERIMENTAL

Single crystals of β-HMX were received from the Naval Weapons Center, China Lake, CA. and were grown by slow evaporation of a room temperature (25°C) saturated solution of neat β-HMX in acetone. Crystallization required 2-4 weeks to produce crystals with lengths of 4-6mm. The assignment of crystallographic axes to these crystals was made by using a Zeiss optical transmission microscope equipped with an x-y grid overlay to digitally record coordinates. This was used to measure interfacial angles and interaxial angles of the crystals. From this information axial assignments were made by comparison with documented dimensions and interaxial angles of β-HMX.(5) The crystals were mounted onto 1mm diameter Macor rods to facilitate handling during irradiation and data collection. Three crystal samples were used. Each crystal was separately mounted for rotation with respect to the polarizing magnetic field direction (H_0) by aligning the crystal with the major axis of the mounting rod perpendicular to the ab or bc* or c*a geometric plane, respectively. Spectra were recorded using a Bruker ER200D spectrometer and a Nicolet 1275 signal processor. The typical instrument settings were a sweep width of 20mT, a sweep time of 0.5 sec (50 time-averaged scans), a power setting of 2 mw, and a modulation of 0.8mT. Each sample was irradiated with unfiltered ultraviolet light using a 500W mercury flashlamp. The irradiation was carried out for 30 minutes at 77K using liquid nitrogen to produce a free radical concentration giving a 20:1 signal-to-noise ratio. The samples were transferred under liquid nitrogen to a finger dewar in a TE_{102} x-band EPR cavity and maintained at a temperature of 77K throughout the experiment. Spectra were recorded at different angles of alignment of the crystal reference axes (a or b or c*) with respect to H_0. The angles varied by increments of 10°. This provided sufficient data to compute the ^{14}N hyperfine coupling tensors and g-value tensors of the free radicals. The g-values and spin concentrations were calculated relative to a 0.00033% pitch in KCl standard having a spin concentration of 2.5×10^{15} spins and a g-value of 2.0028.

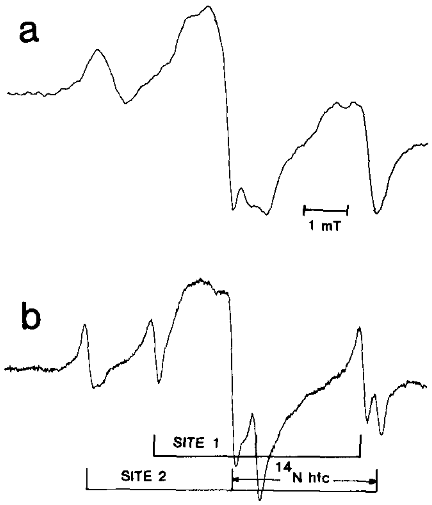

FIG. 1 a) The first-derivative EPR spectrum of a powder sample of β-HMX following ultraviolet photolysis. b) The first-derivative single crystal EPR spectrum of photolyzed β-HMX with H_0 having direction cosines of (0.0, +0.643, +0.766).

EPR SPECTRA

The EPR signal of a photolyzed powder sample of HMX has a pattern which matches the powder spectrum of randomly oriented $\bullet NO_2$ radicals.(6) This spectrum is shown in Fig. 1a. By monitoring this signal, the rate of formation of the $\bullet NO_2$ free radicals in the HMX powder sample was determined. The rate of formation was found to be first-order during the first 30 minutes of photolysis at 77K with a rate constant $k=0.036\ \text{min.}^{-1}$. This gives approximately $3\text{x}10^{13}$ spins/min as the rate of production. After 30 minutes the spin concentration approached $1.6\text{x}10^{15}$ spins as a limit due to mass depletion. The rate of formation will vary depending upon the conditions of irradiation.

The β-HMX single crystals, when photolyzed under the same conditions, gave EPR spectra having highly resolved signals clearly showing two sites of the $\bullet NO_2$ free radicals in the monoclinic lattice. A single crystal EPR spectrum with H_0 having direction cosines of (0.0, +0.643, +0.766) in the bc* plane is shown in Fig.1b. This pattern is easily understood. The fundamental $\bullet NO_2$ spectrum is composed of 3 transitions from the interaction of the unpaired electron spin moment with the ^{14}N nuclear spin moment having I=1.

The space group of β-HMX is $P2_1/c$ with monoclinic unit cell dimensions: a=6.54Å, b=11.05Å, c=8.7Å and β=124.3°.(7) Monoclinic symmetry produces two sites for the same bond when viewed along directions of the ab or bc^* planes of the unit cell. Each site will give an EPR spectrum. Thus, the 6 first-derivative signals of Fig. 1b. are attributed to two sites each having 3 transitions. Plots of the anisotropic hfc values and g-values for the 3 reference planes ab, bc^*, and c^*a are shown in Fig 2. The monoclinic system was transformed into an orthogonal axis system $a'b'c^*$ by using the following relationships:

$$a' = a \bullet x - c' \bullet \tan(\Theta - 90°)$$
$$b' = b \bullet y$$
$$c^* = c \bullet z \cos(\Theta - 90°)$$

where x, y, z are the fractional unit cell dimensions and a', b', c^* are the transformed coordinates having the c^* axis orthogonal to a' and b' axes. This allowed the direction cosines of the bond directions to be directly compared to the principal value directions of the EPR tensors.

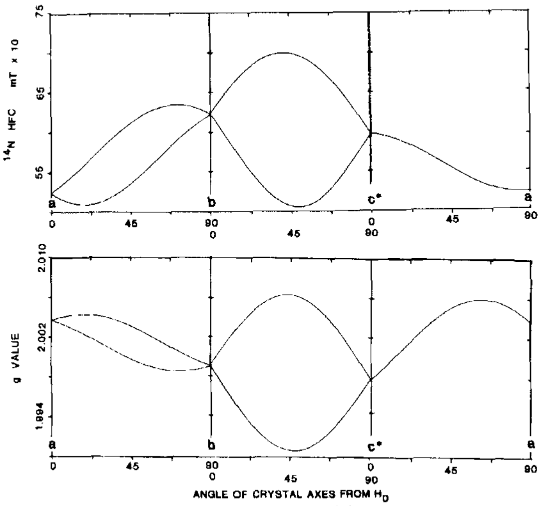

FIG. 2 This figure shows plots of the ^{14}N hyperfine couplings and g-values as a function of the angle of alignment of the β-HMX crystal in the 3 reference planes. Two sites of the $\bullet NO_2$ radicals are observed in the ab and bc^* reference planes.

DISCUSSION

The maximum principal values of the g-tensor and the ^{14}N hyperfine coupling tensor correlate with the C_2 symmetry axis of the $\bullet NO_2$ molecule. The maximum principal value of the ^{14}N hyperfine coupling tensor is parallel to C_2 symmetry axis.(8) The maximum g-value of the g tensor is orthogonal to the C_2 symmetry axis and the O-N-O molecular plane. This provides a way to measure the orientation of the $\bullet NO_2$ free radical from the direction cosines of the g and ^{14}N principal values. The first step in forming the $\bullet NO_2$ free radical is cleavage of an N-N bond by the effect of ultraviolet light. If the orientation of the $\bullet NO_2$ free radical remains unchanged from the orientation of the $-NO_2$ group of the parent molecule, then either the N(1)-N(2) bond direction or the N(3)-N(4) bond direction must correspond to the direction of the maximum value of the ^{14}N hyperfine coupling. There are only two N-N bonds to be considered because the asymmetric halves of the HMX molecule are related by an inversion center. From Table 1. the maximum value of the ^{14}N hyperfine coupling, 7.04 mT, has direction cosines (0.178, -0.752, -0.635). This direction is compared to the N(1)-N(2) and N(3)-N(4) bond directions listed in Table 2. Neither direction exactly matches the maximum ^{14}N hfc direction. However, the

TABLE 1
PRINCIPAL VALUES AND DIRECTION COSINES OF THE ^{14}N HYPERFINE COUPLING TENSOR AND g-VALUE TENSOR OF $\bullet NO_2$

	Direction Cosines		
	a	b	c^*
^{14}N hfc values			
4.89 mT[a,b]	-0.596	∓0.596	+0.538
5.32	+0.783	∓0.283	-0.554
7.04	+0.178	∓0.752	-0.635
g-values			
1.989[c]	+0.290	∓0.628	-0.722
2.004	+0.789	±0.584	-0.190
2.007	-0.541	±0.515	-0.665

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[a] 1mT= 10 Gauss
[b] accurate to ±0.2mT
[c] accurate to ±0.001

TABLE 2
COMPARISON OF $\bullet NO_2$ EPR DIRECTIONS TO THE
β-HMX CRYSTAL STRUCTURE DIRECTIONS

	Direction Cosines			Angle from ^{14}N hfc Direction[a]
Bonds	a	b	c*	
N(1)-N(2)	-0.870	+0.186	-0.458	90°
N(3)-N(4)	+0.678	-0.640	-0.363	30°
Planes				
N(2)-N(1)-O(1)-O(2)				87°
N(3)-N(4)-O(3)-O(4)				11°

---

[a] maximum ^{14}N hfc directon (+0.178, -0.752, -0.635)

maximum ^{14}N hfc direction is much closer to the N(3)-N(4) direction (angle=30°) than to the N(1)-N(2) direction (angle=90°). If the least amount of reorientation of the C_2 symmetry axis of the $\bullet NO_2$ radical is assumed, then the N(3)-N(4) bond is assigned as the location of $\bullet NO_2$ formation.

A similar argument applies if the geometric planes N(2)-N(1)-O(1)-O(2) and N(3)-N(4)-O(3)-O(4) are compared to the maximum ^{14}N hfc direction. An average plane was computed for each set of atoms. The direction orthogonal to the N(2)-N(1)-O(1)-O(2) plane is (-0.200, 0.718, 0.666). The direction orthogonal to the N(3)-N(4)-O(3)-O(4) plane is (-0.467, -0.759, 0.454). The maximum ^{14}N hfc direction makes an angle of 11° with the N(3)-N(4)-O(3)-O(4) plane and an angle of 87° with the N(2)-N(1)-O(1)-O(2) plane. This indicates that the C_2 symmetry axis of the $\bullet NO_2$ radical lies almost within the N(3)-N(4)-O(3)-O(4) plane. This gives additional support for cleavage of the N(3)-N(4) bond assuming minimum reorientation of the C_2 axis.

From the crystal structure data of Choi and Boutin the N(3)-N(4) bond distance (1.373Å) is larger than the N(1)-N(2) bond distance (1.354Å) indicating a weaker N(3)-N(4) bond. The crystal structure data also indicates that there is higher strain along the N(3)...N(3') direction than along the N(2)...N(2') direction. (Primes indicate the atom related by the inversion center of the molecule). This is attributed to closer packing of atoms along the N(3)...N(3') direction. Higher strain and a weaker bond favor N(3)-N(4) bond cleavage.

The formation of $\bullet NO_2$ at only one of the N-N bond positions of β-HMX is surprising when compared with $\bullet NO_2$ formation in single crystals of RDX. Ultraviolet photolysis of single crystals of RDX under the same conditions produces $\bullet NO_2$ radicals at each N-N bond position of the molecule. The higher symmetry and lower strain of the HMX ring may be related to this finding. Another important factor is the counter radical which must be formed by homolytic cleavage during the formation of $\bullet NO_2$. This radical is not clearly observed at 77K. Lower temperatures may help to isolate this radical. Further studies are planned to investigate the influence of symmetry and ring strain on the free radical formation in nitramines.

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