change in electronic configuration between states, nuclear tunneling (vibrational overlap), which is a quantum effect, will dominate electron transfer. This transition is illustrated in Figure 5A. The critical issue in this case is energy disposal and not thermal activation. The form of the energy dependence arises from how the energy gap influences vibrational overlaps for the high- or medium-frequency modes that act as energy acceptors. Low-frequency modes and solvent librational modes play a role but to a much lesser degree.

The requirements for these reactions are quite different from those for thermally activated, classical electron transfer. In the absence of high- or medium-frequency acceptor modes, electron transfer is more nearly classical and thermal activation is required.^{1f,3} This case is illustrated in the energy-coordinate diagram in Figure 5B. In the limit that $\hbar\omega \ll k_{\rm B}T$, the full quadratic dependence of $\ln (k \times 1s)$ on ΔG° predicted by Marcus should be realized.

The impact of high- or medium-frequency acceptor modes is profound. If there were no $\nu(bpy)$ contributors to nonradiative decay in [(4,4'-(X)₂-bpy^{•-})Re^{II}(CO)₃(4-Etpy)]^{+*}, nonradiative lifetimes would be far longer. In the classical limit, the rate constant for nonradiative decay is given by eq 20. In this limit,

$$k_{\rm nr} = \beta_0 (1/k_{\rm B}T\lambda)^{-1/2} \exp[(\lambda + \Delta G^{\circ})^2/4\lambda k_{\rm B}T] \quad (20)$$

 λ is related to the bandwidth parameter, $\Delta \bar{\nu}_{0,1/2}$, by $\lambda \sim$ $(\Delta \bar{\nu}_{0,1/2})^2/16k_BT \ln 2$. At typical values of the energy gap (18000 cm⁻¹), $\Delta \bar{\nu}_{0,1/2}$ (3000 cm⁻¹), and λ (4000 cm⁻¹) and with the value of β_0 obtained from the energy gap law plot in Figure 2 (2 × 10¹⁴ s^{-1}), $k_{nr} = 1.3 \times 10^{-15} s^{-1}$. This is less by a factor of 1.5×10^{21} than the experimental value of $2 \times 10^6 \text{ s}^{-1}$.

The recognition of the role played by high- or medium-frequency modes on electron transfer in the inverted region has important implications for the design of molecular systems for applications in energy conversion and storage at the molecular level. It follows from our analysis that it should be possible to achieve long-lived, redox-separated states at the molecular level by choosing systems in which the energy gap is large and there is weak or no coupling with modes of high or medium frequency. Such an example may have been identified recently by Gray and co-workers.53 We are currently attempting to design such molecules.

The conclusion that electron transfer may be dominated by through-space electronic interactions is also significant in this context. With appropriate control of chemical links in related systems, it may be possible to achieve greatly enhanced lifetimes for the redox-separated state. An observation of this kind has been made in a related complex in which there is a ligand bridge "spacer" between the donor and acceptor sites.⁵⁴

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EPR Spectra of Photochemical NO₂ Formation in Monocyclic Nitramines and Hexanitrohexaazaisowurtzitane

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NO₂ radicals produced by ultraviolet light are studied in three condensed-phase nitramines; cyclotrimethylenetrinitramine (RDX), cyclotetramethylenetetranitramine (HMX), and hexanitrohexaazaisowurtzitane (HNIW), a newly developed nitramine. Electron paramagnetic resonance (EPR) spectroscopy is used to measure NO₂ radical concentrations in polycrystalline samples of each nitramine and to analyze NO₂ conformations in single crystals of HNIW. The results show that HNIW has a quantum yield of formation of NO₂ radicals that is 1 order of magnitude greater than either RDX or HMX. Trapped NO₂ radical sites in an HNIW single crystal are analyzed at 77 K before (I) and after (II) annealing at 298 K. For (I) the nitrogen hyperfine couplings and g values are $A_x = 5.7 \text{ mT}$, $A_y = 5.8 \text{ mT}$, $A_z = 7.0 \text{ mT}$ and $g_x = 2.0062$, $g_y = 1.9952$, $g_z = 2.0020$. For (II) the values are $A_x = 4.9 \text{ mT}$, $A_y = 5.4 \text{ mT}$, $A_z = 7.0 \text{ mT}$ and $g_x = 2.0057$, $g_y = 1.9927$, $g_z = 2.0017$. EPR spectral line shapes indicate different motional correlation times of I and II at 77 K. At 298 K stabilization of NO₂ radicals in the α -polymorph of HNIW is attributed to trapping of NO₂ in clathrate regions of the HNIW crystallites.

I. Introduction

Nitramines are used in rocket propellants and in munitions. Recent synthetic efforts have produced several polynitropolyaza-caged compounds whose properties are being compared with conventional nitramines.¹ In particular this report describes results for 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo-5.5.0.0^{5,9}.0^{3,11}-dodecane, or hexanitrohexaazaisowurtzitane (HNIW, Figure 1), which is an interesting new nitramine molecule.2

Characterization of impurities, including free radicals, is part of a larger effort to investigate the chemical and physical properties

TABLE I: Crystallographic Data for Selected Nitramines

nitramine ^a	space group	nitramine ^a	space group	
RDX HMX	Pbca P2 ₁ /c	HNIW ⁶	Pbca	

"RDX refers to the β -polymorph;³¹ HMX refers to the β -polymorph;³² HNIW refers to the α -polymorph.¹⁴ ^b HNIW has eight sites per unit cell given by the following symmetry operations: molecule 1 (x, y, z); molecule 2 (0.5 - x, 0.5 + y, z); molecule 3 (x, 0.5 - y, 0.5 + y, z)z); molecule 4 (0.5 - x, -y, 0.5 + z); molecule 5 (-x, -y, -z); molecule 6 (0.5 + x; 0.5 - y; -z); molecule 7 (-x, 0.5 + y, 0.5 - z); molecule 8 (0.5 + x, y, 0.5 - z).

of HNIW. The occurrence of free-radical impurities in HNIW is not surprising. Past studies have shown that free-radical products in nitramines form by many different pathways. Photolytic degradation of nitramines and nitroaromatics in solution

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Figure 1. Molecular structure of HNIW. Hydrogens are not shown.

form steady-state concentrations of free-radical products that rapidly decay when the UV light is turned off.³⁻⁵ Thermal decomposition studies have shown that nitramine and nitroaromatic free radicals are formed and decay quickly following heating.⁶⁻⁸ In the solid state, paramagnetic radicals and ions may be stabilized in defect sites of single crystals or polycrystalline powders.^{9,10} Such defects may strongly influence the stability of these materials.

Crystal data for RDX (cyclotrimethylenetrinitramine), HMX (cyclotetramethylenetetranitramine), and HNIW are listed in Table I. Prior studies have established that UV light initiates the formation of NO₂ radicals in RDX and HMX at 77 K.^{11,12} The experimental results herein show NO₂ radicals form during photolysis of HNIW under similar experimental conditions. In this study trapped NO₂ is compared for the series RDX, HMX, and HNIW. The trapped NO₂ radicals are formed at 77 K from an excited electronic state initiated by 320-400-nm light. Nitric oxide (NO) production from ultraviolet light may also be initiated at lower temperature (20 K).¹³ In section IIIA, a quantitative measurement of the production rate of NO₂ radicals is compared for RDX, HMX, and HNIW under identical UV exposure. In section IIIB, an HNIW single-crystal study is reported for NO2 radicals at 77 K before and after annealing an HNIW crystal at room temperature. This study was carried out in order to understand motion and diffusion of NO2 in the defect sites. In section IIIC, polycrystalline EPR spectra of NO2 are analyzed-showing for the first time that this oxidant can be stabilized in a solid "bulk" phase polycyclic nitramine at ambient temperature and pressure.

II. Experimental Section

Hexanitrohexaazaisowurtzitane high-purity samples were supplied by the Naval Weapons Center, China Lake, CA; Aerojet Solid Propulsion, Sacramento CA; and the Naval Surface Warfare Center, White Oak, MD. Although HNIW is known to have at least four polymorphic forms, only the α -polymorph was used in this study.¹⁴ The crystal structure of HNIW has been determined by R. D. Gilardi of the Naval Research Laboratory.¹⁵ Some crystallographic information is given in Table I. For polycrystalline

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TABLE II: NO₂ Concentrations

nitramine	effective no. of molecules ^b	spin concn (spins) ^c	% conversion ^d
RDX	9.8×10^{17}	5.0×10^{13}	0.0051
НМХ	7.7×10^{17}	2.2×10^{13}	0.0029
HNIW	5.4×10^{17}	2.5×10^{14}	0.046

^a Polycrystalline powder samples; UV photolysis at 77 K; spectra re-corded at 77 K. ^b The effective number of molecules in each sample actually exposed to the UV light is estimated by assuming that the flat cell sample approximates a thin film 10 μ m thick and that the film is crystalline. 'The spin concentration measured by EPR relative to weak pitch (10^{13} spins) with 1 spin per free radical; error $\pm 15\%$. ^d Calculated as the ratio of the spin concentration to the effective number of molecules $\times 100$.

studies, HNIW samples were used without further purification. The samples provided were claimed to have greater than 99% purity and to contain no significant synthetic analogues of HNIW. For single-crystal studies, crystals of the α -polymorph were grown from solution of a 1:1 mixture, by volume, of methanol and acetone. A 2-mL volume of the solution was saturated with HNIW at room temperature, and crystals grew from solution within 3 days by slow evaporation. Optical photographs of the crystals were made by using a Zeiss transmission microscope equipped with a 35-mm camera.

The samples were exposed to ultraviolet light from a 1000-W Hg-Xe Hanovia (Electro Powerpacs Inc., Cambridge, MA) high-pressure arc lamp. A constant lamp power of 1000 W was used in all experiments. Corning filters no. 7-60 (λ 300-480 nm) and 3-75 (λ 380-4200 nm) were used to measure the wavelength dependence of radical formation. No EPR signals in solid samples were observed at wavelengths greater than 380 nm. Precise amounts of polycrystalline powders of RDX, HMX, and HNIW were loaded into three separate flat cells, having dimensions of 5 mm (width) \times 0.5 mm (thickness) filled to 4 mm height. All photolyses were carried out under the same conditions of temperature and light flux. The dewar containing the sample cell was located 16 cm from the lamp, and a lens was used to focus the UV light onto the sample with a beam spot of 1-cm diameter, so that the entire sample received uniform exposure to the UV light. Only one side of the flat cell was UV irradiated. EPR spectra were recorded by using a Bruker ER 200 X-band spectrometer and a liquid nitrogen dewar. Variable temperature was achieved by using a resistive heating coil contained in a nitrogen flow-through dewar and an Omega IIB 3083 K alumel-chromel thermocouple inserted near the sample. A Nicolet 1175 signal data processor was used to collect EPR spectra and perform line-shape integrations. The spin concentration measurements were calibrated by using weak pitch (0.00033% pitch in KCl) and a Bruker dual X-band cavity. A manganese reference standard (Mn^{2+}) was used to calibrate the g values.

Signals were observed after only a few seconds of UV irradiation at 77 K, but to maximize the parent-to-radical conversion, approaching the mass depletion limit of the crystalline surfaces, photolysis was carried out for 30 min at 77 K on each sample. The NO₂ EPR signals from the irradiated samples were stable at 77 K. The concentration of NO2 was then measured by double integration of the first-derivative EPR signal and by comparison to the EPR standard. The spin concentrations were normalized by taking into account the density and weight of each sample.

III. Results

A. NO₂ Concentrations of Photolyzed Polycrystalline Samples. To characterize their electronic absorptions, ultraviolet spectra were recorded for solutions of RDX, HMX, and HNIW in acetonitrile (initial concentrations of 0.004 M). Each sample gave a strong absorption at $\lambda = 234$ nm for RDX, $\lambda = 227$ nm for HMX, and $\lambda = 225$ nm for HNIW. No bands were observed in the range 300-400 nm. These results are in agreement with solution spectra recorded by other researchers and indicate that the molar absorptivities of these nitramines are similar.^{16,17} This

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⁽¹⁴⁾ The acronym HNIW refers to the α -polymorph of hexanitrohexaazaisowurtzitane throughout this report. Only the α -polymorph was used for the EPR experiments.

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Figure 2. Photograph of an HNIW crystal. The a axis coincides with the vertical bisector of the obtuse angle formed by the crystal edges. The b axis is assigned perpendicular to the plane of the page. The c axis is the horizontal bisector of the acute angle formed by the crystal edges.

is particularly true for HMX and HNIW, which have a molar absorptivity $\epsilon \approx 20\,000 \text{ cm}^{-1} \text{ L/mol}$ and supports an assumption that solid-phase samples of these nitramines absorb UV light with similar efficiencies.

The trend of increasing NO₂ densities is RDX < HMX < HNIW. On the basis of this relationship and a naive assumption that the more nitramine groups present, the more NO₂ radicals expected, then a corresponding order is predicted for the NO₂ radical concentrations produced by UV photolysis. Table II gives the experimental NO₂ spin concentrations in each of the three nitramine samples studied. This result was reproduced by several experimental runs. Examining column 3 of Table II shows that the trend predicted above is only partly followed. RDX and HMX give about the same number of radicals (with RDX slightly higher), but HNIW produces about an order of magnitude greater concentration of NO₂ radicals than either RDX or HMX under identical conditions of UV irradiation, thus giving the trend of increasing NO₂ radical concentrations as HMX < RDX \ll HNIW.

The NO₂ concentrations are much less than the total number of nitramine groups (\sim 1:10000). A conservative estimate of the depth to which the UV light penetrates the surface of each exposed grain of sample is 10 μ m.^{18,19} The UV light is assumed to penetrate each nitramine crystallite by the same depth before being attenuated based on the similarity of the solution-phase UV spectra, the similar particle sizes, and similar transparencies of RDX, HMX, and HNIW. An estimate of the number of molecules exposed to UV light for each nitramine sample is given in column 2 of Table II. Assuming close packing of the nitramine granules, each sample approximates a thin film. By taking the ratio of the measured spin concentrations to the total number of exposed molecules, an estimate of the percentage of NO₂ radicals produced is achieved (Table II, column 4). The HNIW free-radical concentration is much greater than predicted by the density of this material. To investigate which nitramine bonds are breaking to form NO₂ radicals, a single-crystal study of HNIW was carried out as described in the next section.

B. Single-Crystal EPR Spectroscopy of NO₂ Sites in HNIW. Single crystals of HNIW were grown from a solution of methanol and acetone (1:1 volume ratio) saturated with HNIW at room temperature. Crystals grew from solution slowly over 3 days at room temperature. An optical transmission photograph of a single crystal is shown in Figure 2. The crystals are rhombohedral with an acute angle of 77.5°. The typical dimensions of the major and minor axes of the rhombohedron are 3 and 2 cm, respectively. For these experiments, single crystals were irradiated with UV

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⁽¹⁹⁾ This is probably a low estimate of the penetration depth of the UV light. It has been shown that RDX and HMX solids absorb at $\lambda = 350$ nm (Marinkas, P. L. J. Lumin. 1977, 15, 57) with an absorption coefficient of 10² cm⁻¹, giving a penetration depth of 0.1 mm. This is sufficient to penetrate the samples used in this study. However, experimental factors (lamp-to-sample distance, irradiation times, signal stability, etc.) make precise measurement of the penetration depth difficult in this experimental setup. For penetration depths greater than 10 μ m there would be a proportionate decrease in the radical-to-molecule ratio-in Table II; however, the finding that HNIW produces much more free NO₂ than RDX or HMX would remain unchanged.



Figure 3. First-derivative EPR spectra with H_0 along the direction (0.643, 0, -0.766) as defined by the reference frame in Figure 2. (a) EPR spectrum recorded at 77 K before warming the crystal. Signals are from NO₂, denoted as I, and radical X. (b) EPR spectrum recorded at 77 K after annealing the crystal for several minutes at 298 K showing signals from NO₂, denoted as II.

light under the same conditions as described for polycrystalline samples in section IIIA and studied by using EPR by transferring the crystals to a liquid nitrogen dewar in the EPR cavity.¹³ Between 77 K and room temperature at least two clearly identified radicals are detected. The following equations give the sequence of radical formation and decay (EPR spectra are shown in Figure 3):

parent HNIW
$$\rightarrow$$
 NO₂ + radical X (77 K) (1)

 NO_2 + radical X \rightarrow NO_2 (radical X decays) (298 K) (2)

NO₂ (highly mobile) (298 K) \rightarrow

$$NO_2$$
 (weakly mobile) (77 K) (3)

The EPR spectrum shown in Figure 3a is assigned to NO₂ and an unidentified radical labeled as radical X. The spectral pattern of the EPR signal due to the NO₂ radical consists of three lines, separated by the electron-nuclear hyperfine coupling of the ¹⁴N nucleus (I = 1). Both NO₂ and radical X are stable at 77 K. Warming the photolyzed HNIW crystal to room temperature leads to disappearance of radical X. The orientations of the NO₂ radicals in the crystal lattice before warming the crystal are not significantly different from the NO₂ orientations after warming. However, recooling the crystal to 77 K results in line narrowing of the NO_2 spectrum. A model that accounts for the line-shape changes is discussed in section IV. Tensors for the ¹⁴N hyperfine couplings and the g values were measured by a complete singlecrystal analysis carried out on the NO₂ spectra at 77 K before warming the crystal to room temperature denoted as I and on the NO₂ spectra recorded at 77 K after warming the crystal to room temperature, denoted as II. Results are listed in Table III. The angular dependences of the ¹⁴N hyperfine couplings and g values for II are given in Figure 4.

By comparing the experimental direction cosines of the maximum g value and the maximum ¹⁴N hyperfine coupling value to direction cosines derived from the crystallographic coordinates, a suggested assignment of where the nitramine bond breaks to form an NO₂ radical can be made. When making such comparisons it is essential to keep track of the reference frame of the HNIW crystal with respect to the crystallographic a, b, c axes. The assignment of the reference axes in Figure 2 was used for this purpose. This assignment is based on the calculated angle

TABLE III: ¹⁴N Hyperfine Couplings and g Values for NO₂ Trapped in HNIW

I ^a	II ^b		
2.006 (2) (0.448, 0.751, -0.486)	2.005 (7) (0.777, 0.521, -0.355)		
1.995 (2) (0.130, -0.592, -0.795)	1.992 (7) (-0.128, 0.682, 0.720)		
2.002 (0) (0.885, -0.293, 0.363)	2.001 (7) (0.617, -0.514, 0.596)		
5.7° (-0.896, -0.296, 0.333)	5.4 (-0.776, -0.596, 0.206)		
5.8 (0.698, -0.645, 0.761)	4.8 (0.242, -0.584, -0.775)		
7.0 (0.440, -0.705, 0.557)	7.0 (0.582, -0.552, 0.597)		

^eNO₂ EPR spectra recorded at 77 K before warming the HNIW crystal to room temperature. These signals showed broader line widths than II, making the measurements of g and ¹⁴N hfc (hyperfine coupling) less accurate than for II. ^bNO₂ EPR spectra recorded at 77 K after warming the HNIW crystal to room temperature. ^cUnits in millitesla.



Figure 4. Angular dependence of the ¹⁴N hyperfine couplings (solid line, read from the right vertical axis) and the g values (dashed line, read from the left vertical axis) of EPR spectrum of II recorded at 77 K. Data from only one site are shown. The planes ab, bc, and ca are referenced in Figure 2.

between the planes (102) and (-102) of 77.4°, which is in agreement with the acute angle observed in the crystal.¹³

A complication that arises from vector comparisons between experimental and calculated data is phase ambiguity, introduced by the signs of the direction cosines. In the EPR single-crystal data two NO₂ sites are observed due to orthorhombic symmetry of the *Pbca* space group of HNIW, and the angular dependences of the spectra of these sites vary depending on the plane of rotation of the crystal relative to the polarizing magnetic field direction. The correlation of site assignments among the data sets specified by the axis labels *ab*, *bc*, and *ca* is not determined by experiment.

TABLE IV: Nitramine Bond Directions and NO₂ Planes^a

bonds ^b	planes	
N2-N2a (0.967, 0.191, 0.172)	O2a-N2a-O2b (0.092, -0.062, -0.994)	
N4-N4a (0.183, 0.790, -0.586)	O4a-N4a-O4b (0.586, -0.528, -0.615)	
N6-N6a (0.694, 0.159, -0.703)	O6a-N6a-O6b (-0.210, 0.299, -0.931)	
N8-N8a (-0.648, -0.738, -0.189)	O8a-N8a-O8b (-0.210, 0.299, -0.931)	
N10-N10a (-0.653, 0.005, 0.757)	O10a-N10a-O10b (-0.291, 0.914, -0.281)	
N12-N12a (0.349, -0.360, 0.866)	O12a-N12a-O12b (0.775, 0.632, -0.027)	

^aSigns in this table are for site x, y, z. Other sign possibilities are generated from the symmetry arguments given in Table I. The atom numbers in this table correspond to symmetrically related atoms in Figure 5b, but letters distinguish ring nitrogens (unlabeled) from nitro group nitrogens (labeled a) and nitro group oxygens (labeled a and b). In Figure 5 multiple letter labels are used to distinguish different sites. For example, N(8aa) and N(8ab) in Figure 5b are related to N8a in this table by symmetry operations (0.5 + x, 0.5 - y, -z) and (0.5 - x, 0.5 + y, +z), respectively. ^bSix nitramine bond directions occur in the HNIW molecule. The maximum ¹⁴N hyperfine coupling direction is (0.582, -0.552, 0.597) as given in Table II. ^c Directions perpendicular to the O-N-O planes are given.

Therefore, eight combinations of sign assignments for each of the two sites are possible from experiment. This gives eight different sign combinations of the off-diagonal terms of the g value and hyperfine tensors calculated from these data sets and four possible sign combinations of the a, b, c components of the direction cosines when the tensors are diagonalized.

Direction cosines calculated by using the HNIW crystallographic coordinates for the planes of each of the six NO₂ groups of the HNIW molecule in each of eight sites of the unit cell are shown in Table IV. Four different sign combinations of the a, b, c components arise from the calculated set of vectors after the total number of possible combinations is reduced by symmetry. This means that there are four sets of direction cosines from experiment that must be compared to four calculated sets of direction cosines. The strategy used to correlate the experimental results with the crystallographic data was to compare magnitudes of the a, b, c components of the direction cosines and then consider the sign combinations. For this comparison results from data set II were used.

The maximum ¹⁴N hyperfine coupling coincides with the C_2 symmetry axis bisecting the O–N–O angle.²⁰ This allows one to compare this direction with the nitramine bond directions that are known from the crystal structure. If severe reorientations of the NO₂ groups do not occur during bond cleavage, then the maximum ¹⁴N coupling should match one of the nitramine bond directions. Inspection of the nitramine bond directions (Table IV) shows good agreement between the maximum ¹⁴N hyperfine coupling direction of II and the N12–N12a bond direction (Table IV gives the *xyz* position. Table I gives symmetry arguments for equivalent sites in the unit cell). The angle between these directions is less than 30°. This is the best match of both magnitudes and signs of all allowed choices of the nitramine bonds.

Support for this assignment also comes from examining the g tensor. The maximum g value direction is orthogonal to the NO₂ C_2 symmetry axis and orthogonal to the NO₂ plane as determined by prior studies.²¹ This direction is (+0.775, +0.632, -0.027) for the O(12a)-N(12)-O(12b) plane as calculated from the crystal structure coordinates. The value of g_{max} for II is 2.0057 and lies in the direction (+0.777, +0.521, -0.355). These two direction vectors differ by 20°, but their match is much better than for direction cosines of the alternative NO₂ planes. For example, the angle between N2-N2a and g_{max} is 70°. If minimal reorientation of the NO₂ takes place during radical formation and during



Figure 5. Clathrate site formed by the host HNIW molecules and a guest H_2O molecule shown with two possible positions of H_2O in the inclusion site. (a) This view shows the molecular packing arrangement of four HNIW molecules to form the inclusion center. (b) This expanded view shows nitramine groups involved with formation of this inclusion center. These include molecule 6 (O8aa, N8aa, O8ba, N8b and O10d, N10c, O10c, N10b); molecule 2 (O10e, N10e, O10f, N10d and O8ab, N8ab, O8bb, N8c); molecule 3 (O12h, N12f, O12g, N12g); and molecule 7 (O12k, N12k, O12l, N12j) generated by equivalent positions given in Table 1.

annealing of the crystal at room temperature, then the singlecrystal analysis supports cleavage at the N12–N12a bond location to form the radical.

There is experimental precedence that at or below liquid nitrogen temperature, minimal molecular reorientations occur during cleavage of bonds. One such example is radical pair formation in photolyzed crystalline dibenzoyl peroxide. Radical pair formation in this system has been studied by McBride and co-workers, who have shown that minimal reorientation is associated with the bond cleavage event to form radical pairs.²² Upon warming the sample, reorientations of molecular and atomic fragments can occur, but in the HNIW crystal the direction cosines indicate that the NO₂ orientations before and after warming the crystal are nearly the same (Table III). This suggests that the NO₂ radicals undergo rapid motion at high temperature but relax to an orientation of minimum potential energy upon recooling to 77 K. This appraisal of the stabilization of the NO₂ radicals is preliminary and will be further investigated by using ENDOR.

In the previous discussion the tensor directions reflect the average orientations that the NO_2 radicals have in the lattice sites at constant temperature (77 K). When the temperature is in-



Figure 6. Experimental and simulated first-derivative polycrystalline EPR spectra shown for NO₂ trapped in HNIW at (a) 77 K and (b) 123 K showing the onset of motion and (c) at 173 K showing motional line broadening. The diffusion coefficients indicated were used to simulate the spectra.

creased above 77 K, the NO_2 radicals undergo rapid rotation. The following section discusses the effect of motions on the EPR line shape and details of the radical rotation.

C. EPR Line-Shape Studies of NO₂ in Polycrystalline HNIW. HNIW (α -polymorph) crystallizes with formation of inclusion centers where H₂O or other molecules may be trapped.¹⁵ RDX and HMX do not have such clathrate-like forms. Figure 5 shows how molecular packing in the HNIW crystal creates this solvation cavity with H₂O depicted as the trapped molecule. The cavity is associated with a nonsymmetrical nitro group attached to the N12 position. The cavity is approximately 0.3×0.5 nm, so that it can accommodate other small molecules such as NO_2 . This unusual feature of HNIW may account for the detection of NO2 radicals in HNIW polycrystalline samples that have been stored at room temperature for long periods of time. We have observed significant radical concentrations even with samples of 99% reported purity. Figure 6a shows the experimental and simulated polycrystalline EPR spectra were recorded from HNIW stored at room temperature for 12 weeks. The EPR spectrum must be recorded at temperatures below 220 K because above this temperature rapid motion of the NO2 results in motional broadening of the EPR line shape. We observe this signal from HNIW samples stored in room light but with no prior UV light treatment. suggesting that free NO_2 is trapped during synthesis or formed by degradation during storage.

The EPR line shapes of the NO_2 molecules in the trapped sites have a complex temperature-dependent behavior. To analyze these complex line shapes EPR spectra were computed for variations of the correlation times of rotation about the symmetry axes of NO2. This was accomplished by using the slow-motional EPR theory developed by Freed et al.²³ The EPR theory has been discussed in publications by these researchers and will not be repeated here. A PC-based implementation of this theory was recently reported by Freed and Schneider.²⁴ Studies using the slow-motional theory to simulate nitroxyl EPR spectra, as well as NO₂ EPR spectra, have been recently published.^{25,26}

Other experimental NO₂ EPR spectra recorded at 123 and 173 K are shown side-by-side with simulated spectra in Figure 6. Simulations were carried out by varying the rotational correlation times about the C_2 symmetry axis of the NO₂ molecule (reported as the diffusion coefficients, D_{ZZ} , where $\tau^{-1} = 6D_{ij}$) and about the direction parallel with the O-O bond direction (D_{XY}) . For these calculations the xy plane corresponds to the O-N-O plane. This analysis shows that the molecule undergoes faster motion about the O-O direction than about the C_2 axis.

This result is consistent with previous investigations of NO₂ motion. In one of the first papers describing motion of NO₂ in a polycrystalline N₂O₄ matrix between 77 K and room temperature, it was reported that motion occurs about the O-O direction.²⁷ In that study NO_2 was shown to have mobile and immobile sites that contributed to the polycrystalline spectrum in frozen N_2O_4 . On the basis of comparisons of experimental spectra to simulated spectra, a ratio of mobile-to-immobile components was determined to be 14%. Only at temperatures above 159 K were rotations about the O-O direction observed. It was also noted that annealing the matrix at room temperature for 20-30 s resulted in sharpening of the spectral lines. This is similar to the phenomenon reported in Figure 3 for HNIW spectra, although the HNIW crystal was kept at room temperature for much longer periods of time. In a more recent study, Kevan and co-workers observed NO₂ motion about the O-O axis direction.²⁶ Their study was carried out on SiO₂ surfaces, and by using pulsed EPR the NO₂ was found to be distributed in sites with slightly varying g and hyperfine tensors. These studies suggest that there are specific conditions under which NO_2 is stabilized and that it is unusual to see room-temperature stability as has been observed with HNIW. An assessment of the current understanding of the free radical stability in HMX, RDX, and HNIW is given in the Discussion.

IV. Discussion

The EPR assignment of NO₂ was first reported in γ -irradiated NaNO₂ by Zeldes and Livingston.²⁸ The detection of NO and NO₂ in single crystals and polycrystalline matrices has since been reported by other researchers.^{29,30} In most cases temperatures below 200 K are required in order to observe the EPR signals because of motional and exchange line broadening of the radical signal. Our previous investigations of UV-irradiated single crystals of RDX showed multiple sites of formation of NO₂ radicals.¹¹ The sites did not correspond to a unique bond location, and it was concluded that both axial and equatorial nitramine groups were broken to form the radicals. In HMX similar reasoning led to the conclusion that N3-N4 (atomic labels are in reference to the crystal structure)¹² bond cleavage resulted in the NO_2 signals. In both HMX and RDX the NO₂ signals decayed with warming of the crystals to 298 K. The experimental findings for HNIW suggest that radical processes are much more complicated in HNIW than in RDX and HMX because (i) a greater concentration of NO₂ is produced in HNIW than in RDX or HMX and (ii) the NO₂ is stabilized in the HNIW crystal even at 298 K. We have observed such stability previously only in irradiated guanidine nitrate or guanidine chloride salts.³³

Does the inclusion center in HNIW account for NO₂ longevity at 298 K? The clathrate complex is formed by binding of a guest molecule, which is usually H₂O, with the host HNIW molecules as shown in Figure 5. From the crystal structure there are eight possible H₂O sites per unit cell. These sites occur in close pairs, so effectively there are only four nitramine-enclosed cavities per unit cell. This means that in order to be fully occupied, each cavity would contain two guest molecules. The crystal data show not more than $0.5 \text{ H}_2\text{O}$ molecules per cage site. This indicates that

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the inclusion sites formed by the cavities are not fully occupied by H₂O. Vacancies allow for other molecules such as NO₂ to form clathrates with the HNIW molecules. The EPR results implicate the N12-N12a bond (Table IV) and symmetrically equivalent positions (Table I) as the major position for radical formation. This is one of the nitramine bonds that forms the "cage" inclusion center. For NO₂ radical formation at this position, the NO₂ would effectively be in the cage immediately when formed. This provides an opportunity for trapping NO_2 at the inclusion site, especially if the cavity does not contain a guest H₂O molecule.

Annealing the crystal at room temperature provides kinetic energy to the NO₂ radicals that might be sufficient to induce diffusion into the cage sites from other locations. From section IIIA, it is shown that more NO₂ is produced per quantum of UV from HNIW than from RDX or HMX. There are weak signals (not shown) in I and II spectra that indicate that other NO_2 conformations exist. No attempt was made to study these additional conformations because the signals were too weak and masked by the more intense signals from I or II.

Another factor that might contribute to NO₂ formation and stability is the presence of other nitrate impurities. Studies by Box and Rustgi show that HNO₃ facilitates the formation of NO₂ in X-irradiated nitrate salt crystals of glycylglycine.³⁴ The reaction as shown in eq 4 proceeds by electron scavenging by the

$$RNH_3^+NO_3^- \xrightarrow{c} RNH_3^+ + NO_3^{\cdot 2^-}$$
 (4)

$$2NO_3^{\bullet 2-} \xrightarrow{2H^+} 2NO_2 + 2OH^-$$
(5)

 NO_3^- anion to form $NO_3^{\bullet 2-}$, which is paramagnetic. There are two factors that were shown to contribute to $NO_3^{\bullet 2-}$ stability: (i)

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the $NO_3^{\circ 2^-}$ is stable as long as the temperature is low enough to prohibit proton transfer from a neighboring molecule or (ii) deuteration of neighboring molecules prohibits NO₃^{•2-} decay. Warming the crystal to room temperature facilitates proton transfer from adjacent molecules and results in reduction of NO₁^{•2-} to form NO_2 and the hydroxyl anion. This pathway for NO_2 formation will be investigated in HNIW crystals by the ENDOR technique.

V. Summary

Hexanitrohexaazaisowurtzitane decomposes photolytically to produce more NO₂ than that produced from an equivalent mass of either RDX or HMX. The NO₂ is trapped in crystalline HNIW and remains stable for extended periods at room temperature. The NO₂ stability is suggested to involve clathrate formation with near-neighbor molecules that form an inclusion site.

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Rate Constants (296–1700 K) for the Reactions $C_2H + C_2H_2 \rightarrow C_4H_2 + H$ and $C_2D + C_2D_2 \rightarrow C_4D_2 + D$

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Rate constants for the reactions $C_2H + C_2H_2 \rightarrow C_4H_2 + H$ and $C_2D + C_2D_2 \rightarrow C_4D_2 + D$ have been measured over the temperature range 296-1475 and 1226-1700 K, respectively. For the high-temperature experiments, the method was the laser photolysis-shock tube technique (LP-ST); however, for the room-temperature experiments, the laser photolysis-resonance absorption (LP-RA) technique was used. These techniques utilize the atomic resonance absorption spectroscopy (ARAS) method to monitor H or D atom formation. The results for $C_2H + C_2H_2 \rightarrow C_4H_2 + H$ may be represented by the Arrhenius expression $k_{1H} = 3.02 \times 10^{-10} \exp(-235 \text{ K/T}) \text{ cm}^3$ molecule⁻¹ s⁻¹ or may be represented by the simple average of all values, $k_{1H} = (1.9 \pm 0.8) \times 10^{-10} \text{ cm}^3$ molecule⁻¹ s⁻¹, over the temperature range 296-1475 K. The rate constant for the reaction $C_2D + C_2D_2 \rightarrow C_4D_2 + D$ can be represented by a simple average of the experimental values, $k_{1D} = (1.8 \pm 0.5) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹, over the temperature range 1226-1700 K. The primary quantum yield for H atom production from acetylene by single-photon absorption at 193.3 nm has also been determined to be 0.21 ± 0.04 .

Introduction

The ethynyl radical, C₂H, is known to be an important chemical species in combustion systems, and it apparently plays a key role in the initial stages of soot formation.¹ It has also been detected in several astrophysical environments.²

Rate constants for the reaction

$$C_2H + C_2H_2 \rightarrow C_4H_2 + H \tag{1}$$

have previously been measured three times at room temperature by Lange and Wagner,³ Laufer and Bass,⁴ and Stephens et al.⁵ However, no higher temperature measurements have been reported to date by any absolute technique. Since the room-temperature

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