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ESR study of free radicals in irradiated single crystals of potassium hydroxylamine disulfonate*

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Two free radicals formed when single crystals of potassium hydroxylamine disulfonate are irradiated with gamma rays at 77°K were studied by ESR. The ESR spectra result from a predominant center (radical A) exhibiting large ^{14}N and ^1H hyperfine splittings and from lesser amounts of Fremy's radical $[\dot{\text{O}}\text{N}(\text{SO}_3)_2^-]$. The g and hyperfine tensors of these radicals have been evaluated and are discussed. Radical A, whose identity remains in doubt, may be regarded as the precursor to Fremy's radical; on warming its lines decay and those of Fremy's radical are formed. Lines from radical A decrease in strength and those of the hydroxyl radical ($\dot{\text{O}}\text{H}$) grow in strength when irradiated crystals are photolyzed at 77°K. The reverse reaction occurs in the dark; the hydroxyl radical disappears and radical A is reformed.

INTRODUCTION

Fremy's radical $[\dot{\text{O}}\text{N}(\text{SO}_3)_2^-]$ is a stable free radical which has been the subject of many chemical studies, and its ESR lines in solution have been used widely as magnetic field markers. An early study¹ showed that it could be coprecipitated into a single crystal of its chemical parent, potassium hydroxylamine disulfonate and anisotropic ^{14}N hyperfine splittings were observed. This work was recently extended² to an evaluation of the g and ^{14}N hyperfine tensors. It was also found that the radical is produced when the disulfonate crystals are exposed to x rays at room temperature.

This report is primarily concerned with a precursor to Fremy's radical that is found along with smaller amounts of Fremy's radical when the disulfonate single crystals are irradiated with ^{60}Co gamma rays at low temperatures (77°K). Its hyperfine tensors from ^{14}N and ^1H and its g tensor have been evaluated and are discussed. At 77°K on photolysis with visible light its ESR lines decrease in strength and the hydroxyl radical ($\dot{\text{O}}\text{H}$) is formed. The precursor is stable only at low temperature; on warming it decays irreversibly into Fremy's radical. The ESR spectrum of Fremy's radical has been reinvestigated so that a more direct comparison with the precursor can be made.

EXPERIMENTAL

Potassium hydroxylamine disulfonate $[\text{K}_2\text{HON}(\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}]$ was prepared by the reaction of NO_2^- with HSO_3^- using a modification of Rashig's method.³ Single crystals were grown from unbuffered solutions in H_2O or D_2O made slightly alkaline with KOH. Crystals (monoclinic) were grown both by slow cooling and by evaporation. They usually grew elongated in the c^* direction with a habit more like that described by Groth⁴ than that described by Hamrick *et al.*² X-ray diffraction studies⁵ show that they possess $P2_1/c$ symmetry with four molecules in the unit cell and with cell dimensions $a = 10.16$, $b = 6.56$, $c = 14.72 \text{ \AA}$, and $\beta = 106.1^\circ$. The structure has not been determined.

The crystals were irradiated with ^{60}Co gamma rays while immersed in liquid nitrogen and transferred, without warming, to the ESR spectrometer⁶ operating at 9.2 GHz. Crystals were oriented with respect to the applied magnetic field by making two angular adjustments: a magnet rotation about a vertical axis and a rotation of the crystal, within the cavity, about a horizontal axis. Both rotations were reproducible to 0.2° and could be made while observing the spectrum. Spectra were displayed as second derivatives using a modulation frequency of 35 kHz. Line positions were measured by superimposing a proton NMR signal of known frequency on the ESR signal using an oscilloscope.

All measurements are referred to an orthogonal a^* , b , c axis system. The b axis direction and the ac plane were determined directly from ESR observations by noting the angles at which the more anisotropic symmetry-related lines coalesced to single lines. The a^* and c axes are not fixed by symmetry but were determined by carefully mounting a crystal such that the (100) face was normal to the magnetic field.

GENERAL OBSERVATIONS

Two radicals are formed and stably trapped when potassium hydroxylamine disulfonate single crystals are irradiated with ^{60}Co gamma rays at 77°K. One of these has been identified as Fremy's radical, $\dot{\text{O}}\text{N}(\text{SO}_3)_2^-$. The other will be designed as radical A for purposes of discussion. The concentration of A was estimated to be about three times that of Fremy's radical. This ratio remained constant up to the maximum dose studied, $2 \times 10^{20} \text{ eV/g}$. The initial radiation yield of A was estimated as 2 molecules per 100 eV.

Radical A is the precursor of Fremy's radical. On warming lines from A decrease in strength and those of Fremy's radical grow irreversibly. This transformation is illustrated in Fig. 1. The six strong lines of Fig. 1(a) are hyperfine lines from ^{14}N and ^1H from radical A. Lines from a smaller amount of Fremy's radical are obscured at this orientation. Figure 1(b) is a spectrum

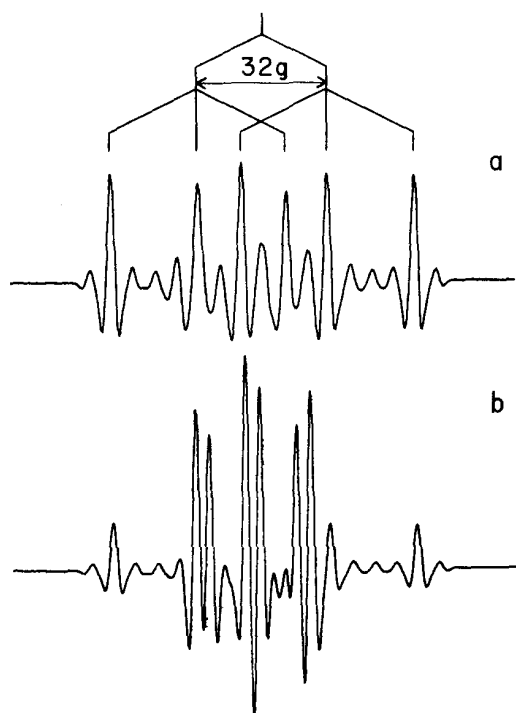


FIG. 1. ESR spectra in potassium hydroxylamine disulfonate at 77 °K. Field orientation: ac plane, 15° from a^* , 105° from c . (a) Radical A after gamma irradiation at 77 °K. (b) Growth of Fremy's radical after brief warming to 130 °K.

at 77 °K and the same orientation obtained after having warmed the crystal to 130 °K for a short time. Lines from A are much weaker, and those from Fremy's radical have grown in. The spectrum of $\text{ON}(\text{SO}_3)_2^-$ shows not only the characteristic triplet from ^{14}N but also a weak doublet splitting that arises from an interaction with a nearby proton. The onset of the transformation was observed at ca. 100 °K. It does not go to completion at any one temperature, but with further warming more Fremy's radical is formed as more of A decays. Small amounts of A were detected after warming to 220 °K. At room temperature only Fremy's radical remains. The transformation is also characterized by a change in color of the crystal from brown to pale blue typical of Fremy's radical.

When irradiated crystals are photolyzed with incandescent light at 77 °K an unusual transformation occurs. Lines from radical A decrease in strength and the hydroxyl radical, $\dot{\text{O}}\text{H}$, is formed [Fig. 2(b)]. The hydroxyl is not stably trapped in the lattice at 77 °K, but slowly decays with an accompanying regrowth of radical A [Fig. 2(c)]. This process may be repeated many times without apparent loss in strength of the lines. The kinetics of this reaction are under study and will be reported separately.

RESULTS AND DISCUSSION

The ESR line positions were analyzed using first order solutions of the spin Hamiltonian

$$\mathcal{H} = \beta_e \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + \sum_i (\mathbf{S} \cdot \mathbf{A}_i \cdot \mathbf{I}_i - g_i \beta_n \mathbf{H} \cdot \mathbf{I}_i). \quad (1)$$

Here \mathbf{g} and \mathbf{A} are the tensors representing the Zeeman and hyperfine interaction, β_e and β_n the Bohr and nuclear magnetons, \mathbf{H} is the magnetic field, \mathbf{S} and \mathbf{I} are the electron and nuclear spin operators. The sum is taken over the magnetic nuclei in the radical. Experimentally measured values of g are related to the tensor \mathbf{g} by

$$g = (\hat{\mathbf{H}} \cdot \mathbf{g} \cdot \mathbf{g} \cdot \hat{\mathbf{H}})^{1/2}, \quad (2)$$

where $\hat{\mathbf{H}}$ is a unit vector describing the orientation of the magnetic field. Line to line hyperfine spacings S are given by

$$S = (k/g^2 \beta_e)(D_+ + D_-)/2, \quad (3)$$

where

$$D_{\pm} = \left[1 + \frac{b^2}{k^2} \pm \frac{2\mathbf{b} \cdot \mathbf{k}}{k^2} \right]^{1/2}, \quad (4)$$

$$\mathbf{k} = \hat{\mathbf{H}} \cdot \mathbf{g} \cdot \mathbf{A}, \quad (5)$$

$$k = (\hat{\mathbf{H}} \cdot \mathbf{g} \cdot \mathbf{A} \cdot \mathbf{A} \cdot \mathbf{g} \cdot \hat{\mathbf{H}})^{1/2}, \quad (6)$$

and

$$\mathbf{b} = g_n \beta_n \mathbf{H}. \quad (7)$$

Equation (3) refers to those transitions which are normally allowed (i.e., those most probable when $k^2 > b^2$).

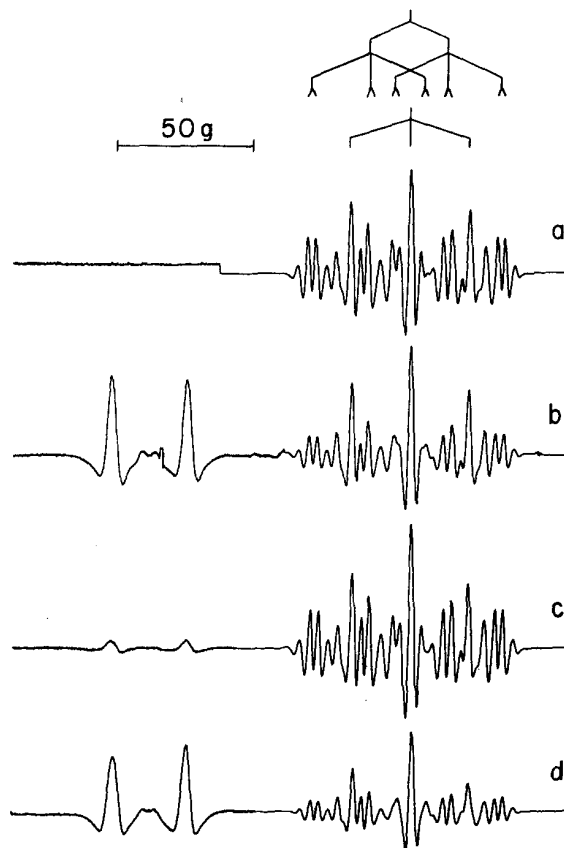


FIG. 2. Formation and decay of $\dot{\text{O}}\text{H}$ in irradiated potassium hydroxylamine disulfonate at 77 °K. Field orientation: ac plane, 5° from a^* , 85° and c . (a) Spectrum of gamma irradiated crystal. (b) Spectrum immediately after photolysis. (c) Decay of $\dot{\text{O}}\text{H}$ and regrowth of radical A on standing in dark. (d) Spectrum after second photolysis.

TABLE I. Principal values of g and A^N for $\dot{O}N(SO_3)_2^-$ at room temperature.

	Principal values ^a		Direction cosines		
	a^*	b	c		
g_1	2.0066	(2, 0055)	-0.538	± 0.597	0.596
g_2	2.0102	(2, 0094)	0.492	± 0.796	-0.353
g_3	2.0025	(2, 0026)	-0.685	± 0.103	-0.722
\bar{g}	2.0064	(2, 0058)			
A_1^N	6.8	(5, 5)	-0.414	± 0.730	0.543
A_2^N	7.1	(7, 7)	0.633	± 0.660	-0.404
A_3^N	28.6	(27, 5)	-0.654	± 0.177	-0.736
$A^N(\text{iso}) = 14.2$, $A^N(\text{dip}) = (-7.4, -7.1, 14.4)$					

^aHyperfine tensor in gauss ($A/2.0023\beta_B$). Principal values in parentheses are taken from Ref. 2.

The factor $(D_+ + D_-)/2$ arises from the third term in the Hamiltonian and deviates significantly from unity only when b is large enough to be comparable to k . Principal values of g and A , and their principal directions were computed from the above equations by a least-squares technique which found those values which minimized the standard error of fit to the data.

Fremy's radical

The g and the ^{14}N hyperfine tensor were evaluated for Fremy's radical from a crystal grown from D_2O so that the weak proton hyperfine splitting [Fig. 1(b)] would not interfere with the measurements. The results are summarized in Table I. The elements of g were evaluated by least squares using Eq. (2). Experimental g values and those back calculated from Eq. (2) agreed to a precision (standard error) of 0.00003. The standard error for ^{14}N splittings [using Eq. (3)] was 0.07 G. The A^N tensor is very close to axial symmetry, hence the principal directions corresponding to A_1^N and A_2^N are not well determined. Principal values obtained by Hamrick, Shields, and Gangwer² are included in Table I for comparison. Corresponding principal directions obtained from the two investigations agree to ca. 20° . The signs of each of the principal elements of A^N have been chosen as positive to obtain best agreement of $A^N(\text{iso})$ with the 13.0 G hyperfine splitting seen in solution.

Using appropriate atomic parameters,⁷ the spin densities as nitrogen $2s$ and $2p$ orbitals are $\rho(2s) = 0.026$ and $\rho(2p) = 0.42$. The distortion of the radical from planarity is estimated using the equation^{8,9}

$$A^N(\text{iso}) = A^N(0) + 550\rho_N(2 \tan^2 \theta),$$

where θ is the out-of-plane bending angle⁸ and where $A^N(0)$ depends on σ - π interaction Q values and the spin densities on nitrogen and oxygen. Using for the total nitrogen spin density $\rho_N = 0.45$ as given above, $\rho_0 = 0.55$ (by difference from unity since the small ^{33}S splittings seen in solution¹⁰ indicate little delocalization of the spin on to the SO_3^- groups), and $A^N(0) = 1.8$ G as determined from the parameters given by Hayat and Silver,⁹ an out-of-plane bending angle of 9° is found. This angle as well as ρ_N and ρ_0 are in excellent agreement with those

determined for other nitroxide radicals⁹ on the basis of ^{14}N and ^{17}O splittings seen in solution.

Hydroxyl radical

The g and 1H hyperfine tensors were evaluated from line positions measured at $64^\circ K$. This temperature was chosen to retard the decay of the $\dot{O}H$. Principal values, direction cosines, and the resolution of the hyperfine tensor into isotropic and dipolar parts are summarized in Table II. The standard error of fit of these parameters to observed g values is 0.0003 and to observed hyperfine splittings 0.2 G. The parameters of Table II are generally in good accord with those of previous investigators (references to previous literature on ESR studies of $\dot{O}H$ may be found in Ref. 11). The principal g value parallel to the molecular axis, 2.1325, is somewhat larger than reported previously and indicates a weaker binding with surrounding molecules.

Radical A

As with Fremy's radical, the six main lines of radical A are split for some orientations into closely spaced doublets due to a weak hyperfine interaction from a nearby proton (see Fig. 2). Because of the complexity of the spectrum, it was not possible to make enough reliable measurements to evaluate the tensors for radical A with crystals grown from normal water. This was particularly true at orientations where the symmetry related radicals gave degenerate spectra. Much of the difficulty was alleviated when measurements were made with crystals grown from 90% D_2O -10% H_2O . Lines were sharper, the hyperfine splitting coming from the neighbor proton was always unresolved, yet the main 1H hyperfine splitting from the small amount of normal hydrogen could still be easily observed and measured. An ESR spectrum obtained with this system is shown in Fig. 3. Lines labelled H are from radicals containing normal hydrogen and those labelled D from deuterated radicals. The weak H lines in the center part of the spectrum were usually not well resolved. Therefore, the 1H hyperfine splitting was calculated from the difference between the overall splitting of the H lines and the ^{14}N splitting which was determined from the D lines.

Principal values of g and the various hyperfine tensors and their directions are presented in Table III. Data ob-

TABLE II. Principal values of g and A^H for $\dot{O}H$ at $64^\circ K$.

	Principal values ^a		Direction cosines	
	a^*	b	c	
g_1	2.0008	0.345	∓ 0.908	-0.238
g_2	2.0070	0.670	± 0.416	-0.615
g_3	2.1326	0.657	± 0.053	0.752
A_1^H	-27.9	0.423	∓ 0.867	-0.263
A_2^H	-43.9	0.636	± 0.491	-0.596
A_3^H	7.7	0.645	± 0.085	0.759
$A^H(\text{iso}) = -21.4$, $A^H(\text{dip}) = (-6.5, -22.5, 29.1)$				

^aHyperfine tensors in gauss ($A/2.0023\beta_B$).

TABLE III. Principal values of g , A^N , A^H , and A^D for Radical A at 77 °K.

	Principal values ^a	Direction cosines		
		a^*	b	c
g_1	2.0056	0.835	∓ 0.543	-0.092
g_2	2.0158	0.281	± 0.278	0.918
g_3	2.0024	0.473	± 0.792	-0.385
\bar{g}	2.0079			
A_1^N	19.0	0.819	∓ 0.495	-0.290
A_2^N	19.2	0.488	± 0.333	0.807
A_3^N	33.3	0.303	± 0.802	-0.514
$A^N(\text{iso}) = 23.8$, $A^N(\text{dip}) = (-4.8, -4.6, 9.4)$				
A_1^H	-35.0	0.880	∓ 0.468	-0.081
A_2^H	7.8	0.249	± 0.310	0.917
A_3^H	-22.2	0.404	± 0.828	-0.390
$A^H(\text{iso}) = -16.5$, $A^H(\text{dip}) = (-18.6, 24.3, -5.7)$				
A_1^D	-36.3	0.868	∓ 0.489	-0.082
A_2^D	4.6	0.302	± 0.392	0.869
A_3^D	-23.6	0.393	± 0.779	-0.488
$A^D(\text{iso}) = -18.5$, $A^D(\text{dip}) = (-17.9, 23.0, -5.2)$				

^aHyperfine tensors in gauss ($A/2.0023\beta_B$). Deuterium couplings have been multiplied by ratio of proton to deuteron nuclear g values.

tained at 30 different orientations were used to derive the parameters. The elements of g were evaluated by least squares using Eq. (2). Experimental g values and values back calculated from Eq. (2) agreed to a precision (standard error) of 0.00006. The standard error for ^{14}N splittings [using Eq. (3)] was 0.07 G. The A^N tensor is almost axially symmetric, thus the principal directions of A_1^N and A_2^N , other than being normal to A_3^N , are not well determined. The signs of the elements of A^N were not determined because of the negligible contribution of the third term of the Hamiltonian. Thus the resolution of A^N into isotropic and dipolar parts could not be made unambiguously. Nevertheless, because of the near axial symmetry of the tensor, only two of the possible resolutions are reasonable. One is to choose all signs the same (positive signs are chosen to yield positive spin density in the region of the nitrogen nucleus). With this choice, the isotropic coupling $A^N(\text{iso})$ is 23.8 G and the elements of the dipolar tensor $A^N(\text{dip})$ are -4.8, -4.6, and 9.4 G. Using appropriate atomic parameters,⁷ the spin densities in terms of nitrogen $2s$ and $2p$ orbitals are $\rho(2s) = 0.043$ and $\rho(2p) = 0.28$. The other possibility is to choose A_3^N as positive and the perpendicular components negative. This alternative yields $A^N(\text{iso}) = -1.6$ G and $A^N(\text{dip}) = (-17.4, -17.6, 34.9)$ from which spin densities $\rho(2s) = -0.003$ and $\rho(2p) = 1.03$ are calculated. This latter resolution does not appear realistic. While the value of $\rho(2p)$ might be taken to indicate the localization of the spin on nitrogen as a pure $2p$ orbital, the small and negative isotropic coupling is not in accord with such a model; positive isotropic cou-

plings of 20 to 30 G would be expected.¹²

The third term of the Hamiltonian has an influence on both the proton hyperfine interactions and their transition probabilities. Because of it, both the magnitudes and the relative signs of the principal values are determinable. The measured proton spacings were fitted to Eq. (3) for various choices of the signs of the principal values. These data could only be satisfactorily fit if the two largest principal values were taken to be of the same sign. Data from line spacings were not adequate to determine the relative sign of the smallest element. With either choice of sign, the observed splittings were fit equally well with a standard error of 0.2 G. At a few orientations, however, with crystals containing only normal hydrogen, weak normally forbidden transitions were sufficiently resolved and of proper intensity to indicate that the sign of the smallest element is opposite that of the others. This assignment, with absolute signs chosen so that $A^N(\text{iso})$ is negative, is shown in Table III.

Deuterium hyperfine splittings were also measured, and principal values of A^D derived assuming they have the same signs as the corresponding hydrogen elements. The values listed in Table III have been multiplied by 6.514 in order to directly compare them with A^H . The smallest principal value A_2^D is subject to a large uncertainty because deuterium splittings for some orientations were unresolved. With this exception, the two sets of parameters, A^H and A^D , are in reasonable agreement and there is no indication of isotope effects that might arise from motions of the hydrogen.

It is apparent from the magnitude and anisotropy of the elements of A^H that the proton interaction results from

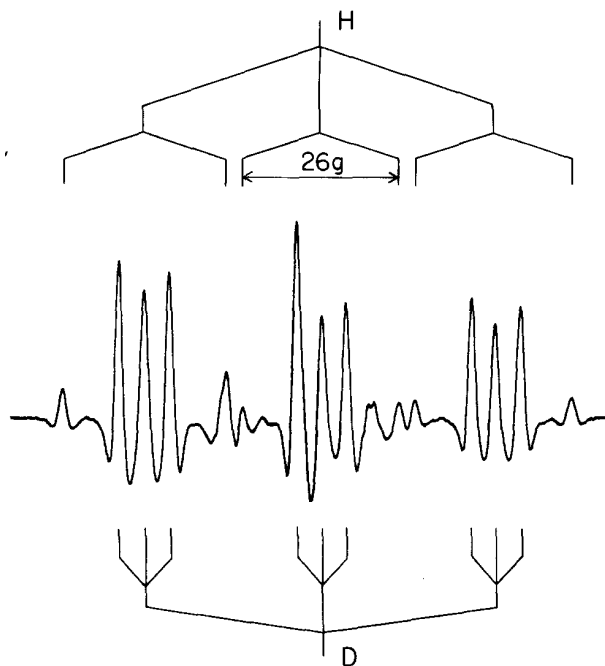


FIG. 3. ESR spectrum of irradiated potassium hydroxylamine disulfonate grown from $\text{D}_2\text{O}-\text{H}_2\text{O}$ solution. Field parallel to b axis. Lines H are from radical A in protonated form; (D) in deuterated form.

high spin density on a neighboring atom and that the spin resides on this atom largely as a πp orbital. While the elements of \mathbf{A}^H are much too large to arise from an $\dot{\text{N}}\text{H}$ fragment with a value of ρ_N of 0.3 as determined above, a consistent interpretation of \mathbf{A}^H can be made assuming that the hydrogen is bonded to an oxygen. This is most simply demonstrated by comparing the proton couplings of radical A with those of $\dot{\text{O}}\text{H}$ (regarding $\dot{\text{O}}\text{H}$ as a prototype for the interaction with unit πp spin density on the oxygen). The ratio of $A^H(\text{iso})$ from radical A to that of $\dot{\text{O}}\text{H}$ is 0.78. Similarly, the ratios of corresponding dipolar elements are 0.82, 0.87, and 0.82. While these ratios are satisfactorily consistent, this approach undoubtedly overestimates ρ_O (note that $\rho_O + \rho_N = 1.1$) because contributions from spin on other atoms is neglected. The ESR results, then, suggest that the radical contains an NOH fragment with the unpaired electron a πp orbital on the nitrogen and oxygen. One would then expect the principal directions corresponding to the most quenched g value, the largest nitrogen coupling, and the proton coupling of intermediate magnitude to all be normal to the NOH plane. The corresponding experimental principal values are g_3 , A_3^N , and A_3^H of Table III. Their principal directions, although not coincident, are closely grouped, spanning an angle of 12° .

Two possible radicals with this NOH structure are suggested. One, $\text{H}\dot{\text{O}}\text{N}(\text{SO}_3)_2^-$, might easily be formed by loss of an electron upon gamma irradiation. The other, $\text{H}\dot{\text{O}}\text{NSO}_3^-$, by loss of SO_3^- . It is also attractive to identify radical A as $\text{H}\dot{\text{O}}\text{N}(\text{SO}_3)_2^-$ in that the formation of Fremy's radical from it on warming can be regarded as a deprotonation reaction. It should be noted, however, that while this identification forms a reasonable basis for the interpretation of the results presented here, it is not without objection. In particular, it is difficult to reconcile the large value of ρ_O estimated above with the electronic structure of the radical. For example, $\text{H}\dot{\text{O}}\text{N}(\text{SO}_3)_2^-$ can be regarded as a protonated form of Fremy's radical. As such it would be expected¹³ that the spin density on the oxygen would be less than in Fremy's radical ($\rho_O = 0.55$) rather than more.

A comparison of the principal directions of the tensors of Fremy's radical with those of its precursor, radical A, shows that they are oriented quite differently in the lattice. Using, for example, the principal directions

corresponding to the largest value of \mathbf{A}^N as indicators of their orientations, we find that the two radicals are twisted by 71° or 88° (the ambiguity arises because there are two distinguishable symmetry related molecules). Because the crystal structure is unknown, we are of course unable to determine which, if either, of the two radicals are trapped in a substitutional position. A knowledge of the crystal structure would also be useful in gaining an understanding of the photolytic formation of $\dot{\text{O}}\text{H}$ from radical A. This process, which will be discussed in detail in a later publication, apparently involves the transfer of a hydrogen from a water molecule to radical A.

Added note: The reviewer has called our attention to a recent similar ESR study¹⁴ in which potassium hydroxylamine disulfonate crystals were irradiated with x rays at 77°K . Strong spectra from Fremy's radical were seen, but lines from radical A were not observed. This difference is most readily understood if warming significantly above 77°K occurred during the x-irradiation. The experimental technique used differed from ours in that the crystals were mounted on a cryotip apparatus in an intense x-ray beam.

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