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Authors

Meinzer, Richard A.
Pratt, David W.
Myers, Rollie J.

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Richard A. Meinzer, David W. Pratt and Rollie J. Myers

Department of Chemistry, University of California
and Inorganic Materials Research Division,
Lawrence Radiation Laboratory,
Berkeley, California 94720

Abstract

At temperatures below 0°C , chemical or electrolytic reduction of S_4N_4 in tetrahydrofuran produces a nine-line ESR spectrum characteristic of a radical with four equivalent nitrogens. The isotropic spin Hamiltonian parameters obtained from the observed spectrum, $A(^{14}\text{N}) = 1.185 \text{ G}$ and $g = 2.0006$, are significantly different from those found by Chapman and Massey, who produced a nine-line spectrum by room temperature reduction of S_4N_4 and assigned it to the radical anion $S_4N_4^{\cdot -}$. Theoretical comparison of the g -values and ^{14}N hyperfine coupling constants of both nine-line radicals shows that only the low temperature species has the characteristics expected for $S_4N_4^{\cdot -}$. This interpretation is supported by the observed chemical behavior of the low temperature radical, which decomposes at higher temperatures with a series of products which appear to be precursors of the radical found by Chapman and Massey.

Introduction

When tetrasulfur tetranitride (S_4N_4) is reduced by alkali metals in dimethoxyethane at room temperature, a series of color changes occur. These colored products were first investigated with electron spin resonance by Chapman and Massey² (CM). They observed a weak ESR spectrum with nine well-resolved hyperfine components. From the number and relative intensity of these lines, the spectrum could be assigned to a radical containing four equivalent nitrogens. It was suggested by CM that this radical was derived from the cyclic S_4N_4 by a simple one-electron reduction. Since aromatic hydrocarbons readily form radical anions, it seemed reasonable that S_4N_4 would also, and CM assigned their spectrum to $S_4N_4^-$.

Our attention was drawn to this problem when Jolly and Ray supplied us with several samples of S_4N_4 which had been reduced by the addition of sodium naphthalenide in tetrahydrofuran (THF) at room temperature. Instead of a single nine-line radical, we observed³ a variety of radicals. With the controlled reduction which was made possible by the use of sodium naphthalenide, we first observed three-line and five-line radicals. Such spectra indicate appreciable hyperfine interaction with only one or two nitrogens. Only after considerably more than one equivalent electron was added did we observe the nine-line species reported by CM, and in addition, this spectrum was significantly weaker than those described above.

In this work, the application of the controlled reduction technique to THF solutions of S_4N_4 at temperatures below 0°C is described.

A new nine-line species has been detected under these conditions, and at temperatures above 0° , it decomposes into a number of radicals including those previously described. On the basis of this behavior and supporting theoretical arguments, the low-temperature spectrum has been assigned to the radical anion of S_4N_4 . It is further concluded that the CM radical is a different species which is formed following the decomposition of S_4N_4 under reducing conditions.

Experimental

The in situ electrolytic reduction experiments were performed using a cell which has been previously described.⁴ It was cooled with a stream of cold nitrogen gas, and several volts were applied between the platinum electrodes during electrolysis. Carefully purified and degassed THF was used as a solvent; 0.1M tetrabutylammonium perchlorate was used as the electrolyte. The potassium reductions were carried out in a vacuum apparatus which allowed small amounts of potassium metal dissolved in THF to react with S_4N_4 . During this reaction, the sample was kept below room temperature. ESR measurements were performed at 9 GHz using 100 kHz field modulation; all spectra were displayed as first derivatives.

Results

The ESR spectrum of the radical formed by electrolytic reduction of S_4N_4 at -25° is shown in Fig. 1. This spectrum was recorded using the digital method described by Bauder and Myers.⁵ Smoothed experimental points are shown as crosses in Fig. 1. Also shown is a solid-line

least-squares fit which assumes four equivalent ^{14}N nuclei in the radical, each with nuclear spin $I = 1$. This fit follows the experimental data very accurately as is illustrated by the error curve (on an expanded scale) in the lower portion of Fig. 1. A similar spectrum can be produced by careful low temperature chemical reduction.

Because of the low conductivity of the solutions, only one or two μA of current are passed through the cell. The nine-line spectrum can first be clearly observed, with nominal spectrometer sensitivity, after about three minutes of electrolysis at -25° . Since the nominal spectrometer sensitivity is approximately 10^{-10} to 10^{-9} moles of radicals, these results are consistent with about one radical per electron of reduction.

After about 30 minutes of electrolysis at -25° , the radical concentration appears to reach a steady-state. At higher temperatures the radical decomposes rapidly, and above 0° , very little of this species can be detected. In the chemical reduction experiments near -25° , other radicals previously observed at room temperature³ are also detected following the appearance of the nine-line spectrum when more potassium is added. Observed first is the superposition of the nine-line spectrum with a three-line spectrum; with further reduction the three-line spectrum disappears and is replaced with a five-line spectrum. This is exactly the order of appearance observed at room temperature, except that the nine-line spectrum shown in Fig. 1 cannot be detected. This is to be expected from its absence during electrolysis above 0° .

The g -value, hyperfine splitting constant and linewidth of the new nine-line radical change little with temperature over the range -25° to -90° . However, the addition of some excess S_4N_4 to the solution

produced an increase in the linewidth of the spectrum, and a linewidth of 0.8 G was obtained. This result is indicative of rapid electron exchange between the radical and the parent S_4N_4 . Such exchange reactions have been observed between aromatic radical anions and their diamagnetic precursors and it is generally assumed that fast exchange is possible only if the anion and the parent species have similar geometries. The existence of this concentration broadening of the nine-line radical is therefore good evidence that the radical is $S_4N_4^-$ in which the ring structure of S_4N_4 is kept intact.

Discussion

Table I lists the ESR parameters of the nine-line radical observed in this work together with those observed for the room temperature species by CM. It is useful to compare the results for the two radicals with those observed for related species. Considering first the A-values; if the unpaired electron in the CM radical were localized on only one of the four nitrogens, the ^{14}N coupling constant would be four times as large or about 13 G. Similarly, for our low temperature radical it would be about 5 G. Coupling constants close to 13 G have been observed for many other nitrogen-containing inorganic radicals⁶ such as NO_2^- , $N(SO_3)_2^-$, $NH(SO_3)_2^-$, $ON(SO_3)_2^-$ and a number of organic nitroxides. On the other hand, the NO_2 radical has an A-value of about 50 G.

Smaller values of the ^{14}N coupling constants can be expected for those radicals whose odd electron occupies a π molecular orbital. The isotropic coupling constant depends almost entirely on the extent of the s orbital participation in the ^{14}N wave function and this is necessarily small

TABLE I.

A COMPARISON OF THE
TWO NINE-LINE RADICALS FROM S_4N_4

Radical Produced by Reduction at:

	<u>Room Temperature</u> (Chapman and Massey)	<u>Low Temperature</u> (-25°, our work)
Hyperfine coupling- A(^{14}N) in gauss	3.22 ±0.04	1.185 ±0.001
Line width- ΔH in gauss	~0.3	0.46
g-value	2.006 ±0.001	2.0006 ±0.0001

for a π radical. In contrast, for σ radicals like NO_2 , larger ^{14}N A-values can be expected because of large s orbital participation. Recent calculations by Cramer and Drago⁷ support this view for NO_2 and other σ radicals. If the odd electron is in a π orbital, some s character will be mixed into the wave function by electron-electron repulsion, and the resulting s orbital spin density produces a non-zero isotropic coupling constant. This mechanism has been discussed in detail by Karplus and Fraenkel.⁸ As a result of the balancing effects of this spin polarization, a ^{14}N A-value in the range 5-15 G is often observed in such cases. On the basis of hyperfine coupling, it appears that both nine-line radicals have their unpaired electrons in π molecular orbitals with only a small amount of s orbital participation.

The g-value of the room temperature species is slightly larger than that of the free electron, 2.0023. The isotropic g-values for NO_2^{2-} and the other radicals listed above are also 2.006 ± 0.001 , whereas for NO_2 it is less than the free electron value and close to 2.000. The difference between these two cases is of particular importance for a similar g-value change is one of the major differences between the two radicals in Table I.

A linear O-N-O molecule would be a $^2\Pi$ radical, and the odd electron would be in a π orbital with two-fold orbital degeneracy. When the molecule bends, to form its lowest electronic state, this cylindrical π orbital splits into one of a_1 symmetry and one of b_1 symmetry.⁹ The odd electron has a lower energy if it stays in the a_1 orbital and the ground state of NO_2 is 2A_1 . While the a_1 orbital is derived from a cylindrical π orbital in the linear case, it has no node in the

molecular plane, and it becomes a σ orbital when the molecule bends. The result is that NO_2 , as we indicated previously, is a σ radical. In NO_2^{2-} on the other hand, the two additional electrons fill the a_1 and the odd electron is in the b_1 orbital. This orbital has a node in the molecular plane and NO_2^{2-} is a π radical.

The shift of the g-value from 2.0023 depends upon matrix elements of the electronic orbital angular momentum between the odd electron orbital and all the other orbitals in the molecule. If the more important terms are to orbitals of lower energy, the g-value will be greater than 2.0023, and if they are to higher energy orbitals the g-value will be less than 2.0023. In NO_2 the g-value is less than the free electron value primarily because of a matrix element of the orbital angular momentum between the a_1 and b_1 orbitals. The same matrix element also serves to insure that NO_2^{2-} has a g-value greater than that of the free electron.

This comparison can now be extended to the two nine-line radicals derived from S_4N_4 . Both the g- and A-values obtained for the room temperature radical are consistent with it being a typical π radical. As long as the stoichiometry is unknown, it is meaningless to propose an actual structure for this radical. The ESR parameters do suggest, however, that the bonding in the room temperature species is not greatly different from that found in ordinary nitroxide radicals. It is interesting to note that the other radicals formed³ by the room temperature reduction of S_4N_4 also seem to be of this type.

The low temperature radical has both a small hyperfine coupling constant and a g-value which is less than that of the free electron. If this radical is derived from S_4N_4 by the simple addition of one electron, then these two properties should be consistent with the fairly well established electronic structure of S_4N_4 . Turner and Mortimer¹⁰ have done an extended Hückel molecular orbital (HMO) calculation for S_4N_4 . These calculations indicate that with a D_{2d} point group, the lowest unoccupied orbital has E symmetry; in $S_4N_4^-$, this is presumably the orbital occupied by the unpaired electron. Assuming that the E orbital is made up of a linear combination of 2s and 2p orbitals, the orbital coefficients obtained by Turner and Mortimer¹¹ show that the contribution of the 2s nitrogen orbital is small, but non-zero. This suggests that the isotropic ¹⁴N coupling constant in $S_4N_4^-$ arises from a mixture of direct and spin polarization contributions. The small A-value observed for the low temperature species would require a partial cancellation of these two contributions; this is quite possible since they may be opposite in sign. The HMO calculation also indicates that the E-orbital is largely delocalized with about equal contribution from the sulfur and nitrogen orbitals. Consequently, spin polarization of the ¹⁴N 2s orbital by the adjacent sulfur spin density should be important and it is all the more probable that some cancellation could occur for the spin density.

Since the odd electron in $S_4N_4^-$ would occupy an E orbital the Jahn-Teller theory¹² should require the radical to have a symmetry lower than that of the original S_4N_4 . Symmetry considerations suggest that the D_{2d} point symmetry be reduced by a distortion corresponding to either ¹² a b_1 or b_2 symmetry coordinate of the group D_{2d} . As a result,

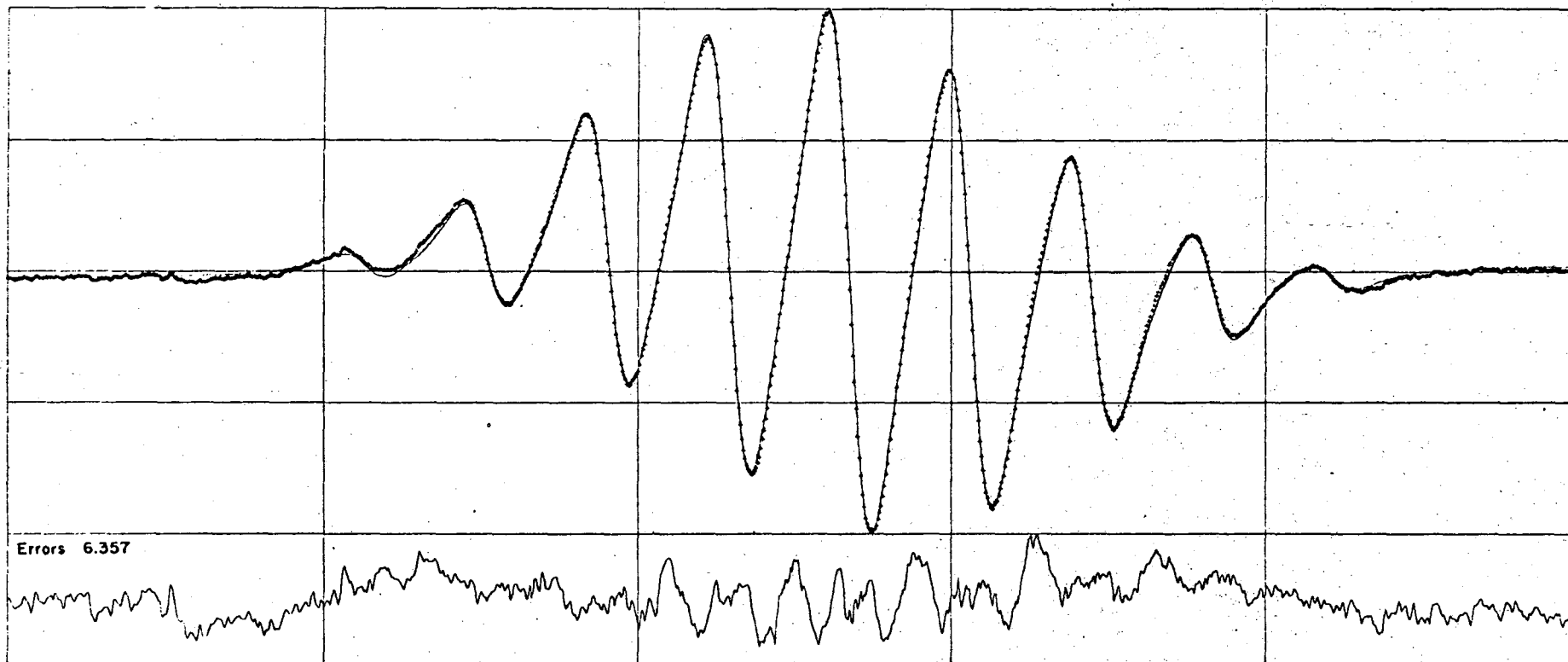
the odd electron would occupy a non-degenerate orbital of a new point group. If the distortion is along a b_1 symmetry coordinate the point group is reduced to C_{2v} , while if it is along b_2 the group would be D_2 . The $S_4N_4^-$ with C_{2v} symmetry would have four equivalent nitrogens, but it would have two sets of two equivalent sulfurs. With D_2 symmetry the sulfurs would be all equivalent, but the nitrogens would fall in pairs.

The observed ^{14}N hyperfine pattern shows that all four nitrogens are exactly equivalent or very nearly equivalent. As a result we must conclude that either $S_4N_4^-$ has C_{2v} symmetry or our simple Jahn-Teller considerations are not correct. Since the C_{2v} symmetry requires that there be two pairs of equivalent sulfurs, ^{33}S hyperfine coupling would be particularly informative. Such experiments are in progress.

The g-value shift for $S_4N_4^-$ can be nicely explained by a Jahn-Teller distortion. In the D_{2d} point symmetry the matrix element $\langle E | L_z | E \rangle$ for the electronic orbital angular momentum is non-zero. With a Jahn-Teller distortion this matrix element is reduced to one between the odd electron orbital and the lowest unoccupied orbital. As a result, the g-value calculation for a distorted $S_4N_4^-$ is similar to that for NO_2^- , and one would expect that a distorted $S_4N_4^-$ would have a g-value less than that of the free electron. It is always difficult to judge the extent of the Jahn-Teller distortion, but if the distortion were very small the matrix element which would determine the g-value would also give a very short electronic spin-lattice relaxation time. As a result of these considerations, it seems most likely that the Jahn-Teller distortions in $S_4N_4^-$ should be fairly large. Further work should be done on this interesting Jahn-Teller case.

Acknowledgements

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Figure 1. The ESR Spectrum of the Low Temperature Radical - The experimental points shown as crosses have been fit by least squares to the theoretical smooth curve following the method of Reference 5. The parameters were: $A(^{14}\text{N}) = 1.1847$ gauss and derivative width $\Delta H = 0.4610$ gauss. The lower error curve has a scale expansion of 6.357. The smooth curve assumes a Lorentz line shape and four equivalent ^{14}N spins.

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