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Electron Paramagnetic Resonance Studies of Tetrasulfur Tetranitride in Sulfuric Acid

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The paramagnetic solutions formed by the reaction of tetrasulfur tetranitride with sulfuric acid have been studied by electron paramagnetic resonance (epr). We have confirmed previous reports that the main radical is positively charged and that its spectrum is a 1:2:3:2:1 quintet corresponding to the presence of two equivalent nitrogen atoms. By using sulfur-33-enriched S_4N_4, we have observed hyperfine coupling ($A_S = 8.9$ G) corresponding to the presence of two equivalent sulfur atoms. We therefore assign the radical the formula $S_2N_2^+$. In 95% sulfuric acid the five-line spectrum decays to a weak three-line spectrum with relative intensities 1:2:1. The splitting is interpreted in terms of coupling to two equivalent hydrogen atoms ($A_H = 1.05$ G). Weak satellite lines due to ^{33}S coupling ($A_S = 8.5$ G) are also observed, but no lines due to nitrogen coupling are observed. Migration of the three-line radical toward the cathode during electrolysis indicates that it is positively charged.

Introduction

The epr spectra of the solutions formed by the reaction of S_4N_4 with concentrated sulfuric acid were first reported by Chapman and Massey[1] in 1962. Freshly prepared solutions gave a spectrum of five lines with an intensity ratio of 1:2:3:2:1 and a separation of 3.32 ± 0.04 G. This spectrum is consistent with a radical containing two equivalent nitrogen atoms. A transference study by Chapman and Massey showed that the species was positively charged, and they suggested that the radical was SN_2^+.

In a later study, McNeil, Murray, and Symons[2] also observed the same five-line spectrum. They calculated nitrogen atom spin populations from the observed hyperfine coupling constants and concluded that there should be an appreciable spin population on the sulfur atom. However, using the method of Walsh[3] they predicted that SN_2^+ would have a linear structure, with no spin population on the sulfur atom. Because the latter prediction was inconsistent with the coupling constant data, they proposed that the radical was the cyclic $S_2N_2^+$ species, which would be expected to have a significant spin population on the sulfur atoms.

Both groups of researchers reported that in 95% sulfuric acid a three-line spectrum appeared as the five-line spectrum decayed. This triplet was reported to have an intensity ratio of 1:1:1 and a splitting of approximately 1 G. Such a spectrum is consistent with the second radical containing only one nitrogen atom. Chapman and Massey were unable to determine the electrical charge of the species and proposed SN as a possible formula.

We have further studied the epr spectra of these solutions to learn more about the nature of these radicals as well as their relative importance in the overall reaction of S_4N_4 with sulfuric acid.

Experimental Procedures

Two solvents were employed: 95% sulfuric acid and 100% sulfuric acid. The reactions were slightly different in these solvents. The 100% sulfuric acid (referred to as "sulfuric acid" unless otherwise specified) was prepared by mixing Baker and Adamson reagent grade 95% sulfuric acid and Baker and Adamson reagent grade 15% fuming sulfuric acid. The composition of the solvent was adjusted until a maximum in the freezing point was obtained.

The S_4N_4 was prepared by the method of Villena-Blanco and Jolly[4] and was recrystallized from benzene until a constant melting point of 186° was obtained.

Tetrasulfur tetranitride enriched in ^{33}S was prepared for some experiments. Three milligrams of sulfur containing 48.6% ^{33}S (obtained from Oak Ridge National Laboratory) was placed in a conical 15-ml test tube equipped with a standard-taper joint. The tube was connected through a stopcock to a vacuum line and was evacuated. Chlorine was introduced to the tube to a pressure of *ca.* 700 Torr, and the stopcock was closed. After several hours all the sulfur had been converted to volatile compounds—presumably a mixture of sulfur chlorides. The tube was cooled to −112°, and the excess chlorine was pumped off. Then 8.5 ml of carbon tetrachloride was condensed into the tube, and the tube was filled with a nitrogen atmosphere, warmed to room temperature, and disconnected from the vacuum line. Purified ammonia was bubbled through the solution for 4 hr, and then the carbon tetrachloride solution was filtered to remove all the ammonium chloride as well as most of the sulfur which are products of the reaction. The filtrate was evaporated to dryness to obtain the crude product which was not further purified. Samples prepared by this technique from ordinary sulfur gave typical epr spectra with no unusual features.

The reaction of S_4N_4 with H_2SO_4 was always carried out under vacuum. Usually the S_4N_4 was added slowly to H_2SO_4 cooled to 0° in order to prevent any local overheating. With the $^{33}S_4N_4$, the smaller sample size made it more convenient to reverse the order of addition.

The polarity of the radicals was determined by electrolysis in a cell containing five compartments separated by sintered-glass disks. Solvent was placed in the four outer compartments, and the solution being studied was placed in the center compartment. In order to obtain an adequate current, 5-V d.c. was applied for 95% H_2SO_4 and 15-V d.c. was applied for 100% H_2SO_4. The charge on a species was deduced from the direction of migration as detected by the epr spectra of the solutions in the adjacent cell compartments.

Epr measurements were made using a Varian V4502 epr spec-

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[1] D. Chapman and A. G. Massey, *Trans. Faraday Soc.*, **58**, 1291 (1962).

[2] D. A. C. McNeil, M. Murray, and M. C. R. Symons, *J. Chem. Soc. A*, 1019 (1967).

[3] A. D. Walsh, *ibid.*, 2260 (1953); see also P. M. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals," Elsevier, Amsterdam, 1967.

[4] M. Villena-Blanco and W. L. Jolly, *Inorg. Syn.*, **9**, 98 (1967).

trometer, equipped with a 9-in. Fieldial-regulated magnet and 100-kHz field modulation and detection. For routine work, samples were held in a quartz flat cell (Varian V4548 aqueous solution sample cell). A V4531 multipurpose cavity was used.

Spectra were recorded both in analog form for routine analysis and in digital form for computer processing of the spectra. The spectra were digitized by attaching a Honeywell Model S6114 automatic data logging system to the spectrometer. This system consists of a frequency counter (HP 5245L), a digital voltmeter (Honeywell-EI-Multimeter, Model 630S), an output control unit (Honeywell-EI, Model 825), and an incremental magnetic tape recorder (Kennedy, Model 1400). A voltage-to-frequency converter (Vidar, Model 240) was used to provide magnetic field information from the x-axis transmitting potentiometer of the Fieldial unit. The magnetic field was calibrated using an nmr magnetometer.

The digitized spectra were processed by computing a least-squares fit to the spectra; this procedure yielded good values for the line width, line position, and line intensity. The least-squares technique is especially important in determining line intensities of unresolved lines which have different line widths. Errors due to base line drift and overlapped lines are automatically accounted for by the line shape analysis. This technique is not subject to the errors (due to approximations) of the usual integration methods.

Radical concentrations were determined by a comparison technique. A resonant cavity (Varian, V4534) was provided with a reference standard by taping a small capillary tube containing MgO doped with manganese(II) to the side of the resonant cavity so that the capillary tube was in both the microwave field and the modulation field. This reference standard gave epr signals which were resolved from those of the radicals of interest. The reference standard was calibrated with a sample of vanadyl acetylacetonate dissolved in dichloromethane, and the radical spectra were compared with the manganese(II) signals. The epr signal intensities were determined by a least-squares fit to the digitized spectra.

Results and Discussion

Five-Line Radical.—The epr study of the reaction products of tetrasulfur tetranitride in 100% sulfuric acid produced the same spectrum that had previously been reported for 95% sulfuric acid. This spectrum consisted of five lines with an intensity ratio of 1:2:3:2:1. The lines showed a trend in line width: the narrowest line was on the low-field side and the broadest line was on the high-field side. This spectrum was fit using a modified version of the least-squares technique described by Bauder and Myers.[5] Assuming Lorentzian lines of variable widths and a second-order spin Hamiltonian, the radical was found to have $g = 2.0107$ and a hyperfine coupling constant of 3.21 G.

Further study of the spectrum revealed several very low intensity lines (each less than 1% of the intensity of the major spectrum) which were symmetrically disposed about the major five-line spectrum. These lines, like the major five lines, showed distinct variations in line widths from low to high field (Figure 1). Moreover, the lines both on the low-field side and on the high-field side were separated by approximately the same splitting as the major lines.

These low-intensity lines appear to have the same g value as the five-line spectrum and are believed to be due to ^{33}S in natural abundance. Sulfur-33 has a nuclear spin $I = {}^3/_2$, and is a stable isotope of 0.74% natural abundance. In principle, the number of sulfur atoms in the radical could be determined by comparing the intensities of the satellite lines and the main lines. However, the low intensity of the satellite lines, the variation in the line widths, and the lack of resolution made the comparison very difficult. The relative intensities of the lines could not be determined with sufficient precision to distinguish between the presence of one and two sulfur atoms in the radical.

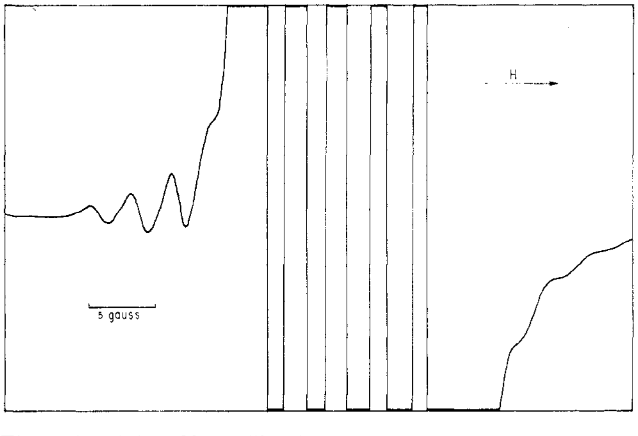

Figure 1.—Sulfur-33 satellite lines in the epr spectrum of $S_2N_2^+$ in H_2SO_4.

In order to establish the number of sulfur atoms in the radical, S_4N_4 enriched in ^{33}S was used. The spectrum resulting from the enriched sample is shown in Figure 2. From this spectrum, it can be concluded immediately that the radical must possess more than one sulfur. The hyperfine pattern is much too complicated for a species with only one sulfur atom. Because of the numbers of parameters required to describe the spectrum, the spectrum could not be fitted with a least-squares technique. However, it was possible to simulate the spectrum quite closely by assuming a radical containing two equivalent sulfur atoms (see

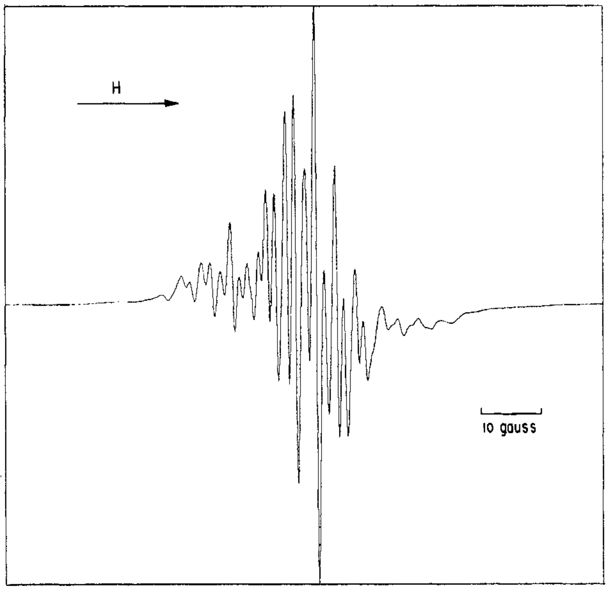

Figure 2.—Epr spectrum of ^{33}S-enriched $S_2N_2^+$ in H_2SO_4.

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[5] A. Bauder and R. J. Myers, *J. Mol. Spectrosc.*, **27**, 110 (1968).

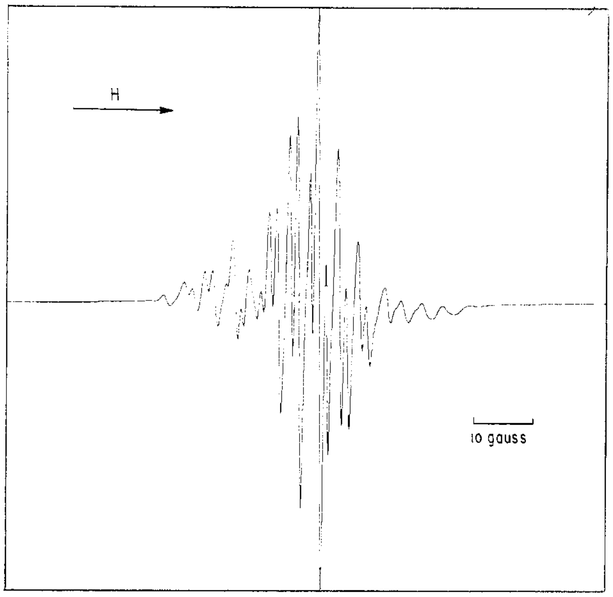

Figure 3.—Calculated epr spectrum of ^{33}S-enriched $S_2N_2^+$.

Figure 3). The sulfur hyperfine coupling constant obtained is 8.9 G.

The concentration of the radical was determined by epr studies of solutions which were nominally about 0.001 *M* in S_4N_4. The spectra were taken at various intervals starting 40 min after the initiation of reaction, and the slow decay was followed. Extrapolation back to zero time indicated that about 0.27 radical was initially produced per S_4N_4. Obviously the formation of the five-line radicals is an important part of the overall reaction of S_4N_4 with H_2SO_4.

The five-line radical can also be made from sulfur-nitrogen compounds other than S_4N_4. Chapman and Massey reported that they observed the same spectrum with S_2N_2, S_4N_2, $S_4N_4H_4$, $Co(S_2N_2H)_2$, and $S_3N_2O_2$ in concentrated sulfuric acid.[1,6] We have confirmed the results with $S_3N_2O_2$ and have shown that with $S_3N_2O_5$ in 100% sulfuric acid the same spectrum is obtained. Thus, it appears that the radical is a common decomposition product of many sulfur-nitrogen compounds in sulfuric acid. All of these initial compounds have one structural feature in common: alternating sulfur and nitrogen atoms.

The charge of the five-line radical was checked using the five-compartment transference cell. When the epr spectra of the three central compartments were examined, it was found that the radical had migrated preferentially toward the cathode. This confirmed the results of Chapman and Massey, who showed that the radical was positively charged.

The epr determinations have shown that the radical has two equivalent nitrogens and two equivalent sulfurs. However, this result cannot preclude the possibility of a species containing oxygen, other nonequivalent sulfurs, or even hydrogen having no appreciable free electron density. Even if there were only sulfur and nitrogen atoms in the radical, the linear structures $SNNS^+$ and $NSSN^+$ would satisfy the epr results, although they both require a rearrangement of S–N fragments. However, the relative ease of formation from so many compounds containing alternating sulfur and nitrogen atoms would indicate that its structure is more probably a ring of alternating sulfur and nitrogen atoms.

Three-Line Radical.—We were able to confirm the earlier investigators' observation of the growth of a relatively weak three-line spectrum during the decay of the five-line spectrum only when S_4N_4 was treated with 95% sulfuric acid (see Figure 4). We were unable to produce the three-line spectrum using 100% sulfuric acid. The five-line species in 95% acid was completely decomposed after several weeks at room temperature or after 2 hr at 100°.

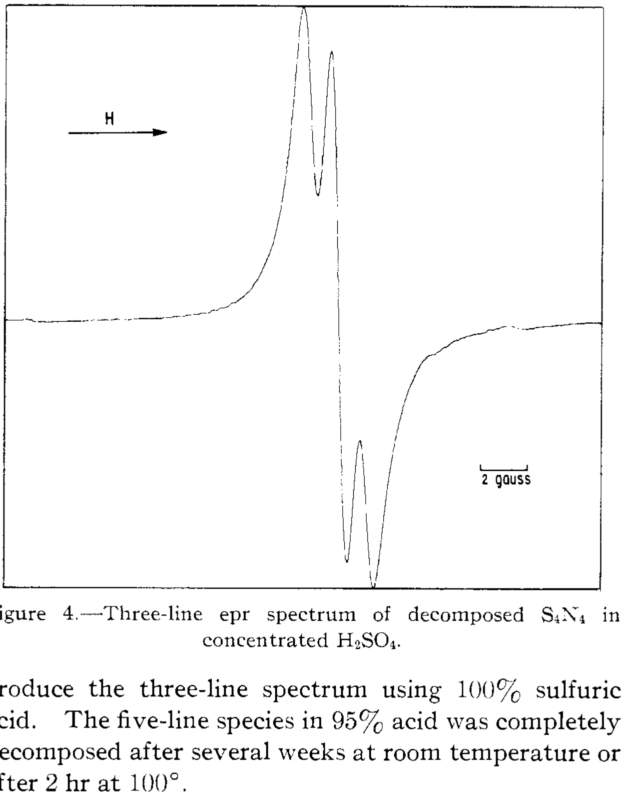

Figure 4.—Three-line epr spectrum of decomposed S_4N_4 in concentrated H_2SO_4.

The present work showed that the relative intensities of the triplet lines are in the ratio 1:1.97:1.35. The high-field line probably has too much apparent intensity because of overcompensation for the small residual five-line spectrum on the high-field side. The measured intensities are essentially 1:2:1 within the probable experimental error. This intensity ratio is consistent with a radical containing two equivalent hydrogen atoms and is in disagreement with the 1:1:1 intensity ratio reported by Chapman and Massey. Furthermore, we have observed some very weak lines on both the low-field and the high-field sides of the spectrum. These lines are equidistant from the three main lines and exhibit the same pattern. Thus, they are thought to arise from a ^{33}S hyperfine interaction. The number of sulfur atoms in the radical species could not be determined because the signal intensities were too weak. The spectral parameters determined from a least-squares fit to the spectrum were $g = 2.0152$, $A_H = 1.07$ G, and $A_S = 8.5$ G.

To substantiate further this interpretation of the three-line spectrum, the radical was prepared in deuterated sulfuric acid. The solution formed by the initial reaction of S_4N_4 with 95% D_2SO_4 gave the same

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[6] D. Chapman and A. G. Massey, *Chem. Ind.* (*London*), 2088 (1962).

five-line spectrum as reported previously. However, when the five-line species decayed, the spectrum observed was a single line with a width less than the spread of the triplet spectrum observed in ordinary 95% H_2SO_4. Because the line did not have a Lorentzian shape, we believe that it probably consists of unresolved hyperfine structure. Indeed, two equivalent deuterons in the radical would be expected to yield a quintet with one-third the spread of the proton triplet. Because the splitting would be smaller than the line width, an unresolved spectrum would be expected. Thus we believe these results confirm the interpretation that the radical contains two equivalent hydrogen atoms.

The three-line radical was observed to migrate toward the cathode of the transference cell. This result established that the species was positively charged.

The concentration of the three-line species was determined by comparison with the manganese(II) standard and was found to correspond to less than 0.0028 spin per original S_4N_4. Obviously the three-line radical is a relatively unimportant species as far as the overall stoichiometry is concerned.

In summary, the data indicate that the three-line radical is formed in small amounts, probably as one of the decomposition products of the five-line radical. It is positively charged and contains two equivalent hydrogen atoms and at least one sulfur atom. Inasmuch as no nitrogen hyperfine coupling is observed, the radical probably contains no nitrogen atoms, and in view of the fact that the radical forms only in sulfuric acid containing appreciable amounts of water, it seems likely that it is a hydrolysis product containing hydroxyl groups. The high g value and the small hydrogen coupling constant indicate that the radical is probably a π radical. From the available data it is impossible to determine its exact composition or structure.

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Formation and Reversal Kinetics of High-Pressure Sulfur XII

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Sulfur phase XII is in equilibrium with the liquidus at pressures above 20 kbars and may be crystallized at these pressures at temperatures above 200–240°. The rate of crystallization increases by a factor of 1.5–2 for each 10° along an isobar but it decreases with increasing pressure. The activation volume for the transition to XII is about +2 cm^3/mol. The very slow rate of formation of XII in the lower temperature region of its apparent stability field renders this phase difficult to detect unless sufficient time is allowed for reaction. For this reason dynamic methods are not successful in locating the lower temperature phase boundary, especially since the enthalpy of transition appears to be small.

Introduction

During a study of the high-temperature high-pressure equilibria displayed in sulfur[1] the authors found evidence for ten new high-pressure phases. Only one of these ten phases could be retained metastably upon quenching to room conditions, but six or more were indicated by quenching to about −30°. The kinetics of the formation of the readily quenchable phase (designated as phase XII) and its metastability both show unusual features and these are reported herein, together with possible explanations for the phenomena.

Earlier, Geller[2] as well as Sclar, Garrison, Gager, and Stewart,[3] publishing almost simultaneously, had reported quite different methods for the preparation of phases which are close to what we call phase XII. Ward and Deaton[4] also reported the synthesis of the same phase. Geller further determined that it crystallizes in the orthorhombic system and that the structure is based on right- and left-handed helical chains of sulfur at least half of which have some disorder about their axes. In the present report we shall call it sulfur phase XII.

Experimental Section

Pressure and temperature were applied in an opposed-anvil system described by Dachille and Roy[5] and calibrated and checked for pressure homogeneity by Myers, Dachille, and Roy.[6] Details of sample assemblies, heating times, and quenching procedures in the sulfur work are given by Vezzoli.[7]

High-purity orthorhombic sulfur (99.999%, prepared by American Smelting and Refining Co.) was used as the starting material and was stored in a vacuum desiccator. The quenched products were examined by using a petrographic microscope, Norelco X-ray diffractometer, and Debye–Scherrer film methods.

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[1] G. Vezzoli, F. Dachille, and R. Roy, *Science*, **166**, 218 (1969).

[2] S. Geller, *ibid.*, **152**, 644 (1966).

[3] C. Sclar, L. Garrison, W. Gager, and O. Stewart, *J. Phys. Chem. Solids*, **27**, 1339 (1966).

[4] K. Ward, Jr., and B. Deaton, *Phys. Rev.*, **153**, 947 (1967).

[5] F. Dachille and R. Roy, "The Physics and Chemistry of High Pressures," Society of Chemical Industry, London, 1963, p 77–85.

[6] M. Myers, F. Dachille, and R. Roy, *Rev. Sci. Instrum.*, **34**, 401 (1963).

[7] G. C. Vezzoli, Ph.D. Dissertation, The Pennsylvania State University, University Park, Pa., March 1969.