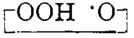
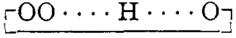
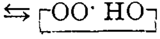
monomer rather than iron(II). Thus of all monomers investigated at both 25 and 40°, there was only one instance in which there was a significant tendency for the radical to react with iron(II) rather than with monomer (MMA at 40°). This is in marked contrast to the monohydroperoxy radicals investigated which normally react 500 to 1000 times as rapidly with iron(II) as with monomer. The reason for this lies in the variation of $E_{1i} - E_{1o}$ and A_{1i}/A_{1o} with the electronegativity of the *p*-substituent. Below is a comparison of the differences in activation energy for initiation and iron(II) oxidation as a function of Hammett σ-value, using some data previously reported[8] for solutions of acrylonitrile, in conjunction with the data above

σ	−0.191	0	0.778	4.5
$E_{1i} - E_{1o}$	8.0	0	−2.5	−20

There is a marked increase in the activation energy of iron(II) oxidation relative to that of reaction with monomer. Change in A_{1i}/A_{1o} values with σ tends to compensate for this effect. The compensation is by no means complete, with a resultant increase in activity toward monomer.

It is possible that a portion of this reactivity change is caused by resonance of the unpaired electron between the adjacent OOH and ·O group on the molecule which appear to be sufficiently close together to make hydrogen bonding possible. Under these conditions an electron only need shift to yield a resonance system which appears to represent a shift of hydrogen:  ⇆  ⇆ .

(IV). Utility as a Catalyst in Emulsion Polymerization.—It is believed[8] that variations in the yield of polymer obtained from emulsion polymerizations when initiated by hydroperoxides of differing structure could be explained by the tendency of the hydroperoxy radical to indulge in non-polymerization side reactions. These side reactions comprise attack on iron(II) or hydroperoxide. With this catalyst, both of these have been suppressed with the result that it should be a superior initiator, if the above hypothesis is correct. Such was actually found to be the case, especially in recipes where conditions were so stringent that even the reasonably effective DIP failed.

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SARNIA, ONTARIO, CANADA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Paramagnetic Resonance of Liquid Sulfur: Determination of Molecular Properties[1]

BY DONALD M. GARDNER[2] AND GEORGE K. FRAENKEL

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Paramagnetic resonance spectra have been obtained from liquid sulfur at temperatures from 189 to 414°. The paramagnetism, which increases reversibly with temperature, provides direct confirmation for the existence of long-chain sulfur polymers, and the results obtained are in quantitative agreement with the predictions of the theory due to Gee that postulates an equilibrium between long chains and S_8 rings. The heat of scission of sulfur–sulfur bonds in a long chain was found to be 33.4 ± 4.8 kcal./mole. The concentration of radicals at 300° was found to be $(1.1 \pm 0.6) \times 10^{-3}$ mole/l. and the average chain length is estimated to reach a maximum value of $(1.5 \pm 0.7) \times 10^6$ at 171°. Good agreement exists between these values and the estimates obtained from interpretation of the heat capacity data. The line width of the resonance increases markedly with temperature, but the spectroscopic splitting factor (*g*-value) is independent of temperature. The behavior of the line width is interpreted as evidence for a rapid radical displacement reaction giving for the rate constant $k = 2.8 \times 10^8 \exp(-3100/RT)$ l. (g.-atom)$^{-1}$ sec.$^{-1}$. Paramagnetic resonance spectra have also been observed from the black specks obtained by heating sulfur of ordinary purity. A description is given of the techniques of high temperature paramagnetic resonance spectroscopy and of the methods of obtaining absolute and relative paramagnetic intensities.

I. Introduction

For many years interest has been evoked by the occurrence of a transition in the physical properties of liquid sulfur at temperatures in the neighborhood of 160°; perhaps the most striking anomaly is the 10,000-fold *increase* in viscosity that takes place when the temperature is raised from 159 to 187°.[3] Studies have been made of the heat capacity,[4,5] the molecular aggregations,[6] the vapor pressure,[7] the composition of the vapor,[8,9] and the density.[10] Some of these measurements have been reviewed recently by Gee.[11] A number of investigators have also examined the properties of sulfur which has been quenched from a temperature above 160°: only a portion of the quenched sulfur dissolves rapidly in CS_2[12]; the material is elastic; repeated stretching increases the tensile strength by a factor of ten[13]; and after stretching a fiber X-ray diagram

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[1] Supported in part by Squier Signal Laboratory, U.S. Army Signal Corps.

[2] U. S. Army Signal Corps. Research Assistant.

[3] R. F. Bacon and R. Fanelli, THIS JOURNAL, **65**, 639 (1943).

[4] G. N. Lewis and M. Randall, *ibid.*, **33**, 476 (1911).

[5] H. Braune and O. Möller, *Z. Naturforsch.*, **9a**, 210 (1954).

[6] A. H. W. Aten, *Z. physik. Chem.*, **86**, 1 (1914).

[7] W. A. West and A. W. C. Menzies, *J. Phys. Chem.*, **33**, 1880 (1929).

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[9] H. Braune, S. Peter and V. Neveling, *Z. Naturforsch.*, **6a**, 32 (1951).

[10] A. M. Kellas, *J. Chem. Soc.*, **113**, 903 (1918).

[11] G. Gee, *Sci. Prog.*, 193 (1955).

[12] D. L. Hammick, W. R. Cousins and E. J. Langford, *J. Chem. Soc.*, 797 (1928).

[13] K. Sakurada and H. Erbring, *Koll.-Z.*, **72**, 129 (1935).

is found.[14] This X-ray work of Meyer and Go was the first data that was recognized as an indication of polymer formation.

The polymer model has served as the basis for a successful explanation of the peculiar properties of liquid sulfur. Powell and Eyring[15] developed the first detailed theory and gave an interpretation of the careful viscosity measurements of Bacon and Fanelli[3] on highly purified sulfur. This theory was superseded, however, in 1952 by the work of Gee[16] who was able to apply to the problem the advances made during the previous decade in the understanding of the statistical thermodynamics of polymer solutions. Gee's development, which is based on the assumption of an equilibrium between octatomic sulfur rings and linear-chain polymers, is in good semi-quantitative agreement with the viscosity and heat capacity[17] data. The only discrepancy which may exist in Gee's theory is in the temperature region below the transition.[17] The polymer model also accounts qualitatively for the changes that occur in crystalline character, tensile strength, and solubility, after the sulfur is quenched from high temperatures.[18] Krebs[19] has advanced the notion, in opposition to the chain model, that the polymeric material is composed primarily of large rings; this is ruled out by statistical considerations.[20]

The conventional rules of valence theory and the assumption of linear chains imply that polymeric sulfur molecules should contain an unpaired electron at each end,[21] and thus, if the polymer theory is correct, the liquid should be paramagnetic above the transition temperature (*ca.* 160°). Although measurements of the magnetic susceptibility of liquid sulfur have been performed,[17,22] the experiments were not of sufficient sensitivity to detect any paramagnetism, and the first direct indication of the existence of radicals was made by the more sensitive technique of paramagnetic resonance absorption spectroscopy.[23]

In the present report a detailed description is given of the paramagnetic resonance absorption measurements. The spectral data are used to evaluate the radical concentration, the heat of scission of a sulfur–sulfur bond, and the average chain length. In addition, evidence has been obtained that indicates the sulfur radicals are in rapid chemical reaction with their environment, and an estimate has been made of the rate of this reaction. The results, which provide data for a critical evaluation of the polymer model of liquid sulfur, have been compared with the predictions of Gee and his collaborators.[16,17]

II. Experimental

a. Apparatus.—All the paramagnetic spectra were obtained on the magic tee, heterodyne bridge spectrometer described by Hirshon and Fraenkel.[24] This spectrometer uses a Type 2K25 klystron at a wave length of about 3.2 cm.

1. Cavities.—The microwave cavities were of the reflection type similar to those described in reference 24 and were operated in the TE_{102} mode. They were made from silver-plated wave guide and had nominal inside dimensions of 0.400 × 0.900 × 1.750 in. The sulfur sample, contained in a 7-mm. o.d. sealed Vycor tube, was inserted vertically through clearance holes at the center of the narrow sides of the cavity. Small holes were also drilled at the back end of the cavity for the insertion of standard samples.

The cavities exhibited a weak, magnetic-field dependent, absorption which occurred even when the cavity was "empty"; similar effects have been reported previously.[24,25] At the lowest temperature at which a sulfur resonance was detected, 189°, the amplitude of the cavity absorption was equal to approximately one-half of the amplitude of the sulfur resonance, but the unwanted absorption did not appreciably affect the measurements made on liquid sulfur above about 240°.

2. Temperature Control and Measurement.—The sample temperature was controlled by heating the entire cavity with an electric heating coil placed outside the magnet gap. This coil radiated to a surrounding metal pipe which served to conduct the heat to the cavity. The temperature was measured by copper–constantan thermocouples set close to the walls of the cavity and the gradient over the sample was estimated to be 1° at 200° and about 4° at 420°.

3. Intensity Measurements. i. General Principles.—A paramagnetic resonance absorption spectrum, which typically consists of a plot of either the magnetic absorption or its derivative *versus* magnetic field,[24,26] can be used to evaluate the paramagnetic part of the magnetic susceptibility if the area of the absorption curve is computed.[27,28] The number of paramagnetic molecules is proportional to this area and, if the Curie law holds, is directly proportional to the absolute temperature. There is no reason to expect the Curie law to be violated in the present work because the usual effects that cause departures from this law[29] are absent.

A linear sulfur chain presumably contains an unpaired electron localized in the neighborhood of each end of the chain and, if the coupling between these two electrons were negligible, the state would be fourfold degenerate, *i.e.*, the two spins could be treated as if they were independent. On the other hand, if the two electrons interact appreciably, the ground state could be either a singlet or a triplet. From the data given below it can be shown that the number of short chains in liquid sulfur (perhaps of ten atoms or less in length) is inappreciable; thus the coupling between spins can be neglected and the number of independent spins is twice the number of chain molecules.

ii. Practical Considerations.—Since it is difficult to evaluate precisely the instrumental parameters which determine the sensitivity of a paramagnetic resonance spectrometer, intensity measurements are usually made relative to an internal standard. A convenient absolute standard is the solid free radical 1,1-diphenyl-2-picrylhydrazyl, but this material is unstable at elevated temperatures, and we therefore employed as a relative standard a sample of amorphous carbon.[30] Various forms of amorphous carbon

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[14] K. H. Meyer and Y. Go, *Helv. Chim. Acta*, **17**, 1081 (1934).

[15] R. E. Powell and H. Eyring, THIS JOURNAL, **76**, 648 (1943).

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[19] H. Krebs and E. F. Weber, *Z. anorg. allgem. Chem.*, **272**, 288 (1953).

[20] H. Jacobson and W. H. Stockmayer, *J. Chem. Phys.*, **18**, 1600 (1950); H. Jacobson, C. O. Beckmann and W. H. Stockmayer, *ibid.*, **18**, 1607 (1950).

[21] The first explicit mention of this conclusion appears to have been made by K. H. Meyer, "Natural and Synthetic High Polymers," 2nd Ed., Interscience Publ., New York, N. Y., 1950, p. 96.

[22] T. Ishiwara, *Science Repts. Tôhoku Imp. Univ., First Ser.*, **9**, 233 (1920); see also K. Honda, *ibid.*, **1**, 1 (1911) and M. Owen, *Ann. Physik.*, **37**, 657 (1912).

[23] D. M. Gardner and G. K. Fraenkel, THIS JOURNAL, **76**, 5891 (1954).

[24] J. M. Hirshon and G. K. Fraenkel, *Rev. Sci. Instr.*, **26**, 34 (1955).

[25] G. Feher and A. F. Kip, *Phys. Rev.*, **98**, 337 (1955).

[26] B. Bleaney and K. W. H. Stevens, *Repts. Progr. Phys.*, **16**, 108 (1953).

[27] R. Kubo and K. Tomita, *J. Phys. Soc. Japan*, **9**, 888 (1954).

[28] Throughout the following discussion, it is assumed that microwave power saturation does not occur.

[29] J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, London, 1932.

[30] Mn(II) activated cubic ZnS phosphor [W. D. Hershberger and H. N. Leifer, *Phys. Rev.*, **88**, 714 (1952)] would be an ideal standard because of the values of the magnetic field at which the resonances occur, but we found that it shows microwave power saturation.

exhibit a moderately weak but narrow absorption with approximately the free-electron g-value[31]; the sample used in this work had a width of about 2 gauss and $g = 2.004$. The intensity of the paramagnetism of the carbon sample at room temperature was determined by comparison with hydrazyl and the temperature dependence of its intensity was evaluated by measurements using anhydrous polycrystalline $CrCl_3$ as a standard. $CrCl_3$ is the only material we have found which has a relatively narrow resonance absorption[32,33] and for which the magnetic susceptibility has been measured at high temperatures.[34] Its width is too large, however, for convenient use directly with sulfur. (In the present work the width between points of extreme slope was found to be 78 ± 4 gauss.)

Our experimental observations are of the derivative of the paramagnetic absorption spectrum and thus, to obtain the area of the absorption *vs.* magnetic field curve, and from the area the number of unpaired electrons in a sulfur sample, a double integration is required. This integration is particularly inaccurate, however, for the absorption observed in liquid sulfur because the line decays quite slowly in the wings. In principle, direct evaluation of the area can be avoided if the line-shape function is known, since then the maximum values of the derivative can be related analytically to the number of unpaired electrons. In this work, therefore, it was assumed, on the basis of measurements of the line shape, that (1) the sulfur resonance did not change in form with temperature, and (2) the shape was adequately represented by a Lorentz-type curve. Only the first assumption is required for evaluation of the temperature dependence of the resonance, but the assumption of Lorentz shape is the main source of uncertainty in the determination of the absolute radical concentration.

The preceding assumptions are sufficient to derive an equation relating the number of unpaired electrons, n_u, in an unknown sample contained in the spectrometer to the number in a standard sample, n_{st}, and the measured properties of the spectrum. The measured quantities are the width, w, of the resonance of the unknown, which is the separation in gauss between points of inflection on the absorption curve, and the peak-to-peak amplitudes of the spectrum of the unknown, A_u, and the standard, A_{st}. The peak-to-peak amplitude is the displacement between the maximum and minimum amplitudes of the first derivative of a spectral line. The calibration of the peak-to-peak amplitude of the standard (carbon) as a function of temperature indicated that an adequate fit to the data could be obtained in the form of a Curie–Weiss law and, since the considerations of Sect. 3, i, indicate that radicals in liquid sulfur should obey the Curie law, one can show that

$$n_u/n_{st} = k(A_u/A_{st})w^2T/(T - \theta_{st}) \qquad (1)$$

where T is the absolute temperature and θ_{st} is the Weiss constant of the standard. If the amplitude of the magnetic field modulation[35,36] used to obtain the derivative of the two spectra is the same, the quantity k is constant and depends only on the form of the shape functions and the locations in the microwave cavity of the standard and the unknown. Since the portion of the Vycor sample tube in the cavity was always filled with sulfur, the volume of sulfur in the cavity remained essentially independent of temperature and the quantity n_u is directly proportional to the radical concentration. Equation 1 has formed the basis in the present work for the evaluation of the paramagnetic intensity as a function of temperature.

iii. Calibration of the Standard.—An evacuated sample of powdered $CrCl_3$ diluted with KCl served as the reference for the determination of the temperature dependence of the paramagnetic intensity of the carbon standard. Since, within experimental error, the width of the $CrCl_3$ line was independent of temperature up to 370°, it was presumed that the line shape was also invariant, and we therefore assumed that the peak-to-peak amplitude of the derivative of the absorption was proportional to the magnetic susceptibility. The intensity of the paramagnetic resonance of the $CrCl_3$ sample, which was checked at room temperature after each heating cycle, was found to be constant except after the final run at the highest temperature (370°). In this run, the intensity decreased by about 30% due to decomposition or sublimation.

Comparisons of the carbon standard with the $CrCl_3$ sample were made by measuring peak-to-peak amplitudes at constant magnetic-field modulation in the temperature range from 25 to 370°. The width of the carbon resonance was independent of temperature and the amplitude results, which were not of high precision, could be fitted by a Curie-Weiss law with a Weiss constant of $\theta_{st} = 100 \pm 28$. The amplitude of the modulation field was the same as used for the measurement of the sulfur resonance.

The absolute radical concentration was determined by comparing at room temperature the peak-to-peak amplitude of the derivative of the carbon resonance with the area of the absorption signal from a known weight of 1,1-diphenyl-2-picrylhydrazyl. The hydrazyl was diluted with powdered sulfur and placed in a Vycor tube of the same nominal dimensions as the tubes used for the liquid sulfur. Since the carbon and hydrazyl resonances occur at the same value of magnetic field, for constant microwave frequency, it was necessary to use a substitution method employing dummy samples. The dummy samples were made to duplicate closely the paramagnetic ones in all properties except their magnetism and all samples were carefully located at definite positions in the cavity. Insofar as possible, the average *r-f* magnetic field at the liquid sulfur samples was made identical to the average field at the hydrazyl standard.

iv. Amplitude Measurements.—The ratio A_u/A_{st} in eq. 1 (u = sulfur, st = carbon) at the different temperatures was obtained from recordings of the spectra taken when both the sulfur and the standard samples were present in the cavity. Since the carbon spectrum obscured the high-field extremum of the sulfur resonance, the amplitude A_u of the sulfur resonance was taken as twice the magnitude of the low-field extremum; the overlap of the carbon spectrum on the sulfur resonance was negligible in the vicinity of the low-field extremum of the latter.

The amplitude of the modulation field was maintained constant throughout the measurements by continually monitoring the voltage across the modulation coils; this voltage was held constant to within about 1% as measured with a vacuum-tube voltmeter. Direct measurement gave for the peak amplitude of the modulation $H_m = 9.5 \pm 0.2$ gauss ($H_{mod} = H_m \cos \omega_m t$) and showed that there was no detectable variation of modulation amplitude with gap width over the range of gaps used. This value of the modulation was chosen by calculation to ensure faithful reproduction of the derivative,[37–39] and direct experimental tests were performed to confirm the results of the calculations. Although the carbon resonance was distorted by over-modulation, any systematic error from this source was eliminated by the over-all calibration procedure.

Experiments were performed to check the reversibility of the paramagnetic resonance absorption as a function of temperature. All but one of the experimental points were obtained from sulfur which had been preheated to about 120–140° before being placed in the spectrometer cavity at the measuring temperature since, in order to prevent breakage of the Vycor sample tube, the sulfur had to be melted carefully. After a sample was inserted in the cavity, approximately five minutes were required for adjusting the instrument and for the sulfur to attain the temperature of the cavity. The resonance, thereafter, was found to be independent of the time of heating. In one experiment a sample was heated for five hours at 320° and then placed in the cavity at 220°; no detectable difference was observed between the resulting resonance and the resonance obtained when the sample was heated to 220° directly from room temperature.

Only a single resonance line was found in liquid sulfur at all temperatures investigated. A careful search for additional lines was repeatedly made over a range of 1000 gauss centered about the sulfur resonance. Less careful

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[31] D. J. E. Ingram and J. E. Bennett, *Phil. Mag.*, **45**, 545 (1954).

[32] D. M. S. Bagguley, B. Bleaney, J. H. E. Griffiths, R. P. Penrose and B. I. Plumpton, *Proc. Phys. Soc.* (*London*), **61**, 551 (1948).

[33] Y. Ting, L. D. Farringer and D. Williams, *Phys. Rev.*, **97**, 1037 (1955).

[34] K. Honda and T. Ishiwara, *Science Repts. Tohôku Imp. Univ., First Ser.*, **4**, 215 (1915).

[35] N. Bloembergen, E. M. Purcell and R. V. Pound, *Phys. Rev.*, **73**, 679 (1948).

[36] G. E. Pake, *Amer. J. Phys.*, **18**, 438, 473 (1950).

[37] W. D. Hershberger, *J. Appl. Phys.*, **19**, 411 (1948).

[38] E. R. Andrew, *Phys. Rev.*, **91**, 425 (1953).

[39] R. Beringer and J. G. Castle, *ibid.*, **81**, 82 (1951).

scanning occasionally extended to a range of about 3000 gauss.[40]

Since the sulfur resonance did not change relative to our intensity standard when the microwave power was reduced, it was assumed that the sulfur absorption did not undergo power saturation, *i.e.*, the (thermal) equilibrium population distribution of the spin states was not appreciably disturbed under the conditions of our experiments.

The lowest temperature at which measurements could be made was limited by the magnetic field dependent absorption which occurs even in an "empty" cavity and by the weakness of the resonance at low temperatures. At high temperatures difficulties were encountered with early modifications of our heating apparatus and with bumping of the evacuated sulfur sample.

4. **Measurement of *g*-Value, Line Width and Line Shape.**—Spectroscopic splitting factors (*g*-values) were measured to about 0.1% by using a calibrated wave meter to measure the microwave frequency and a proton resonance apparatus to determine the magnetic field.[24,41] Greater accuracy, which can be readily attained with the existing apparatus, was not attempted in the present work.

Line widths were usually determined directly by using the proton resonance apparatus to measure the spacing between points of extreme slope. In a few cases, however, measurements were made from pen recordings of the spectrum.

Under certain conditions, symmetric paramagnetic absorption lines about one gauss wide were found to give rise to systematically asymmetric absorption signals and although this apparent asymmetry could be eliminated by closing down the magnet gap, many of the measurements on liquid sulfur were performed with a heater that required a large gap. This inhomogeneity of the magnetic field, however, was found to be too small to cause any appreciable asymmetry in the sulfur resonance.

Since the internal intensity standard overlapped the sulfur spectrum, the determination of the variation of line shape with temperature required that recordings of the derivative of the paramagnetic spectrum of sulfur be made without any internal standard. These spectra were replotted in reduced units by normalizing the peak-to-peak amplitudes to two and by employing as abscissa the reduced-field units $(H - H_0)/w$, where H is the magnetic field and H_0 the resonant value of the magnetic field.

b. **Materials.** 1. **Sulfur.**—All results reported in this work have been obtained from samples of highly purified sulfur "SP-71" supplied by Dr. Fanelli. This sulfur had been purified by the procedure of Bacon and Fanelli.[42] Considerable care was necessary to avoid the development of black specks[43] after heating the sample; these were presumably formed from contamination by dust particles. A closed system was used for final purification: the sulfur was boiled for about 20 hours, degassed under vacuum (about twenty cycles of fusion and solidification at 10^{-5} mm. were required before no bubbles appeared upon fusion), and then distilled into and sealed in the Vycor sample tube. The samples that were filled with nitrogen and air were treated similarly except that after preliminary degassing they were flushed, filled with gas, and then sealed; the air-sample was sealed under one atmosphere of air and the nitrogen sample was sealed under a pressure of 0.57 atm. of prepurified nitrogen, both at room temperature. The high purity of these samples was confirmed by the complete absence of any (visible) black specks or discoloration after long periods of heating: the evacuated sample was heated at temperatures between 200 and 400° for a total of about 75 hours; the air sample was heated for 20 hours at 450°; the nitrogen sample was heated for 12 hours at about 500°.[44]

2. **1,1-Diphenyl-2-picrylhydrazyl.**—Two samples of hydrazyl from different sources were recrystallized from chloroform (m.p. 138–139.5°). The results of microchemical analysis of one sample were: Calcd. for $C_{18}H_{12}N_5O_6$: C, 54.8; H, 3.07; N, 17.8. Found: C, 50.2; H, 2.99; N, 15.9. The results for the other sample were comparable and, although the discrepancies were not explained, a recent report[45] indicates that part of the difficulty may be due to chloroform of crystallization. In any event, it appears unlikely that the radical content differs by more than 10–20% from the value calculated for pure hydrazyl, and considering the other errors inherent in measuring the absolute radical concentration in liquid sulfur, the poor analysis of the hydrazyl is not of too serious concern.

3. **Amorphous Carbon.**—Fifteen miscellaneous samples of decolorizing charcoal were examined and found to give resonance absorptions that varied in width from several hundred gauss to about 5 gauss. Preliminary tests showed that the paramagnetic intensity of a carbon sample depended on its thermal history, but after evacuation to 10^{-5} mm. with a heat treatment similar to those suggested in Dushman,[46] a sample with a reproducible magnetic absorption was obtained.

4. **$CrCl_3$.**—Samples of $CrCl_3$ were prepared by mixing Kahlbaum anhydrous $CrCl_3$ with J. T. Baker reagent grade KCl, the latter serving as a diluent, followed by evacuation to 10^{-5} mm. and sealing of the sample tube. In the absence of air, $CrCl_3$ was found to be relatively stable at temperatures up to 350° (see Section II, a.3.iii).

III. Results

The intensity of the paramagnetic resonance absorption of highly purified liquid sulfur was found to increase with increasing temperature; the resonance was determined only by the temperature of the liquid and was independent of the thermal history of the sample. All the experiments indicated that thermal equilibrium was established as soon as the sample attained the temperature of its surroundings. Only a single resonance line was found at all temperatures investigated.

The measurements were conducted primarily on samples of pure sulfur which were thoroughly degassed and sealed in Vycor tubes at a pressure of 10^{-5} mm. Less extensive data has been obtained from samples sealed under air and nitrogen.

a. ***g*-Value.**—As indicated in Section II, no attempt was made to obtain results more precise than about 0.1%, and within this precision the results are constant over the entire temperature range. The average value is $g = 2.024$. The magnetic-field dependent absorption present in an "empty" cavity had no significant effect on the *g*-value measurements.

b. **Line Width.**—The measured values of the line width (displacement in gauss between points of extreme slope) are tabulated in Table I. Direct measurement of the field displacement of the derivative extrema from the point of zero slope at the center of the line indicated that the high-field displacement was usually slightly greater than the low-field displacement. The apparent asymmetry in the resonance is believed to be due to the absorption of the empty cavity and is not considered to be a property of liquid sulfur; except at the lowest

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[40] In agreement with E. L. Yasaitis and B. Smaller, *Phys. Rev.*, **92**, 1068 (1953), we found a weak resonance from Vycor glass with a *g*-value of about 4.

[41] B. Venkataraman and G. K. Fraenkel, THIS JOURNAL, **77**, 2707 (1955).

[42] R. F. Bacon and R. Fanelli, *Ind. Eng. Chem.*, **34**, 1043 (1942).

[43] These black specks are paramagnetic at elevated temperature and remain paramagnetic at room temperature. The line widths were usually found to be of the order of 7 gauss and the *g*-values were approximately 2.010. The only other data available for this black material is its empirical composition, C_2S; *cf.* ref. 42 and "The Sulphur Data Book," W. N. Tuller, editor, McGraw-Hill Book Co., Inc., New York, N. Y., 1954, p. 102.

[44] The measurements reported in the preliminary communication, ref. 23, were made on imperfectly purified sulfur which developed a thin ring of black material at the upper surface of the liquid after heating in a sealed tube for about 20 hours at 350°.

[45] J. A. Lyons and W. F. Watson, *J. Polymer Sci.*, **18**, 141 (1955).

[46] S. Dushman, "Scientific Foundations of Vacuum Technique," John Wiley and Sons, Inc. New York, N. Y., 1949, pp. 466–471.

temperatures, the errors introduced by this effect are not significantly greater than the reproducibility of the data.

TABLE I

LINE-WIDTH DATA FOR LIQUID SULFUR

Temp., °C.	Chronological[a] sequence	Line width[e] (gauss)
189	5	. . .
216[b]	12 (2)	40 ± 6
218	4	37.2
243	3	36.1
243	7	42.9
244	8	49.2
279	11 (5)	62.4 ± 1.9
295	2	63.4
296	10 (5)	63.0 ± 3.0
306[c]	14 (4)	68.2 ± 2.7
310[d]	15 (2)	75.6 ± 1.0
320	6	64.9
335	13 (4)	71.2 ± 3.4
373	9 (4)	83.5 ± 1.6
414	1	102.4

[a] Figures in parentheses indicate number of replicate measurements. [b] The data at this temperature were obtained from pen-recordings of the spectrum. [c] Refers to sample sealed under nitrogen. [d] Refers to sample sealed under air. [e] The indicated estimates of precision are standard deviations for $(n - 1)$ degrees of freedom where n is the number of replicates.

The line-width data, shown in Fig. 1, have been fitted to the equation

$$\log w = a_w + b_w/T = 2.9812 - 673.0/T \qquad (2)$$

by the method of least squares. The points at 216 and 218° were excluded because of the uncertainties introduced by the absorption in the "empty" cavity, and each point was weighted in accordance with the number of replications. The standard deviation of b_w is $\sigma(b_w) = 90.6°\text{K}$. There is no *a priori* reason for using a semi-logarithmic plot here independent of the interpretation given below for the mechanism of line broadening and for convenience in calculating the intensity data.

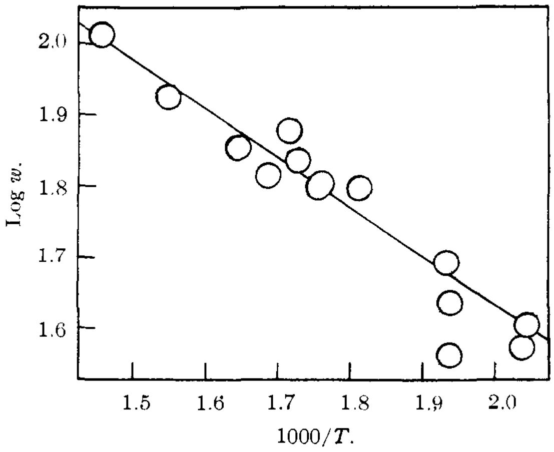

Fig. 1.—Logarithm of line width of sulfur resonance *vs.* reciprocal of absolute temperature.

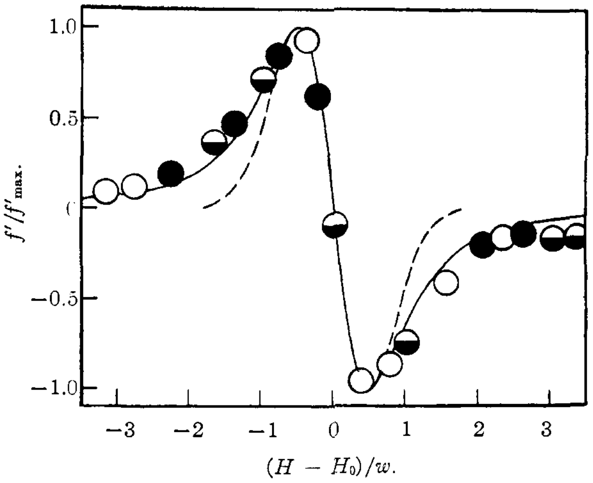

Fig. 2.—Normalized amplitude $f'/f'_{\text{max.}}$ of the derivative of the absorption function *vs.* the reduced field coördinate $(H - H_0)/w$; expt. pt. at 295° ○, 328° ◒, and 367° ●; Gaussian - - -; Lorentzian ———.

c. **Line Shape.**—The line shape was studied by replotting the spectra in reduced units. Figure 2 shows representative points from spectra obtained at 295, 328 and 367°. The dashed curve is a plot of the derivative of a Gaussian line-shape function and the full curve is a plot of the derivative of a Lorentzian line-shape function. No systematic variation of the line shape with temperature was found, and in agreement with the line-width data, the lines are symmetric within the experimental errors. It should be noted, however, that experiments such as these are difficult to evaluate quantitatively and considerable uncertainty is introduced by the large error in determining the amplitudes in the wings of the curve.

Figure 2 shows that, although a Gaussian line-shape function does not fit the data, there is an approximate but rather imperfect fit to a Lorentz shape. We do not believe that the absorption in the wings in excess of that predicted by a Lorentz function is caused entirely by the absorption of the "empty" cavity, but some contribution from this source may be present. Since no refined measurements directed toward the elucidation of the line shape have been carried out, it is not at present certain whether the deviation from the Lorentz shape is real or instrumental.

d. **Intensity.**—On the basis of the evidence in the preceding paragraph concerning the constancy of the line shape as a function of temperature, eq. 1 has been used for the evaluation of the intensity of the paramagnetism. The data for the peak-to-peak amplitudes of sulfur relative to carbon (A_u/A_{st}) are given in Table II. Although the widths of the resonance were not evaluated at the same temperatures as the peak-to-peak amplitudes, the dependence of the number of unpaired electrons on temperature can be expressed through eq. 1 by using eq. 2 for the width together with an equation fitted to the peak-to-peak amplitude data. It is shown in Section IV that the logarithm of the radical concentration, and therefore the quantity n_u/n_{st} of eq. 1, should be approximately linear in the reciprocal of the absolute temperature and thus, using eq. 2, the quantity $y = [\log (10A_u/A_{st})T/(T - \theta_{st})]$ should also be approximately linear in $1/T$. The experimental data in the form of this

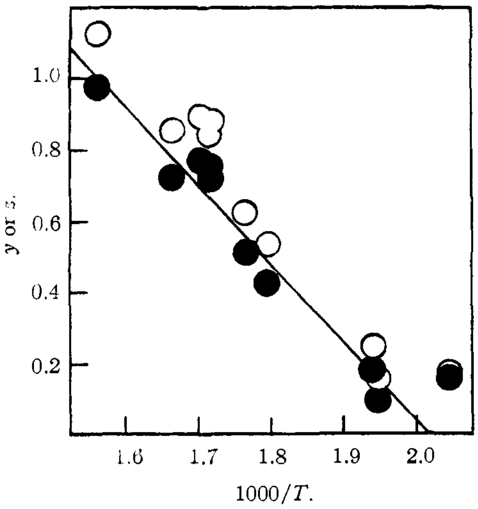

Fig. 3.—Amplitude of sulfur resonance as a function of temperature: expt. data ○ given by $y = \log (10A_u/A_{st}) (T)/(T - 100)$; corrected data ● given by $z = y - {}^1/_2 \log \varphi - \log \rho$; z-data fitted by $z = 4.509 - 2243.4/T$ ———.

quantity y, using $\theta_{st} = 100 \pm 28$°K., is plotted *versus* $1/T$ as the open circles in Fig. 3. The actual evaluation of the intensity of the resonance as a function of temperature will be deferred to Section IV where the significance of the solid circles and the straight line in Fig. 3 will be discussed.

TABLE II

PEAK-AMPLITUDE DATA FOR LIQUID SULFUR

Temp., °C.	Chronological[a] sequence	A_u/A_{st}
216[b]	7 (2)	0.120 ± 0.026
240	2	.115
242	3	.142
284	6 (2)	.282 ± 0.031
294	5 (2)	.349 ± 0.030
308[c]	9 (2)	.602 ± 0.001
310[d]	10	.581
315	1 (2)	.654 ± 0.013
329	8 (2)	.599 ± 0.033
368	4 (2)	1.10 ± 0.05

[a] Figures in parentheses indicate number of replicates. [b] Data corrected for effect of cavity absorption. [c] Refers to sample sealed under nitrogen. [d] Refers to sample sealed under air.

The experimental points in Fig. 3 were fitted to the equation

$$y = a_1' + b_1'/T = 4.985 - 2451.2/T \qquad (3)$$

by the method of least squares. The standard deviation of b_1' is $\sigma(b_1') = 215.9$°K. The point at 216° was excluded because of the effect of the absorption of the "empty" cavity, and the points were weighted in accordance with the number of replications. The large uncertainty in θ_{st} is unimportant since the entire factor $T/(T - \theta_{st})$ contributes only about 1% to the temperature coefficient.

The absolute concentration of unpaired electrons in liquid sulfur was estimated to be $(1.1 \pm 0.6) \times 10^{-3}$ mole/l. at 300°. On the assumption that there are two independent unpaired electrons per sulfur chain, the concentration of chains at 300° is $C_c = (6 \pm 3) \times 10^{-4}$ mole/l. Although the precision of this measurement is about 10%, a value of 50% has been assigned to the uncertainty because of our inadequate knowledge of the line shape of the sulfur resonance.

IV. Interpretation

a. Intensity. The S–S Bond Strength.—The elucidation of the significance of the experimental resonance intensity data for liquid sulfur requires that a specific model be assumed for the composition of the liquid. As a first approximation, it is sufficient to assume that the liquid is an equilibrium mixture of long chains

$$S_i = S_{i-j} + S_j \qquad (I)$$

where S_i is a linear chain of i sulfur atoms. From elementary considerations it can be shown that, if C_c is the concentration of chains, ln C_c should vary with temperature as $-\Delta H_s^\circ/2RT$. Here ΔH_s° is the heat of reaction (I), *i.e.*, the strength of a sulfur-sulfur bond in a long chain. ΔH_s° can thus be obtained from the slope of the semi-log plot of radical concentration *versus* the reciprocal of the absolute temperature.

The detailed analysis of the molecular properties of liquid sulfur by Gee,[16] as modified by Fairbrother, Gee and Merrall,[17] supplements these considerations by taking into account the equilibrium between S_8 rings (S_r) and chains

$$S_{i+8} = S_i + S_r \qquad (II)$$

From a slight modification of Gee's analysis,[47] it can be shown that the concentration of chains, C_c, is given by

$$\ln C_c = \text{const.} - \Delta H_s^\circ/2RT + (1/2) \ln \varphi + \ln \rho \qquad (4)$$

where φ is the weight fraction of polymer and ρ is the density of the liquid. The weight fraction can be calculated by the methods of Gee[16] if a value of ΔH_r°, the heat of reaction (II), is known. We have used the results of Fairbrother, Gee and Merrall[17]

$$\Delta H_r^\circ = -3180 + 9.98(T - T_\varphi) \text{ cal./mole} \qquad (5)$$

where $T_\varphi = 432$°K. is the temperature at which the transition in the viscosity takes place. Since C_c is one-half the radical concentration, it is proportional to the experimentally measured quantity n_u/n_{st}, and a plot of the quantity $[\log (n_u/n_{st}) - ({}^1/_2) \log \varphi - \log \rho]$ *versus* $1/T$ will have a slope

$$b = -\Delta H_s^\circ/(2)(2.303R) \qquad (6)$$

The experimental evaluation of ΔH_s° thus requires that the data for the intensity of the paramagnetic resonance be corrected by the terms $[({}^1/_2) \log \varphi + \log \rho]$. The temperature dependence of the density was found from the data of Kellas[10] and introduces a correction to the temperature coefficient of

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(47) Gee's treatment can be considered to be based on the general ideas of Flory's theory of the thermodynamics of polymer solutions [P. J. Flory, *J. Chem. Phys.*, **12**, 425 (1944), and "Principles of Polymer Chemistry," Cornell University Press, Ithaca, New York, N. Y., 1953], but it is interesting to note that a formal application of the latter theory agrees with Gee's results only when it is assumed that an eight-atom chain segment has the same volume as an S_8 ring and that the heat of mixing of rings and chains is zero. Minor modifications involving the density are introduced into Gee's equations by using the Flory formulation; thus it can be shown that eq. 5 and 15 of reference 16 actually hold even if the density is not assumed to be constant. The Flory formulation is used in the present treatment and, following Gee, we have neglected the volume change accompanying reaction (II).

only about 1%. The weight fraction has a somewhat larger effect, but introducing the combined correction for the density and weight fraction lowers the value of ΔH_s° by only about 4%.

The value of the slope b was determined by separate treatment of the line-width and peak-intensity data. The former were fitted by eq. 2. Each point of the peak-intensity data was corrected for the density and weight fraction effects and the function

$$z = \log [(10A_u/A_{st})T/(T - \theta_{st})] - (1/2) \log \varphi - \log \rho \qquad (7)$$

was fitted by the method of least squares to a function of the form

$$z = a_I + b_I/T \qquad (8)$$

As in Section III, the 216° point has been omitted and the points have been weighted by the number of replications. The corrected amplitude data are shown in Fig. 3 as the shaded circles, and the line is drawn in accord with the fitted equation.[48] The coefficient b_I of eq. 8 is found to be $b_I = -2298$°K., and its standard deviation is $\sigma(b_I) = 209$°K.

From the above considerations, and eq. 1 and 2, it follows that the slope b of eq. 6 is given by $b = b_I + 2b_w$, so that

$$\Delta H_s^\circ = -(9.154 \times 10^{-3})(b_I + 2b_w) = 33.4 \text{ kcal./mole}$$

The standard deviation of ΔH_s° is found to be $\sigma(\Delta H_s^\circ) = 2.5$ kcal./mole. Assuming seven degrees of freedom, which is the smaller of the degrees of freedom entering into b_I and b_w, the 90% confidence limits are 4.8 kcal./mole. This measure of precision is also considered to be an adequate measure of the accuracy of the result. The accuracy is limited not only by uncertainties in evaluating some of the experimental data, but also by the fundamental assumption concerning the constancy of the form of the line-shape function.

Before comparing this result for ΔH_s° with other data, it is convenient to determine the average chain length; the number-average chain length is given by $p = (1000/32)\ (\rho\varphi/C_c)$. The concentration of radical chains at 300° was found experimentally to be $C_c = (6 \pm 3) \times 10^{-4}$ mole/l., and the weight fraction at 300° is calculated to be 0.517. Using $\rho = 1.70$ g./ml., we find that the average chain length at 300° is $p = (5.0 \pm 2.5) \times 10^4$ With the value of ΔH_s°, the weight fraction φ_m and the temperature T_m at the temperature corresponding to the maximum average chain length can be calculated by the methods of Gee[16] to give $\varphi_m = 0.0899$ and $T_m = 444$°K. (at this temperature $\Delta H_r^\circ = -3060$ cal./mole). From T_m and ΔH_s° together with the values for p and φ at 300°, it is found, following Gee, that the average chain length reaches the maximum value of $p_m = (1.5 \pm 0.7) \times 10^6$ at 171°.

No other direct measurement of p_m is available for comparison with the above value, but Gee[16] estimated a value of 10^6 from the effect of added iodine on the viscosity of sulfur. Our value of 1.5×10^6 is equally consistent since it is not possible to ascertain p_m from the viscosity with any certainty. Rather qualitative conclusions about p_m can also be reached from the heat-capacity data discussed below.

The result that $\Delta H_s^\circ = 33.4 \pm 4.8$ kcal./mole obtained from the paramagnetic resonance data can be compared with estimates from three other sources: thermochemical data, the viscosity of liquid sulfur and the heat capacity. The available thermochemical data deal with S–S bonds in S_2, S_8 (rings), or disulfides, whereas measurements by paramagnetic resonance, viscosity or heat capacity, relate to long chains.

The value of ΔH_s° estimated by Gee[16] from the viscosity is 35 kcal./mole. This value is considered to be an upper limit[17] and one must bear in mind it is admittedly a rather crude estimate because of the many assumptions which are necessary to obtain an expression for the viscosity.[49] The analysis of the heat capacity data of Braune and Möller[5] by Fairbrother, *et al.*,[17] shows that the only contribution to the heat capacity from the breaking of sulfur–sulfur bonds in the polymer molecules takes the form of a term

$$(1/64R)(\varphi/p)(\Delta H_s^\circ/T)^2 \text{ cal. g.}^{-1} \text{ deg.}^{-1}$$

The magnitude of the contribution to the specific heat from this term depends very critically on the value of ΔH_s° through the exponential dependence of p on ΔH_s° and Fairbrother, *et al.*, show that if $p_m = 10^6$, ΔH_s° must be less than 35 kcal. The exact numerical limit depends on the assumed values of the temperature dependence of the heat capacity of liquid S_8 rings and of ΔH_r°, but our values $\Delta H_s^\circ = 33.4$ kcal. and $p_m = 1.5 \times 10^6$ are clearly consistent with the heat capacity.

Fairbrother, Gee and Merrall,[17] and Gee,[11] have pointed out that a value of $\Delta H_s^\circ = 35$ kcal./mole for the heat of breaking a sulfur–sulfur bond in a long chain is not consistent with the thermochemical data for sulfur–sulfur bonds in small molecules. Values of about 70 kcal./mole for the dissociation energy of the S–S bond in H_2S_2 and aliphatic disulfides are given in a recent summary[50] and the bond energy term obtained from S_8 rings is 64 kcal./mole. Recently D(HS–SH) has been estimated to be about 60 kcal./mole[51] and although 50 kcal./mole has been used for the bond energy term of S_8,[52] this latter result depends on the choice of D(S–S) in S_2, a quantity about which there has been considerable controversy.[50] Gee and his collaborators conclude that the heat of breaking a sulfur–sulfur bond in a long chain is definitely not the same as the bond strength in a disulfide; they account for a reduction in the heat of scission of long chains by a delocalization of the odd electrons at the chain ends with possible formation of a 3-electron bond with the adjacent sulfur atom.

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(48) The actual corrections applied in the figure correspond to a calculation in which ΔH_r° is taken to have the constant value of −3.18 kcal./mole, and the equation is $z = 4.509 - 2243.4/T$. Using this value of ΔH_r° gives $\Delta H_s^\circ = 32.9$ kcal./mole instead of the value 33.4 obtained when eq. 5 is used for ΔH_r°.

(49) One specific assumption involves the choice of n in the Staudinger relation for the intrinsic viscosity, $[\eta] = Ap^n$. Gee shows that the viscosity can be fitted approximately with a value of $n\Delta H_s^\circ = 23$ kcal./mole. The result $\Delta H_s = 35$ follows if $n = 2/3$, and although this is a reasonable value for n, it is not one sufficiently well known to give a precise value of ΔH_s.

(50) T. L. Cottrell, "The Strengths of Chemical Bonds," Academic Press, Inc., New York, N. Y., 1954.

(51) A. H. Sehon, THIS JOURNAL, **74**, 4723 (1952).

(52) M. L. Huggins, *ibid.*, **75**, 4123 (1953).

Although the measured properties of the paramagnetic spectra provide a direct quantitative test of the long-chain polymer model of liquid sulfur and of the chemical equilibrium between sulfur chains, the experiments do not present a means for a critical evaluation of the ring-chain equilibrium. The test provided by the values of the radical concentration and the heat of scission of a sulfur chain determined in the present work shows that the theory of Gee and his collaborators is essentially correct at temperatures above the transition point.

Our knowledge of the behavior of liquid sulfur can probably be extended by a number of additional experiments employing paramagnetic resonance spectroscopy. Perhaps the most interesting results would be obtained if radicals could be observed in the material obtained by rapid quenching of the high temperature melt, since successful investigations of this nature would provide a means of checking the weight-fraction data obtained from solubility studies. The range of temperatures examined could undoubtedly be extended by careful measurement with improved apparatus. Experiments at temperatures below 200° would serve as a critical test of the equilibrium between rings and chains as postulated in Gee's theory, and might also give a direct value of the heat of reaction ΔH_r°, while high temperature measurements would permit an improvement in the precision of the determination of the heat of scission, ΔH_s°. Although precise studies of the line shape of the resonance and its variation, if any, with temperature, would be extremely difficult, such an investigation would enable improved accuracy to be attained in the evaluation of ΔH_s° and the radical concentration.

b. Line Width. Reactivity of Sulfur Radicals.—The line width of the paramagnetic spectrum of liquid sulfur is unusual in two respects: the width is much larger than expected, the narrowest line observed being about 40 gauss wide at 216°, and it increases rapidly with temperature, reaching 100 gauss at the highest temperature attained, 414°. Resonance lines in paramagnetic spectra can be broadened either by unresolved structure and shifts in the spin energy levels, or by the finite lifetime of a spin state which, in accordance with the Heisenberg uncertainty principle $\Delta E \cdot \Delta t \sim h/2\pi$, causes the energy levels to have a non-zero width. Although broadening can also arise from microwave power saturation, this effect did not take place in our experiments (see Section II).

One contribution of the first type is known as dipolar broadening and arises from the interaction of each spin with the local magnetic fields produced by all the neighboring spins.[35,53] Kittel and Abrahams[54] have estimated the magnitude of the dipolar width for spins placed at random on the sites of a cubic lattice and it can be shown from their results that, except at the highest temperatures, the contribution from the dipolar broadening is much smaller than the width observed in liquid sulfur. Even at the high temperatures, the observed width is about ten times this estimate of the dipolar width, and actually, since the motional narrowing[35] is not taken into account by these authors, the true dipolar width is still smaller than this estimate of one-tenth of the observed width. Another type of broadening may arise if the *g*-tensor is sufficiently anisotropic, but these effects are likely to be small in polyatomic free radicals containing only light atoms. That there is nothing inherent in sulfur radicals that could cause large anisotropic contributions to the *g*-tensor not found in other polyatomic radicals containing light atoms follows from the investigations on ultramarine[55a] and sulfur in oleum.[55b] The lines observed in the latter mixture, including the solid formed from the reaction of sulfur with sulfur trioxide, are 4 to 7 gauss wide. As a further argument against anisotropy broadening, it should be noted that this type of effect would not be expected to increase with increasing temperature. Nuclear hyperfine interactions, which can also cause broadening, are absent in liquid sulfur because of the low abundance of sulfur isotopes with a non-zero nuclear spin.

There are two mechanisms that ordinarily contribute to the shortening of the lifetime, or relaxation, of an electron spin state. Relaxation can occur through the action of motional effects on the dipolar interaction[35] or through the coupling of the spin to the lattice by means of spin-orbit coupling. The dipolar relaxation produces broadening of the same order of magnitude as the direct dipolar broadening, thus being negligible in the present case, and the spin-orbit lattice relaxation is likely to be small since the *g*-value shows that the spin-orbit effects in general are small.

This survey indicates that the usual physical effects contributing to the line breadth are too small to account for the experimental results. A specific interaction between sulfur radicals and their environment, such as a chemical reaction, appears to be the only remaining possibility: by annihilating a sulfur radical, chemical reaction would terminate the life of a spin state and thus, if it were sufficiently rapid, the reaction would affect the breadth of the spin energy levels. A similar interpretation has been given by Ward and Weissman[56] to the variation of the width of the paramagnetic resonance spectrum of the naphthalene negative-ion free radical with naphthalene concentration. These authors attributed the width to an electron transfer reaction between naphthalene and its negative ion.

A sulfur radical in liquid sulfur can participate in a radical combination reaction

$$\text{------S}\cdot + \cdot\text{S-------} \rightarrow \text{-------S–S--------}$$

or a radical displacement reaction

$$\text{--------S}\cdot + \text{------S–S-------} \rightarrow \text{---------S–S------} + \cdot\text{S------}$$

Although energetically favored, the former process is probably negligible compared to the displacement reaction because the concentration of radical ends [S·] is much less than the total concentration of atoms [S]. Furthermore, if the radical combination reaction were predominant, the radical

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(53) J. H. Van Vleck, *Phys. Rev.*, **74**, 1168 (1948).

(54) C. Kittel and E. Abrahams, *ibid.*, **90**, 238 (1953).

(55) (a) D. M. Gardner and G. K. Fraenkel, THIS JOURNAL, **77**, 6399 (1955). (b) D. M. Gardner and G. K. Fraenkel, unpublished results.

(56) R. L. Ward and S. I. Weissman, *ibid.*, **76**, 3612 (1954).

lifetime would depend on the concentration of radicals. From an analysis of the kinetic equations, it can be shown that the logarithmic derivative of the lifetime with respect to temperature is proportional to $-(1/2RT^2)(2E + \Delta H_s^\circ)$ where E is the activation energy of the combination reaction, and thus, contrary to experiment, the lifetime of this reaction would vary at least as rapidly as $\exp(\Delta H_s^\circ/2RT) = \exp(8500/T)$. The rate of disappearance, Rt, of the radical ends is therefore given by

$$Rt = -\mathrm{d}\,[S\cdot]/\mathrm{d}t = k[S\cdot][S] \qquad (9)$$

and the rate constant k can be evaluated from the lifetime of the radicals, τ, by using the relation $[S\cdot]/\tau = Rt$ to give

$$k = 1/\tau[S]\cdot \qquad (10)$$

If the lifetime of a radical end, τ, can be identified with the lifetime of a spin state, τ', and if the width of the paramagnetic resonance spectrum is determined by τ', the rate constant k can be evaluated from the width by using the Van Vleck–Weisskopf theory of pressure broadening of spectral lines.[57] In this theory the lifetime τ' is the mean time between the interruption of a quantum state by strong collisions and, since it is unlikely that a spin state would be undisturbed by a chemical reaction, the spin-state lifetime cannot be greater than the radical lifetime. The true spin-state lifetime τ' cannot be determined from the spectrum if mechanisms other than relaxation effects contribute to the line width but, aside from these effects, there are two factors which might cause the lifetime calculated from the width to be less than the radical lifetime τ. In the first place, a transition may be induced in the spin state at energies of interaction insufficient to allow the reactants to form an activated complex and, secondly, although the spin state may be destroyed when the activated complex is formed, not all activated complexes decompose to the products of the reaction. These effects are difficult to estimate quantitatively, but it is unlikely that they are large.

Van Vleck and Weisskopf[57] have shown that the shape of a spectral absorption line that takes place between energy levels disturbed by strong collisions is Lorentzian and has a half-width at half-maximum intensity on a frequency scale of $\Delta\nu = 1/(2\pi\tau')$. The particular result that the shape should be Lorentzian applies to the present problem since the width is much less than the center frequency of the line,[57] and the observed line shape, Fig. 2, for liquid sulfur, indicates that the resonance is at least approximately Lorentzian. Thus the shape is in agreement with the proposed mechanism of broadening. By using the relation $h\nu = g\beta H$, the half-width at half-maximum intensity on a magnetic-field scale can be written as $\Delta H = h/(2\pi\tau' g\beta)$ or, if numerical values are inserted and the width w between points of extreme slope [$w = (2/\sqrt{3})\Delta H$ for a Lorentz line] is used, one obtains

$$\tau' = 6.47 \times 10^{-8}/w \qquad (11)$$

where τ' is in seconds and w is in gauss.

To calculate the rate constant k we use eq. 10 and 11, identifying τ with τ', and obtain w from eq. 2 for log w. The sulfur atom concentration is found by using 1.7 g./ml. for the density[10]: $[S] = 53$ g.-atom/l. The result, in units of l. (g./atom)$^{-1}$ sec.$^{-1}$, is

$$k = (2.8 \pm 1.9) \times 10^8 \exp[-(3.08 \pm 0.75) \times 10^3/RT] \qquad (12)$$

If the radical combination rather than the displacement reaction were the important mechanism and if the activation energy for the former reaction were close to zero, this result would imply that ΔH_s° could not be greater than $2 \times 3.1 = 6.2$ kcal./mole.

Although there are no data available on completely analogous reactions, these results are in general agreement with previously obtained data. The activation energy of 3.1 kcal. is in accord with the low activation energies usually found in radical displacement reactions. The only other reaction investigated that involves sulfur radicals is the reaction between styrene radicals and sulfur at 45°, studied by Bartlett,[58] who found that the rate of propagation is 460 times the rate in pure styrene. With the aid of the data of Matheson, *et al.*,[59] for the polymerization of styrene, we find that the rate constant for the reaction of styrene radicals with sulfur at 45° is about 4×10^4 while our rate constant for the sulfur radical-sulfur reaction at this temperature is 2×10^6. Comparison can also be made with the second-order rate constant obtained by Ward and Weissman[56] for the reaction between naphthalene and its negative ion referred to above. These authors obtained a rate constant at 30° of 1.0×10^6; our result for the sulfur reaction at 30° is 1.7×10^6.

The value obtained for the rate constant thus seems to be generally consistent with the interpretation of the line width of the resonance in terms of the chemical reactivity of the sulfur radicals. The hypothesis of chemical reaction could be checked quite conclusively by performing paramagnetic resonance experiments on the material quenched from high temperatures since the radical lifetime in the quenched material should be much larger than in the liquid. The effect of diluents would also serve as a means of checking this hypothesis.

c. *g*-Value.—The spectroscopic splitting factor for the liquid-sulfur resonance, $g = 2.024$, differs by only 0.022 unit from the free-electron value of 2.0023. This shift in g-value from the free-electron value can be compared with the shifts of 0.004 unit or less observed in this and other laboratories for polyatomic organic free radicals containing only elements of the first row of the periodic table, and with the shifts of tenths of units or more often found in the spectra of crystalline salts of the transition metals.[26] Although no quantitative theory of the small shifts found in molecules containing only light atoms has been developed, the

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[57] J. H. Van Vleck and V. F. Weisskopf, *Revs. Mod. Phys.*, **17**, 227 (1945). See also R. Karplus and J. Schwinger, *Phys. Rev.*, **73**, 1020 (1948), and C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

[58] P. D. Bartlett, private communication.

[59] M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, THIS JOURNAL, **73**, 1700 (1951).

general interpretation is clear: the shift in *g*-value for molecules in non-degenerate orbital ground states increases with the magnitude of the spin-orbit coupling and decreases with the separation between the ground and excited states.

The spin-orbit coupling in atoms increases rapidly with atomic number and thus the shift in *g*-value for sulfur radicals (0.022 unit) would be expected to be larger than the shift in radicals containing only first row elements (< 0.004 unit), as indeed is the case. The authors know of only two other systems that appear to involve sulfur radicals: ultramarine[55a] and sulfur in oleum.[55b] Both materials have *g*-values of about 2.02, and thus the data suggests the very tentative inference that all polyatomic free radicals in which the odd electron is primarily associated with a sulfur atom will have a *g*-value of about 2.02. When the odd electron is in a sulfur-containing compound but is not primarily localized on a sulfur atom, the *g*-value should be closer than this to the free electron value. Sulfur-containing free radicals have been observed in the presence of Lewis acids,[60,61] and the *g*-value obtained from the spectrum of a sulfuric acid solution of diphenyl disulfide was found to be 2.008.[24] It is also interesting to note that the black specks obtained from impure sulfur, corresponding to the empirical formula C_2S, have a *g*-value of 2.010.[43]

V. Acknowledgments.—We are indebted to Dr. Rocco Fanelli of the Texas Gulf Sulfur Company for his generous gift of highly purified sulfur. We would like to thank Professor Cheves Walling for suggesting this application of the technique of paramagnetic resonance and for innumerable helpful conversations during the course of this research.

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(60) J. M. Hirshon, D. M. Gardner and G. K. Fraenkel, THIS JOURNAL, **75**, 4115 (1953).

(61) J. E. Wertz and J. L. Vivo, *J. Chem. Phys.*, **23**, 2193 (1955).

NEW YORK, N. Y.

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

The Bromine Pentafluoride–Hydrogen Fluoride System. Solid–Liquid Equilibria, Vapor Pressures, Molar Volumes and Specific Conductances[1]

BY MAX T. ROGERS, JOHN L. SPEIRS AND MORTON B. PANISH

RECEIVED FEBRUARY 29, 1956

Various physical properties of the bromine pentafluoride-hydrogen fluoride system have been investigated. The solid-liquid phase diagram shows a eutectic point at −85.61° and 95.2 mole per cent. hydrogen fluoride. The vapor pressure-composition diagram shows large positive deviations from Raoult's law. The deviations from ideality become larger at higher temperatures, and at 25° there is probably an azeotrope with maximum vapor pressure. Average molar volumes observed are lower than calculated for an ideal solution, the contraction on mixing being 2-3%. The specific conductance of a carefully purified sample of bromine pentafluoride was 9.1×10^{-8} ohm^{-1} cm.$^{-1}$. Conductances of bromine pentafluoride-hydrogen fluoride mixtures were studied over a range of temperatures and compositions.

Introduction

The physical properties of bromine pentafluoride and of bromine pentafluoride–hydrogen fluoride mixtures have been little investigated. In order to extend the knowledge of these systems, we have measured freezing points, densities, vapor pressures and specific conductances of various mixtures of hydrogen fluoride and bromine pentafluoride.

Experimental

Materials.—The method for purification, storage and handling of bromine pentafluoride and hydrogen fluoride has been described.[1,2]

Cryoscopic Measurements.—The freezing point cells for bromine pentafluoride-hydrogen fluoride solutions and the technique used have been described.[2] Difficulty was encountered with stirring pure bromine pentafluoride since the reciprocating stirrer froze in when less than half the liquid had frozen. A new cell was therefore constructed in which the liquid could be completely frozen. This cell was constructed entirely of fluorothene and was closed by a tapered plug held in place by a clamping device. A copper-constantan thermocouple was introduced through the plug and the leads were wound in a helix around a fluorothene rod which extended into the liquid. Materials could be introduced into the cell on the vacuum line by a connection through the plug. In use the cell was filled, closed and the entire assembly attached to a single-cylinder reciprocal-action air motor which provided very vigorous shaking of the contents.

Density, Vapor Pressure and Conductance Measurements.—The techniques were the same as used previously.[1] A new dipping-type conductance cell was employed which largely eliminated the use of fluorothene wax as a sealant around leads. This was important since the wax is dissolved by bromine pentafluoride. Measurements at −60° to −70° were made using a Dry Ice-acetone cooling bath; the cell was calibrated at low temperatures with solutions of salts in alcohol or acetone. The conductances of the latter were measured in a conventional glass cell fitted with platinized platinum electrodes.

Results

Solid–liquid Equilibria.—Cooling curves obtained with various mixtures of bromine pentafluoride and hydrogen fluoride provided the initial and final freezing temperatures which are presented in Table I. The only definite feature is a eutectic point at −85.61° and 95.2 mole per cent. hydrogen fluoride. The freezing point of pure bromine pentafluoride calculated by the method of Witschonke[3] is −60.50 ± 0.10°, and the concentration of impurity in our starting material was about 0.02 molal. A slight discontinuity in the freezing point curve at 18 mole per cent. hydrogen fluoride does not seem to be a peritectic but might arise from a phase transition in the solid state.

The heat of fusion of bromine pentafluoride esti-

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[1] Physical Properties of the Halogen Fluorides. VIII. For the preceding article of this series see M. T. Rogers, J. L. Speirs, M. B. Panish and H. B. Thompson, THIS JOURNAL, **78**, 936 (1956).

[2] M. T. Rogers and J. L. Speirs, *J. Phys. Chem.*, in press.

[3] C. R. Witschonke, *Anal. Chem.*, **24**, 350 (1952).