475. *Solutions of Sulphur in Oleum. Part I. Electron-spin Resonance of Solutions of Sulphur in Oleum.*

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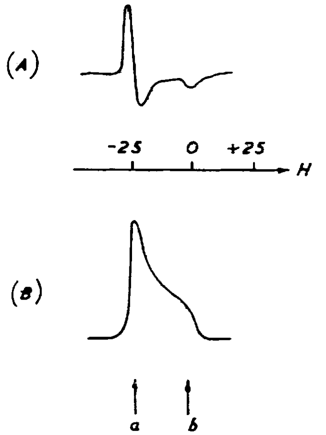
Blue solutions of sulphur in concentrated oleum, although diamagnetic by conventional susceptibility measurements, show a strong electron-spin resonance absorption and must therefore contain a little of some species having unpaired electrons. At 90° K the absorption curve has a sharp peak with a *g*-value of 2·018 and a shoulder having a *g*-value of 2·003. Measurements at two different wavelengths show that this asymmetry is due to a variation in the *g*-value and is not a fine or hyperfine structure. On addition of aqueous sulphuric acid to the solution this line diminishes in intensity and a new line appears having a peak and shoulder with *g*-values of 2·025 and 2·032, respectively. It is postulated that this second line is caused by polymeric sulphur radicals similar to those present in liquid sulphur.

It has been stated[1] that the cause of the colour in blue solutions formed by dissolving sulphur or iodine in oleum is sulphur sesquioxide, and this work was undertaken to investigate this statement. The postulate that blue iodine solutions contain free iodine cations[2] is based largely on the observation that the solutions contain a paramagnetic species in large concentration. This paramagnetic species, which was detected by conventional magnetic-susceptibility measurements. does not give an observable electron-resonance absorption at 90° K, presumably because the absorption is too broad at this temperature, or because there is a large zero-field splitting of the triplet levels. In contrast, blue solutions of sulphur, which are found by susceptibility measurements to contain no bulk paramagnetic component,[3] have a strong electron-resonance absorption,

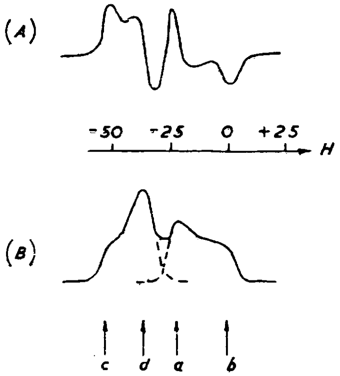
FIG. 1. *Absorption line obtained from a solution of sulphur in concentrated oleum* (65% SO_3).



(*A*) Derivative as traced out.
(*B*) Reconstructed absorption with *g*-values : $a \equiv 2{\cdot}018$, $b \equiv 2{\cdot}003$.

Magnetic field strengths are quoted in gauss centred on the free-spin value.

FIG. 2. *Absorption line obtained from a solution of sulphur in dilute oleum* (20% SO_3).



(*A*) Derivative as traced out.
(*B*) Reconstructed absorption with *g*-values : $a \equiv 2{\cdot}018$, $b \equiv 2{\cdot}003$, $c \equiv 2{\cdot}032$, $d \equiv 2{\cdot}025$.

Magnetic field strengths are quoted in gauss centred on the free-spin value.

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[1] Masson and Argument, *J.*, 1938, 1705.
[2] Symons, *J.*, 1957, 387, 2186.
[3] Symons, following paper.

and therefore contain some species with unpaired electrons in such low concentrations that it cannot be detected satisfactorily by conventional methods.

When these solutions are treated with aqueous sulphuric acid the colour changes from blue, *via* green, to brown, and ultimately sulphur is precipitated. During this process the strong resonance absorption characteristic of the blue solution rapidly decreases and loses its well-defined peak, and a new, weak absorption line appears at a slightly lower field strength. Both bands vanish when sulphur is precipitated.

Typical results obtained from blue and brown solutions are shown in Figs. 1 and 2, respectively. In each case (*A*) represents the derivative of the absorption curve and (*B*) an integrated reconstruction of the actual absorption curve. These curves were obtained from solutions at 90° K. When the brown solutions were allowed to warm the two bands changed markedly as soon as the glassy solvent became fluid. The shoulders of both lines vanished leaving two narrow lines. The brief reference made by Gardner and Fraenkel to the detection of two radicals in solutions of sulphur in oleum probably relates to these narrow, symmetrical lines.[4]

EXPERIMENTAL

Sulphuric acid and oleums were purified as described earlier,[2] and their purity checked by spectrophotometric measurements in the 200—300 mμ range with a Unicam SP500 spectrophotometer. Oleum strengths were estimated by the "fog-clear" method described by Kunzler.[5] Sulphur was purified by the procedure of Bacon and Fanelli.[6] Samples for measurement in the 3 cm. wavelength spectrometer were placed in thin-walled test tubes (3 mm. diam.) and rapidly cooled in liquid oxygen so that a homogeneous glass was formed. These tubes were placed directly in the apparatus. Since only small quantities of solution were required for measurement in the 1·25 cm. wavelength spectrometer, and since it was necessary to avoid attack on the inside of the cavity by sulphur trioxide vapour, the following procedure was adopted. A thin mica sheet was stuck to the bottom of the adjustable short-circuiting plunger of the cavity, which was then cooled in liquid oxygen. Immediately after removal from the liquid oxygen a small drop of oleum solution was placed in the centre of the mica, and the cavity plunger rapidly screwed into position in the apparatus. In this way it was possible to re-cool before the frozen oleum became fluid.

Apparatus.—A 3-cm. wavelength electron resonance spectroscope was employed for most of the measurements, the rectangular H_{012} resonator being surrounded with an evacuated jacket containing liquid oxygen. In order to obtain a high sensitivity, phase-sensitive methods of detection were employed,[7] a small amplitude 100 kc./sec. field sweep being applied across the sample, while the d.c. value of the main magnetic field was slowly swept through the resonance value. The output from the phase-sensitive mixer is thus proportional to the derivative of the absorption line, and it is passed to a pen-recorder *via* a d.c. amplifier chain. The electron resonance spectrum is thus continuously recorded, and two examples of observed spectra are shown in Figs. 1*A* and 2*A* together with the calculated *g*-values. The horizontal axes of these figures thus correspond to changing value of d.c. magnetic field, while the magnitude of the deflection parallel to the vertical axis is equal to the derivative of the absorption line at that point. A maximum in this trace therefore corresponds to a point of maximum slope on the actual absorption curve, while an intercept with the axis indicates a point of inflexion on the absorption line. The actual shape of the resonance absorption can therefore be deduced from the derivatives, and such are reconstructed in Figs. 1*B* and 2*B*. Fig. 1 is for solutions containing a high concentration of SO_3 (65%), while Fig. 2 is for a solution containing the same amount of sulphur (*ca.* 0·1M) but less SO_3 (20%).

The determination of the resonance field strengths and *g*-values (for definition see ref. 8)

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[4] Gardner and Fraenkel, *J. Amer. Chem. Soc.*, 1956, **78**, 3279.
[5] Kunzler, *Analyt. Chem.*, 1953, **25**, 193.
[6] Bacon and Fanelli, *Ind. Eng. Chem.*, 1942, **34**, 1043.
[7] Ingram, "Spectroscopy at Radio and Microwave Frequencies," Butterworths, 1955, p. 35.
[8] Ingram, *ibid.*, pp. 142 and 66.

was effected by affixing a small amount of free-radical marker, αα-diphenyl-β-picrylhydrazyl, to the specimen tube and observing the superimposed spectra. The sharp peak was found to fall on the high-field edge of the main absorption line as indicated in Fig. 1*B*. The *g*-values corresponding to the other peaks could then be calculated directly from the measured field increments.

Some measurements were also made at 1·25 cm. wavelengths at liquid-air temperatures, by use of a standard H_{111} low-temperature cavity.[8] These were performed to check whether the asymmetry of the line shape was due to an anisotropic *g*-value or a zero-field electronic splitting of triplet state levels. The former would give a line width which increased with increasing frequency of observation, whereas the line width would remain constant if due to the latter effect. In fact it was found that a large increase in width was obtained at the higher frequencies, indicating that the shape of the main absorption curve is due to an anisotropic *g*-value. Unfortunately this test could not be applied to the second band because the methods used for detection were less sensitive and the shoulder was not observable with 1·25 cm. radiation. However the fact that both bands changed to single narrow lines when the glass softened suggests that this asymmetry is also due to variation of the *g*-value, since this effect is characteristic of anisotropic transitions when the medium changes from being rigid to fluid.[9]

DISCUSSION

Since one absorption band increases when the other decreases they must be caused by two different radicals and cannot be two transitions of a single species with two unpaired electrons. Gardner and Fraenkel [4] have not observed a *g*-value variation for any of the sulphur radicals studied and they state that anisotropic contributions are unlikely : their failure to observe it in oleum solutions may be because they used fluid solutions.

The high *g*-value of about 2·02 shows that spin–orbit coupling must be appreciable, and, as suggested by Gardner and Fraenkel, may be characteristic of free radicals in which the odd electron is located primarily on sulphur.

These radicals form only a very small component of solutions whose bulk composition is uncertain, and therefore precise identification is impossible. However, the second line appears just before the solid sulphur separates, and since the polymeric radicals present in liquid sulphur have a *g*-value of 2·024,[4] it is suggested that this same radical may be formed as a precursor to the formation of solid sulphur.

The distinction between the sulphur and iodine solutions is clear, the former having no major paramagnetic content but one or two radical species in small concentration readily detectable by their electron-resonance absorption, the latter containing large concentrations of a paramagnetic species which, however, is not detectable by electron resonance techniques at 90° K.

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[9] Bennett, Ingram, and Schonland, *Proc. Phys. Soc.*, 1956, *A*, **69**, 556.