476. *Solutions of Sulphur in Oleum. Part II.* Visible and Ultraviolet Absorption Spectra.*

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Spectra of freshly prepared, blue solutions of sulphur in concentrated oleum show absorption bands with maxima at 590 and 335 mμ, but on storage the latter slowly increases in intensity at the expense of the former. At ∼50° this effect is reversed. A reversible equilibrium between monomeric and polymeric sulphur sesquioxide is postulated to explain these changes, high temperature favouring the monomer. Corresponding changes in magnetic susceptibility show that, after warming, there is a marked increase in the concentration of some paramagnetic species, and the nature of this species is discussed.

WHILST the green-blue solid which is precipitated when sulphur trioxide and sulphur interact has been studied extensively [1-4] and shown to be sulphur sesquioxide with the empirical formula S_2O_3, little attention has been paid to the deep blue, homogeneous solutions formed when sulphur or the sesquioxide is dissolved in concentrated oleum. Partington and Vogel [1] established that these solutions, in contrast with the green or brown solutions obtained when the concentration of sulphur trioxide is small, are not colloidal, and naturally assumed that they are simply solutions of the sesquioxide; they state that the solutions are very unstable.

The colour of the sesquioxide is always described as green-blue, although Wohler and Wegwitz [2] found that when excess of sulphur trioxide was removed, the residual solid was brown. In contrast, the solutions are deep blue owing, as can be seen from curve *a* in Fig. 1, to a band at 590 mμ. Since these solutions contain an unidentified paramagnetic substance [5] in low concentration their electronic absorption spectra and magnetic susceptibilities have been studied. Although the concentration of paramagnetic material is too small for conclusive detection by the Gouy technique because of unascertainable diamagnetic corrections, the results reported in Part I [5] show that in concentrated solutions it should contribute a pull of several milligrams to the overall change in weight and hence any change in concentration of the paramagnetic species, unaccompanied by large changes in the bulk composition of the solution, should be readily detectable.

The results are summarised in Figs. 1 and 2. Two spectral effects may be distinguished; treating a blue solution with sulphuric acid so that the concentration of sulphur trioxide is lowered, changes the colour from blue to brown, and later sulphur is precipitated. Vogel and Partington [1] established that the brown solutions are colloidal, and the spectrum (curve *c*) is characteristic of such a solution. Also, the spectra of fresh solutions (curve *a*) containing a large concentration of sulphur trioxide change with time, the intensity of the peak at 590 mμ slowly decreasing, with a corresponding increase in that of the 335 mμ band, until after several days (curve *b*) dilute solutions appear colourless. If the solution is then warmed to about 50°, an intense blue colour slowly develops and is retained on cooling. The spectrum of the resulting solution is similar to that of the original solution (curve *a*), and again changes with time in an identical manner. With care, very little sulphur dioxide is evolved during this cycle, and a colourless solution, kept at room temperature for many weeks, still assumes an intense blue colour on warming. However,

* Part I, preceding paper.
[1] Vogel and Partington, *J.*, 1925, 1514.
[2] Wöhler and Wegwitz, *Z. anorg. Chem.*, 1933, **213**, 129.
[3] Appel, *Naturwiss.*, 1953, **40**, 509.
[4] Murthy, *Nature*, 1951, **168**, 475.
[5] Ingram and Symons, preceding paper.

overheating causes vigorous evolution of sulphur dioxide and total loss of both bands (curve *d*).

Magnetic-susceptibility measurements showed an apparent increase in the overall diamagnetism of the solutions corresponding with the decay in the 590 mμ peak (Fig. 2). Since the susceptibility of the aged solutions was nearly the same as that of the pure solvent
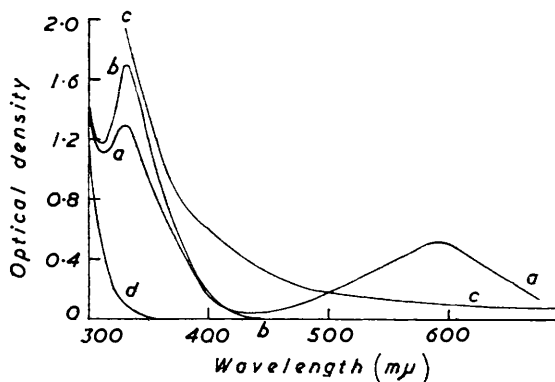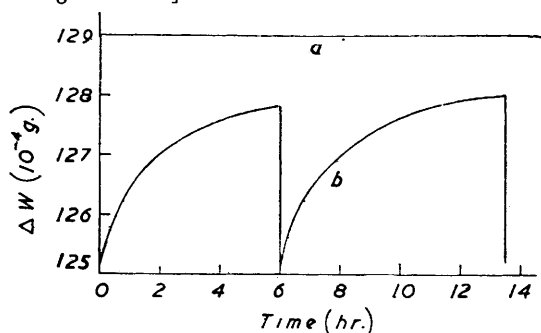

FIG. 1. *Absorption spectra of solutions of sulphur in oleum.*

a, *Freshly prepared solution in concentrated oleum (65%).* b, *Same solution after 24 hours.* d, *Same solution after prolonged heating.* c, *Solution of sulphur in dilute oleum (10%).*

FIG. 2. *Effect of heat on the magnetic susceptibility of a solution of sulphur in oleum (65%).* [ΔW is the difference between the weight of the tube and its contents in the presence and in the absence of the magnetic field.]

a, ΔW *for pure solvent and for the solution remaining after thermal decomposition of the sulphur sesquioxide.* b, *Variation in* ΔW *with time of a freshly prepared solution, and the effect of heat on* ΔW. *All readings were made at the same temperature. The readings obtained 6 and 13·5 hours after preparation were made as soon as possible after warming.*

FIG. 3. *Absorption spectra of various oleums and of sulphur dioxide in sulphuric acid.*

a, *Sulphur dioxide in sulphuric acid (98·4%).* b, *34% Oleum.* c, *40% Oleum.* d, *60% Oleum.*

and of the residual solvent after total decomposition of the solute by heat, it is concluded that the decrease in diamagnetism found immediately after the restoration of the blue colour is caused by the presence of a paramagnetic substance.

The simplest inference is that the blue compound is paramagnetic. A rough estimation of the radical concentration shows that, on this assumption, the extinction coefficient at 590 mμ lies between 10^3 and 10^4, showing that the transition is a permitted one. It is equally reasonable to postulate that the concentration of the paramagnetic species is directly dependent upon the concentration of the blue compound, or even that they are produced by two completely separate processes when the solution is heated. There is insufficient evidence available for an unequivocal conclusion, but certain alternative interpretations seem sufficiently well founded to warrant discussion.

DISCUSSION

It has been concluded that two distinct radical species may occur in solutions of sulphur in oleum, one being favoured by high and the other by low concentrations of sulphur trioxide.[5] These two radicals will be considered in turn. When the oleum is dilute the solutions are colloidal,[1] and precipitation of the sulphur is probably prevented because the solvent is able to protonate S_x molecules. If protonation can occur it is possible that polymeric diradicals, such as are thought to be present in liquid sulphur,[6] will be stabilised by protonation near the ends of the molecules, since repulsive effects would then inhibit cyclisation. These diradicals will behave essentially as two separate radicals since conjugation through the sulphur chain would be impossible provided there are more than three atoms in the chain. However, the unpaired electron will not be localised entirely on the end sulphur atom and may be in part on the second or even the third sulphur atom. Thus the structure resembles in some ways the superoxide or ozonide systems,[7] and the observation of an ill-defined variation [5] in the *g*-value is in agreement with this postulate. (The *g*-value is a measure of the rate of divergence of the electronic levels with magnetic field, and a spread in the electron resonance absorption curve caused by magnetic anisotropy is known as a *g*-value variation.)

These radicals are destroyed when sulphur trioxide is added, but a new one is formed in very much greater concentration. This time, the *g*-value variation is very well defined and spread over a considerable range. There can be little doubt therefore that the radical is axially symmetrical.[8] Certain possibilities arise. In several, the radical considered has two unpaired electrons, and it has already been stressed [5] that such species are somewhat less probable than radicals possessing only one electron or in which one is effectively insulated from the other, since only one transition is observed.

Perhaps the simplest postulate is that monomeric sulphur sesquioxide is both blue and paramagnetic, and that this slowly disappears by polymerisation at room temperature. It has been postulated [9] that S_2O_3 should be diamagnetic, in contrast to SO_4, since the three-fold degeneracy of the highest-energy orbital of sulphate is lifted when one oxygen atom is replaced by sulphur. This argument was based on calculations made by Helmholz, Brennan, and Wolfsberg [10] relating to the electronic structure of the fluorochromate ion. They concluded that the three-fold degenerate orbital of the chromate ion (designated as t_1) is split when the symmetry is reduced by the introduction of fluorine or chlorine to a doubly degenerate level of symmetry e and a non-degenerate level a_2. Since the a_2 level is found to lie above the e level, the compound formed by loss of two electrons from this ion would be diamagnetic. However, extrapolation from this case to sulphur sesquioxide is not short and it is conceivable that these levels are inverted, the doubly degenerate level lying below the non-degenerate level in the S_2O_3 molecule. This would mean that there are two unpaired electrons in S_2O_3, which could therefore possibly be the paramagnetic species in question. This radical has axial symmetry as required by the electron-resonance spectrum.

It has been reported that the monomeric compound SO_4 is colourless in solution.[11] This is in accord with the scheme proposed by Wolfsberg and Helmholz [12] for the perchlorate ion, since the first permitted electronic transition of an ion formed by the loss of two electrons would be $(t_1)^4 \longrightarrow (t_1)^3(3t_2)$ which would be of great energy. However in the S_2O_3 molecule, transition between the e and the a_2 level would be allowed, and hence there should be an intense absorption band of relatively low energy. This is in accord with

[6] Gardner and Fraenkel, *J. Amer. Chem. Soc.*, 1956, **78**, 3279.
[7] Bennett, Ingram, Symons, George, and Griffiths, *Phil. Mag.*, 1955, **46**, 443.
[8] Sands, *Phys. Rev.*, 1955, **99**, 1222.
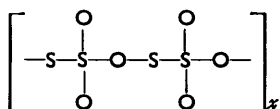[9] Symons, *J.*, 1957, 387.
[10] Helmholz, Brennan, and Wolfsberg, *J. Chem. Phys.*, 1955, **23**, 853.
[11] Schwarz and Achenbach, *Z. anorg. Chem.*, 1934, **219**, 271.
[12] Wolfsberg and Helmholz, *J. Chem. Phys.*, 1952, **20**, 837.

the postulate that the band at 590 mμ is caused by monomeric sulphur sesquioxide and that the molar extinction coefficient is between 10^3 and 10^4.

If this concept is correct, the slow decrease in colour and paramagnetism could be interpreted as a polymerisation process $xS_2O_3 \longrightarrow (S_2O_3)_x$. The new band at 335 mμ would then be ascribed to the polymer, which probably has the symmetrical "head to tail" structure (A) analogous to that of polymeric sulphur trioxide. Evidence for this structure is provided by Appel's work.[3] Each unit within the polymer is structurally analogous to a disubstituted sulphate ion. Thus the situation resembles that discussed by Helmholz et al.,[10] and the fact [13] that the first electronic transition for sulphonyl chloride is at 303 mμ is in accord with this picture. At high concentrations the edge of the 335 mμ band would extend into the visible region, causing the polymer to appear yellow or brown. However, surface decomposition caused by moisture would involve the formation of monomer as in solution, and hence the solid might appear green.

Recently Brayford and Wyatt [14] concluded, on the basis of cryoscopic measurements, that sulphur dissolved in oleum (45%) is present largely as sulphur sesquioxide. They observed a slow increase in the measured i-factor before a constant value was obtained, and attributed this to either the slow dissolution of sulphur or a slow conversion of colloidal sulphur into the sesquioxide. If either interpretation is correct the phenomenon is not related to the changes described here. Brayford and Wyatt state that the sulphur sesquioxide may not be entirely monomeric.

A consideration of the nature of the end groups in such a polymer leads to an alternative theory. In polymeric sulphur trioxide the end groups are almost certainly H and OH, and the polymerisation, which is catalysed by traces of water,[15] must be ionic in type. However, polymeric sulphur appears to be formed by a radical process, the ends of each molecule being neutral radicals. Since polymeric sulphur sesquioxide is half-way between these extremes either type of polymer seems reasonable. By analogy with sulphur
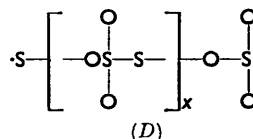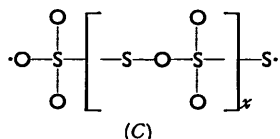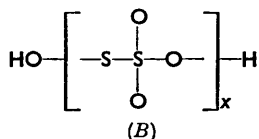
trioxide one could formulate the polymer as (B) or, by analogy with sulphur, as (C) or (D). There are at least four alternative end groups for such polymeric radicals, each of which would be expected to have a characteristic electron-resonance absorption spectrum. It is conceivable that two radical structures are more stable than the remainder, and that their structural similarities are such that the electron-spin resonance spectra merge to give the curve recorded in Part I.[5]

Two further possibilities exist, namely, that the paramagnetic species is monomeric sulphur monoxide or the diradical HS+. Both have axial symmetry and probably two unpaired electrons. Evidence that sulphur monoxide is one of the decomposition products of solid sulphur sesquioxide has been presented by Murthy.[4] Both monomer and dimer have absorption maxima in the 320 mμ region but no transition in the visible region. It is conceivable therefore that the band at 335 mμ is caused by sulphur monoxide, but in that case, since the paramagnetism decreases as this band increases, the monoxide would have to be present in the dimeric form.[16]

The formation of the radical HS+ is postulated because of the similarities between this

[13] Thompson, *Nature*, 1933, **132**, 896.
[14] Brayford and Wyatt, *Trans. Faraday Soc.*, 1956, **52**, 642.
[15] Bigeon, *Ind. chim.*, 1953, **40**, 106.
[16] Jones, *J. Chem. Phys.*, 1950, **18**, 1263.

system and that of iodine in oleum.[9] The iodine cation, thought to be present in the latter solution, could react with sulphur trioxide to form ISO_3^+.[9] The analogous equilibrium $S_2O_3 \rightleftharpoons SO_3 + S$ is far less probable, not only because iodine cations are intrinsically more probable than free sulphur atoms, but also because the former will be stabilised by solvation, whilst sulphur atoms would immediately combine to form solid sulphur. However. if the sesquioxide were capable of accepting a proton to form $HS_2O_3^+$, then this might reversibly dissociate to form HS^+ in very low concentration. The main objection to this theory is that interaction between the unpaired electrons and the proton would be expected and should manifest itself as a splitting of the magnetic resonance line into a doublet which has not been detected.

EXPERIMENTAL

Materials were purified, and solutions prepared as described in Part I.[5] Because of the difficulties involved in the preparation of pure sulphur the following alternative procedure was used in addition to that already described. " AnalaR " sodium thiosulphate was dissolved in concentrated sulphuric acid. The resulting suspension was warmed to expel sulphur dioxide, and sulphur trioxide was added as required. The results were identical with those obtained from solutions prepared from the element.

Spectroscopic measurements were made with a Unicam S.P.600 glass spectrophotometer, and a Unicam S.P.500 quartz spectrophotometer. Calibrated quartz cells of 1 mm. and 1 cm. thickness were used, the latter equipped with stoppers. The 1 mm. cells were not covered since absorption of small amounts of water on the surface of the solution resulted in the formation of an upper layer which effectively sealed the solution from the atmosphere. The spectra recorded in Figs. 1 and 2 were measured against pure solvent as a control material. Measurements were usually made down to 220 mμ and in every case a pronounced peak at 280 mμ was found. This was almost certainly caused by dissolved sulphur dioxide, which is fairly soluble in sulphuric acid. The spectrum of a solution of sulphur dioxide in sulphuric acid is recorded in Fig. 3, curve *a*.

Also recorded in Fig. 3 are the absorption spectra for oleums of various strengths measured against pure sulphuric acid as control material. By comparison with the spectrum for sulphur trioxide in the gaseous state [17] it may be seen that the concentration of free sulphur trioxide must be very small indeed in dilute oleum,[18] but that as the percentage of sulphur trioxide is increased the absorption at low wavelengths increases very rapidly, as does the vapour pressure of the solutions; [19] and it seems probable that this increased absorption is caused by free sulphur trioxide.[14]

Magnetic measurements were made with a conventional Gouy balance at room temperature, as described earlier.[9] The results are recorded in Fig. 2.

[17] Fajans and Goodeve, *Trans. Faraday. Soc.*, 1936, **32**, 511.
[18] Gillespie, *J.*, 1950, 2493.
[19] Yost and Russell, " Systematic Inorganic Chemistry," Prentice-Hall Inc., New York, 1944, p. 340.