Electron Spin Resonance Studies of Sulphur in Oleum. The Ion S_8^+

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Summary E.s.r. studies of blue solutions of sulphur in oleum using sulphur enriched in ^{33}S show that in the liquid phase S_8^+ has eight effectively equivalent sulphur atoms while at 77 K, the electron is largely confined to one atom.

CONSIDERABLE attention has recently been focussed on the cations of elemental sulphur, selenium, and telurium.[1-5] One of us[6] has shown that two of the components of the solutions of sulphur in oleum were paramagnetic, having characteristic e.s.r. spectra, and it was suggested that the blue species (E_{max} *ca.* 17,000 cm^{-1}) might be one of them. These ideas have been extended,[7] and apparently confirmed,[1] but Gillespie and his co-workers contend that the blue species is in fact the diamagnetic S_8^{2+} cation.[2,3] Giggenbach maintains that it is S_4^+, which dimerises to S_8^{2+} on cooling. The present situation for the sulphur cations, together with optical band assignments, is summarised in Table 1.

We have identified the species responsible for the e.s.r. absorption in concentrated oleum solutions, and studied its electronic structure using sulphur enriched with 10% and 25% ^{33}S. The liquid-phase spectra (see Figure) support a

TABLE 1

Optical parameters and assignments for various cations of sulphur

Species	S_4^{2+}	S_4^+	S_8^{2+}	S_8^+	S_{16}^{2+}
Average optical band ..	30,000	17,000	17,000 (i)	17,000	23,500
Maxima (cm^{-1})	—	—	23,500 (ii)	—	—
Ref.	3, 4	1	3 (i) 1 (ii)	[a]	3

[a] This work: based on the optical studies of Giggenbach,[1] and our earlier assignment.[6]

structure with eight equivalent sulphur atoms, *i.e.*, S_8^+. A reconstruction shows that the alternative, S_4^+,[1] is excluded, even allowing for considerable error in the analyses. $2S_8^+ \rightleftharpoons S_{16}^{2+}$, with a weak σ-bonding between the rings comparable with that between the sulphur atoms in the dithionite ion, $S_2O_4^{2-}$ is possible.

TABLE 2

E.s.r. data assigned to S_8^+ *at room temperature and* 77 K

	g_{sol}	$g_{\parallel}$	$g_{\perp}$		
g-Values	2·013	2·004	2·020		
	A_{sol} (G)	$A_{\parallel}$ (S_1) (G)	$A_{\perp}$ (S_1) (G)	$A_{\parallel}$ (S_2) (G)	$A_{\perp}$ (S_2) (G)
^{33}S Hyperfine coupling constants	7·2 ± 0·4	*ca.* 46	*ca.* 20	*ca.* 16	*ca.* 10·5

This conclusion is based particularly on the intensities of bands associated with species containing two and three equivalent ^{33}S atoms.

However, a symmetrically delocalised structure is not expected for S_8^+, and we suggest a rapid charge-transfer mechanism around the ring to explain the results. Such a structure is supported by the e.s.r. spectra of frozen solutions. Although the ^{33}S hyperfine features are poorly defined, and spectral interpretation consequently is difficult, the relative intensities of the parent ^{32}S features are undoubtedly many-fold greater than in the liquid phase and the possibility of eight equivalent sulphur atoms per radical is excluded. The results suggest either one or possibly two equivalent atoms and the large number of poorly resolved features suggests at least two types of sulphur atoms. We tentatively offer the following model. The electron is largely confined to one sulphur atom (S_1) with slight delocalisation on to its two immediate neighbours (S_2 and S_3). The data based on this analysis are given in Table 2. If the orbital on S is pure $3p$ (π), then the magnitude of the isotopic coupling suggests nearly unity spin-density, whilst the anisotropic coupling indicates only about 30%. Since the spin-density on S_2 and S_3 is low, the most probable explanation for this result is a fairly large libration or vibration such as to reduce the measured anisotropy at S_2. Another possibility, of course, is that the hyperfine and *g*-tensors are not coaxial.

Giggenbach has established that this species is in equilibrium with a diamagnetic species. The dimerisation,

Since S_8^+ is the parent cation of elemental sulphur, it plays a role in conduction mechanisms in solid and liquid sulphur;[8]

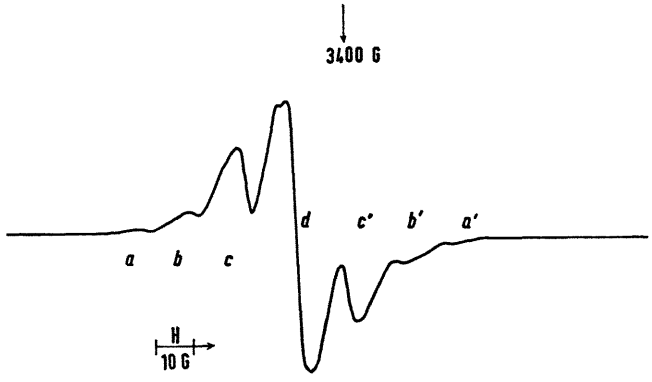

FIGURE. *E.s.r. spectrum of a dilute solution (ca.* 3×10^{-4}M) *of sulphur enriched to* 25% *in* ^{33}S *in oleum* (65%) *at room temperature. Outermost features assigned to* a *radicals containing three equivalent* ^{33}S *atoms,* b *two equivalent* ^{33}S *atoms,* c *one* ^{33}S *atom,* d *radicals containing no* ^{33}S *and two equivalent* ^{33}S *atoms.*

a similar structure has previously been suggested by one of us for the hole carrier.[9]

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