The Radical Cations of Sulphur ($S_8^{\bullet+}$) and Tetrasulphur Tetranitride ($S_4N_4^{\bullet+}$): A Radiation–Electron Spin Resonance Study†

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Exposure of dilute solutions of S_8 and S_4N_4 in trichlorofluoromethane to ^{60}Co γ-rays at 77 K gave the corresponding radical cations. The first formed species from sulphur, (**A**), thought to be S_8^+, had $g_x = 2.069$, $g_y = 2.057$, and $g_z = 1.997$. Enrichment (99%) with ^{33}S gave greatly broadened x and y features, with $A(^{33}S) \approx \pm 4$ G. The z features showed a clear central line flanked by others with $A_z \approx 28$ G. The results suggest the presence of two equally coupled sulphur atoms. On annealing, species (**A**) changes irreversibly into species (**B**) ($g_x = 2.044$, $g_y = 2.034$, $g_z = 2.0035$). It is suggested that (**B**) is also $S_8^{\bullet+}$ in a relaxed form in which two opposite atoms have formed a weak three-electron bond. The e.s.r. parameters for (**B**) are very similar to those previously assigned to S_8^+, formed from S_8^{2+} in oleum. A clear spectrum was produced from S_4N_4 which showed little g-value variation ($g_{av.} = 2.004$) and no evidence for ^{14}N splitting. It is concluded that the $S_4N_4^{\bullet+}$ cation has a relatively isolated semi-occupied molecular orbital, with low spin density on nitrogen.

The primary radical cation of elemental sulphur, $S_8^{\bullet+}$, has had a chequered history, which has been largely associated with the bright blue solutions formed by sulphur dissolved in 65% oleum.[1] Nearly 30 years ago, one of us established the presence of a major paramagnetic species in these blue solutions,[1] but it was only after Gillespie's pioneering work on a range of dications of sulphur and selenium,[2,3] and the use of ^{33}S, that convincing identifications were forthcoming.[4–7]

Using 10 and 25% enrichment of ^{33}S, we put forward a case for $S_8^{\bullet+}$, which was in accord with the poorly defined liquid- and solid-state e.s.r. spectra.[6] However, Giggenbach[4] favoured assignment to $S_4^{\bullet+}$ cations, as did Gillespie and Ummat.[5] Using highly enriched material, Beaudet and Stephens[7] obtained far better resolution in the liquid phase, and concluded firmly that the $S_4^{\bullet+}$ formulation was correct, the four sulphur atoms being equivalent. Unfortunately, this interpretation gave a $g_{av.}$ value of 2.0163, whereas the ^{32}S derivative has $g_{av.} = 2.0130$.[1] We then pointed out that if the species had an even rather than an odd number of lines, the appropriate g value was obtained.[8] Of the two possible formulations, $S_5^{\bullet+}$ and $S_7^{\bullet+}$, we gave several reasons for favouring $S_5^{\bullet+}$, the five sulphur atoms being 'equivalent' on the e.s.r. time-scale at room temperature, but markedly inequivalent at 77 K. Our subsequent, unpublished, studies were in accord with the $S_5^{\bullet+}$ formulation, which was later strongly supported by Low and Beaudet.[9]

Clearly the species having $g_{av.} = 2.013$ formed in 65% oleum cannot be $S_8^{\bullet+}$. However, as sulphuric acid is added, a second species is formed, having $g_{av.} \approx 2.027$. Gillespie and Ummat[5] have argued that this species is $S_8^{\bullet+}$, formed reversibly from the dimer, S_{16}^{2+}. This suggestion is considered below. With the advent of a good routine method for preparing primary radical cations,[10] it seemed worthwhile to return to this topic. This procedure, which involves exposing dilute solutions of the parent molecules in halogenated solvents such as $CFCl_3$, invariably results in the formation of primary radical cations, or unimolecular breakdown products thereof, provided the ionization potential is less than that of the solvent and the substrate does not form aggregates. The only major caveat to this rule is that, under certain circumstances, the primary cations form weak complexes with a solvent molecule.[11]

Thus, we can have considerable confidence that the species detected in this way from S_8 and S_4N_4 are the primary cations, so that the otherwise very difficult assignment problem is overcome. The cation $S_4N_4^+$ has not, so far as we are aware, been studied by e.s.r. spectroscopy although there has been extensive work on solutions in acidic solvents[12,13] and on electron-addition products.[14,15]

Experimental

Dilute solutions of sulphur (99.999%; Aldrich, Gold Label), of ^{33}S (99%, Oak Ridge National Laboratory), and of S_4N_4 (high purity, kindly supplied by Professor C. W. Rees) were prepared in $CFCl_3$ which had been dried, passed down an alumina column, and degassed. Mole fractions were always less than *ca.* 0.001.

Solutions, as small beads, were exposed to ^{60}Co γ-rays at 77 K using doses up to *ca.* 1 Mrad and were studied at this temperature on a Varian E-109 spectrometer calibrated with a Hewlett-Packard 5246L frequency counter and a Bruker B-H12 field probe, which were standardized with a sample of diphenylpicrylhydrazyl (dpph).

Solutions were annealed either by decanting the coolant and allowing the samples to warm in the sealed Dewar until significant changes in the e.s.r. spectra were observed, or in steps of 5° using a Varian variable-temperature accessory.

Samples were exposed to X-rays at *ca.* 4 K using an Oxford Instruments cryostat and an Andrex NDT Products (UK) Gemini 160-kV constant-potential X-ray generating unit fitted with a beryllium window and water cooler.

Results and Discussion

Sulphur Cations.—Although only one major radical, (A), was formed at 77 K a second minor species, (**A**′), with similar parameters was also detected together with a few unrelated features (Figure 1 and Table), which we do not discuss. On annealing, species (A′) became better defined and relatively more intense, before both were lost, with concomitant growth of species (**B**) (Figure 2). On further annealing, species (**B**) decayed, with no further change. Attempts to obtain isotropic spectra failed.

When sulphur enriched with ^{33}S was used, there were very marked changes in the spectra, as indicated in Figure 3.

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† *Non-S.I. units employed:* rad = 10^{-2} J kg^{-1}, G = 10^{-4} T.

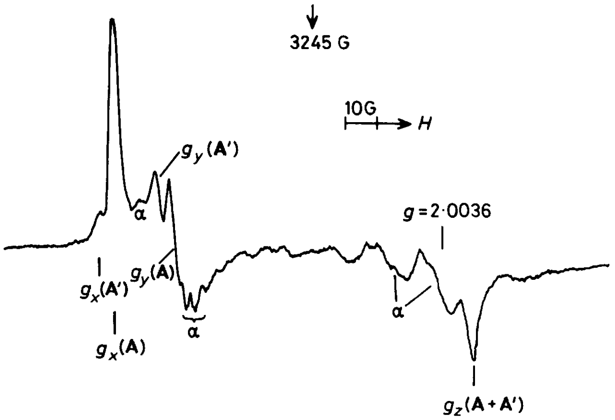


Figure 1. First-derivative X-band e.s.r. spectrum for sulphur in $CFCl_3$ after exposure to ^{60}Co γ-rays at 77 K, showing features for species (**A**) ($S_8^{\cdot+}$) and (**A′**); extra features α, due to impurities, remain unassigned

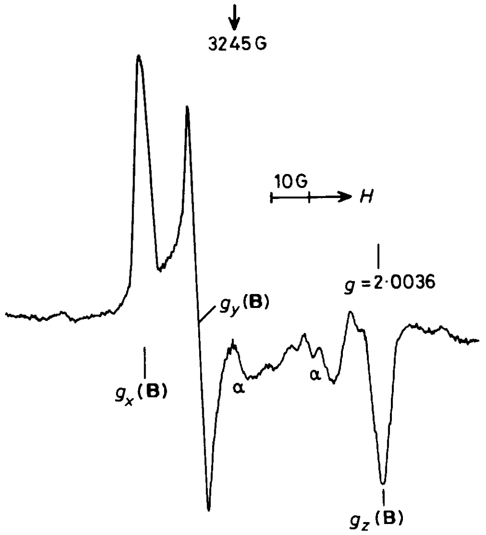


Figure 2. As for Figure 1 but after annealing to *ca.* 120 K, showing the loss of species (**A**) and gain of species (**B**). Note that the microwave frequencies differ in Figures 1 and 2

Table. E.s.r. parameters assigned to $S_8^{\cdot+}$ [radicals (**A**), (**A′**), and (**B**)] and some related sulphur-centred radicals

Radical	Solvent	g_x	g_y	g_z	$g_{av.}$
(**A**)[a]	$CFCl_3$	2.069	2.057	1.997	2.041
(**A′**)	$CFCl_3$	2.074	2.060		
(**B**)[b]	$CFCl_3$	2.044	2.034	2.0035	2.027
$S_5^{\cdot+}$	65% oleum[c]	2.020	2.020	2.002	2.0134
$S_8^{\cdot+}$	25% oleum[d]	2.042	2.031	2.0024	2.025
$(S)_n$	*e*	2.042	2.028	2.002	2.024

[a] $A_x(^{33}S)$ ± 4 ≈ A_y *ca.* ±4 G, A_z ≈ 28 G. [b] ^{33}S Splittings not resolved. [c] Ref. 8 ($g_{av.}$ is the liquid-phase value). [d] Ref. 5. [e] 'Polymer' radical on rapidly frozen molten sulphur.

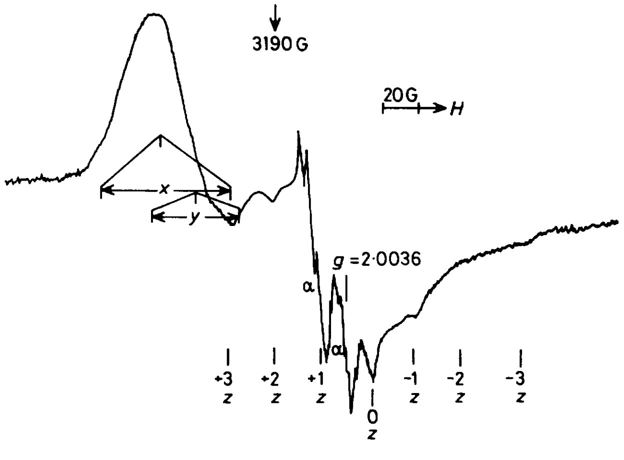


Figure 3. As for Figure 1 but using $^{33}S_8$ (99%)

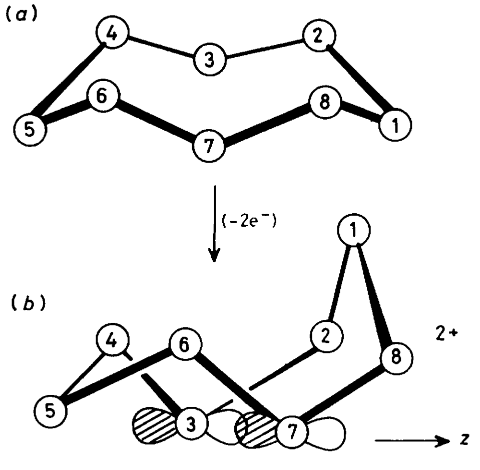


Figure 4. Structures of S_8 (*a*) and $S_8^{\cdot 2+}$ (*b*), the latter showing a weak bonding interaction between S(3) and S(7)

Unfortunately, the x and y features were severely broadened but not resolved. However, despite the presence of impurity signals (α), definite new z features assignable to (**A**) were obtained, the most important being the narrow component in the centre of the multiplet, at g_z = 1.997. This establishes an odd number of lines, which must be at least seven. Unfortunately, the intensity of (**B**) (^{33}S) was such that the z features were never sufficiently well defined for us to be sure of the assignments. The x and y features were broadened in a manner similar to that seen in Figure 3 for (**A**) (^{33}S).

Identification and structure of species (**A**). Since irradiation at very low temperatures gave primarily species (**A**), we are confident that this is the elusive radical cation, $S_8^{\cdot+}$. Species (**A′**) is most likely to be a conformational variation of the major species. If this assignment is accepted, then we can use the e.s.r. parameters to deduce some aspects of structure.

As can be seen from the Table, the g value variation for $S_8^{\cdot+}$ is greater than that for most other sulphur centres. (This does not include RS$^{\cdot}$ radicals for which $g_{max.}$ is largely controlled by the effective 'crystal-field' splitting induced by the medium, and hence is not a characteristic of the radical itself.) This result means that there is strong but not quite equal coupling to filled orbitals in the plane normal to the symmetry axis of the s.o.m.o. (semi-occupied molecular orbital). The fact that g_z is close to the free-spin value means that the symmetry axes of the 3p orbitals which comprise the s.o.m.o. are effectively the same.

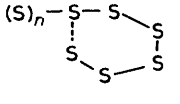
A clue to the electronic and geometric structure of the monocation comes from the known structure of the dication, S_8^{2+}.[3] As shown in Figure 4, on going from S_8 to S_8^{2+} two *trans* sulphur atoms (3 and 7 in Figure 4) move together, their separation falling from 468 to 286 pm in the dication. (There is also a conformational flip, as indicated in Figure 4.) As a working model, we suppose that electron addition to the dication will utilize the σ^* orbital, which will be quite strongly localized in $3p$ orbitals on S(3) and S(7). This model leads to the requirement that $g_x \sim g_y > 2.0023$ and that g_z is close to the free-spin value. (In fact, the large positive shift for g_x and g_y results in a small negative shift for g_z.) This model also requires small values for A_x and A_y and a large positive A_z. If the approximate experimental data for ^{33}S are processed in the usual way,[16] we get $A_{\text{iso}} \approx 9 \pm 3$ G and $2B \approx 19 \pm 3$ G, giving a $3p$ spin density of $33 \pm 5\%$ and the expected very low $3s$ character of *ca.* 1%. The remaining spin density (*ca.* 33%) is expected to be largely equally divided between the four adjacent sulphur atoms. These results are in qualitative accord with the proposed s.o.m.o.

The most probable alternative that would equally well accommodate the data is that the s.o.m.o. is largely confined to two adjacent sulphur atoms. The resulting distortion would bear no relationship to that observed for S_8^{2+} but, as discussed below, is worthy of consideration.

The minor species, (**A′**), seems to be closely related to species (**A**) and we suggest that, in the rigid lattice, there are alternative conformations with local barriers that are large enough to prevent interconversion.

Identification and structure of species (**B**). The results leave no doubt that species (**A**) changes irreversibly into (**B**) on annealing. The general form of the g-tensor components is the same as that for species (**A**) but the s.o.m.o. is more isolated from other filled levels and g_z is now clearly > 2.0023.

The data are close to those for radicals in rapidly frozen molten sulphur (Table) which are usually written as $(S)_n$–S–S, where n is large. Unfortunately, this representation for these polymer radicals has severe limitations both with respect to the e.s.r. data and chemical expectation. On the one hand, with no environmental effects, we expect Δg_x and Δg_y to be greater than the values observed, as can be judged by comparison with data for other sulphur-centred radicals.[17,18] Secondly, in view of the propensity for RS$^{\cdot}$ radicals to form 'σ^*' species[19] such as $RS \dot{-} SR^-$, we would expect this to occur in molten sulphur, giving centres such as (**I**). This bonding would tend to isolate the s.o.m.o. by raising the energy above those of other coupled bonding orbitals and hence give rise to smaller g shifts.



(**I**)

This is also a possible model for the species ($g_{\text{av.}} \approx 2.026$) formed in dilute oleum solutions. Because this species is formed at low SO_3 concentrations at which there is a tendency for sulphur to precipitate from the solution, it seemed reasonable to assign it to polymer radicals[1] and this has generally been accepted.

The e.s.r. data for species (**B**) are very similar and hence (**B**) could be a 'polymer' radical. However, we need to consider the evidence given by Gillespie and co-workers that the species in dilute oleum is actually $S_8^{\cdot+}$. We stress that our results for species (**A**), which we consider to be correctly described as $S_8^{\cdot+}$, do not rule out this possibility, since (**A**) could well be a 'hot' form of $S_8^{\cdot+}$ which on annealing can relax to its preferred, thermodynamically stable form.

The evidence put forward by Gillespie and Ummat[5] is strong. It hinges on equilibrium (1) which, they propose, leads to

$$2S_8^{\cdot+} \rightleftharpoons S_{16}^{2+} \tag{1}$$

dimerization on cooling. Not only do their optical measurements fit in well with this formulation but also the fact that crystals of the diamagnetic compound $S_{16}(AsF_6)_2$ contain appreciable concentrations of the paramagnetic centre assigned to $S_8^{\cdot+}$. Thus, although the paramagnetic species in concentrated oleum cannot be $S_4^{\cdot+}$ as claimed,[5] we feel that the evidence for $S_8^{\cdot+}$ in dilute oleum is strong.

In that case, we favour the idea that initial loss of an electron from S_8 at low temperatures in a constraining matrix such as $CFCl_3$ leads to 'hot' $S_8^{\cdot+}$ with little σ bonding between S(3) and S(7). On annealing, these atoms move together to give a three-electron bond. This will raise the energy of the σ^* oribital thus reducing Δg. Unfortunately, the e.s.r. signals lose intensity at the temperature of interconversion and little can be said about the ^{33}S hyperfine coupling except that it seems to be similar in form to that for species (**A**). However, as stressed above, the reduction in $\Delta g_{x,y}$ is in good accord with the onset of σ bonding. Also the shift in g_z to a value slightly greater than 2.0023 suggests that the $3p$ orbitals involved do not lie exactly along the z axis so that some mixing can occur.

We tentatively conclude that (**A**) and (**A′**) and 'hot' forms of $S_8^{\cdot+}$ with geometric structures close to that of S_8, whilst (**B**) is $S_8^{\cdot+}$ in its stable configuration more closely related to that of S_8^{2+}.

The Radical Cation of S_4N_4.—Although we are satisfied that the e.s.r. spectrum obtained from S_4N_4 in $CFCl_3$ is due to the cation, it is disappointingly uninformative, comprising a symmetrical singlet with $g_{\text{av.}} = 2.004$ and an overall width of *ca.* 45 G. If all four nitrogen nuclei contributed equally and their axes were parallel (z), then $A_{\parallel}(^{14}N) \leqslant 5$ G. With $A_{\perp} \approx 0$, we calculate a maximum $2p_z$ orbital population of *ca.* 10% on each nitrogen. Thus we can conclude that the s.o.m.o. is located more on sulphur than on nitrogen but, from the small g shift, this must be strongly isolated from other filled levels.

These results are in broad accord with predictions derivable from m.o. theory for S_4N_4 and $S_4N_4^{2+}$ cations.[20] If we consider electron addition to planar $S_4N_4^{2+}$ (D_{4h}), the s.o.m.o., before relaxation, is a $2e_g$ orbital having π^* character, which is well removed from the filled orbitals (Figure 1 and ref. 20). Population analysis for this virtual orbital gives 0.128 for nitrogen and 0.202 for sulphur. Thus, provided distortion towards the D_{2d} structure for S_4N_4 is not too great, this π^* orbital would appear to be quite acceptable in terms of the limited e.s.r. results.

However, starting from S_4N_4, electron loss is from the $2a_2$ orbital which is close to other filled orbitals and moves down to become the deeper $1b_{2u}$ level as the molecule approaches planarity. The latter is a non-bonding π orbital on nitrogen, which is clearly unsatisfactory. Thus, based on the limited evidence available, we favour the idea that the cation approaches the planar structure of the dication.

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