# Unstable Intermediates. Part CXXIII.[1] Electron Spin Resonance Spectra of Radicals in γ-Irradiated Sulphuryl Chloride: The $SO_2Cl_2^-$ Radical

By **K. V. S. Rao** and **M. C. R. Symons,*** Department of Chemistry, The University, Leicester LE1 7RH

The major species detected by e.s.r. spectroscopy in $\gamma$-irradiated sulphuryl chloride at 77 K is thought to be $SO_2Cl_2^-$. The $^{33}S$ and $^{35}Cl$ hyperfine components and the $g$-tensor components are in accord with this suggestion, and show that the radical anion is comparable with others in this class, having the unpaired electron primarily on sulphur (*ca.* 76%) with a very high 3*s*-character (*ca.* 29%), and on the two equivalent chlorine atoms with a high 3*p*-character (*ca.* 23%). The form of the molecular orbital involved is discussed.

THE radical $SeO_4^{3-}$ has $^{77}Se$ hyperfine coupling parameters[2] comparable with those for isostructural phosphorus radicals such as $PF_4$[3] and $PO_4^-$,[4] with the unpaired electron largely on the selenium atom (*ca.* 62%), in contrast with the isostructural ion $ClO_4^{2-}$, which has, apparently,[5] only a small spin-density on the chlorine atom (*ca.* 7·4%). In order to probe this unusual structural difference further, we have endeavoured to prepare the radical $SO_4^{3-}$ in yields sufficient to enable us to detect features from radicals containing $^{33}S$ in natural abundance. All our experiments, including the use of phosphate crystals doped with sulphate, which might have been expected to give good yields of $SO_4^{3-}$,[6] have so far failed. We therefore turned our attention to other radicals of this type with sulphur as the central atom, and found that sulphuryl chloride gave $SO_2Cl_2^-$ radicals in good yield. Meanwhile Kerr and Williams[7] published an excellent e.s.r. spectrum for this radical in irradiated sulphuryl chloride, and reported values for $A_z$($^{35}Cl$ and $^{37}Cl$) and $g_z$. However, they were not able to define the $^{35}Cl$ $A_x$ and $A_y$ values or the $g_x$ and $g_y$ values, although they suggested that $A_\perp$($^{35}Cl$) lies between 0 and 16 G.[7] They were also unable to detect $^{33}S$ satellite features. This work is of interest since[7] they suggest that the radical $SO_2Cl_2^-$ does not resemble the others of its kind, such as $PF_4$, but can best be thought of as a resonance hybrid between $SO_2^- + Cl_2$ on the one hand, and $SO_2 + Cl_2^-$ on the other, with $Cl_2^-$ as the major component.

Since this approach to the electronic structure of such radicals might shed further light on the anomalous data

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[1] Part CXXII, A. Begum and M. C. R. Symons, *J.C.S. Faraday II*, 1973, in the press.

[2] K. V. S. Rao and M. C. R. Symons, *J.C.S. Dalton*, 1972, 147.

[3] P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, Amsterdam, 1967.

[4] M. C. R. Symons, *J. Chem. Phys.*, 1970, **53**, 857.

[5] M. B. D. Bloom, R. S. Eachus, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1970, 1235.

[6] R. S. Eachus and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1968, 790.

[7] C. M. L. Kerr and F. Williams, *J. Amer. Chem. Soc.*, 1971, **93**, 2805.

assigned to $ClO_4^{2-}$,[5] we have extended this study to include the use of $Q$-band frequencies to aid in the determination of $g$-values, and very high gains and doses, to reveal features for radicals containing $^{33}S$ isotopes.

## EXPERIMENTAL

Sulphuryl chloride (Fisons) was frozen to 77 K by adding droplets directly to liquid nitrogen. The resulting beads were irradiated at 77 K in a Vickrad $^{60}Co$ $\gamma$-ray source having a nominal dose rate of 4 Mrad $h^{-1}$. For observation of $^{33}S$ satellites, the irradiation had to be carried out for *ca.* 12 h.

E.s.r. spectra were run at 77 K on a Varian E.3 spectrometer at $X$-band and at $Q$-band on a home-made spectrometer.[8]

The irradiated samples were bright green in colour.

## RESULTS AND DISCUSSION

A typical e.s.r. spectrum of the species thought to be $SO_2Cl_2^-$ is given in Figure 1, and at high gain and high modulation in Figure 2, whilst the resulting magnetic data are in Table 1, together with those for some isostructural radicals. Orbital populations, estimated by use of the best available atomic wavefunctions[9] in the usual way,[3] are in Table 2.

We agree with Kerr and Williams[7] that this species must be $SO_2Cl_2^-$. It contains two equivalent chlorine atoms and at least one sulphur atom, the latter having a large hyperfine coupling characteristic of such radicals. The only other structurally and chemically reasonable species, in our view, would be the pyramidal radical $SOCl_2^+$, isoelectronic with $POCl_2$, previously described.[10] However, the latter had a far smaller hyperfine coupling to two equivalent chlorine atoms (*ca.* 18 G).[10] Also we would have expected $SO_2Cl$ rather than $SOCl_2^+$ to be formed from $SO_2Cl_2$, under the action of $\gamma$-rays. Unfortunately, the results for radicals containing $^{33}S$ are equivocal in this regard, since it is not certain that the features we have labelled $\pm\frac{1}{2}$ in Figure 2 are correctly identified. Were these, in fact, the $\pm\frac{3}{2}$ features, then the resulting hyperfine coupling could at least conceivably arise from $SOCl_2^+$ radicals. We doubt this assignment because the less anisotropic $\pm\frac{1}{2}$ features would be too intense for $^{33}S$ satellites, as gauged from the outer features. On the other hand, if these are, as we suppose, the $\pm\frac{1}{2}$ features, then the more anisotropic $\pm\frac{3}{2}$ lines would have intensities below the noise level of our instrument. In fact, we have only been able to accommodate the very unusual form of the satellites

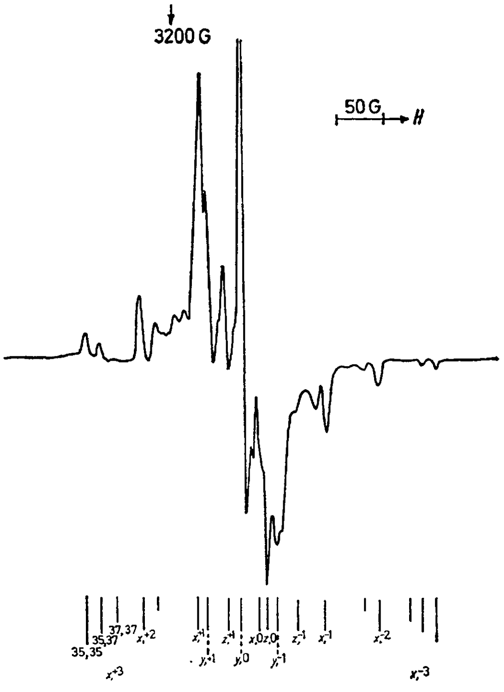

FIGURE 1 First derivative $X$-band e.s.r. spectrum for sulphuryl chloride after exposure to $^{60}Co$ $\gamma$-rays at 77 K. Except for the $\pm3(x)$ components, only the $^{35}Cl$ lines are indicated in the stick diagrams. Also, only the $+1$, 0, and $-1$ $y$ and $z$ components are indicated since these are clearly resolved

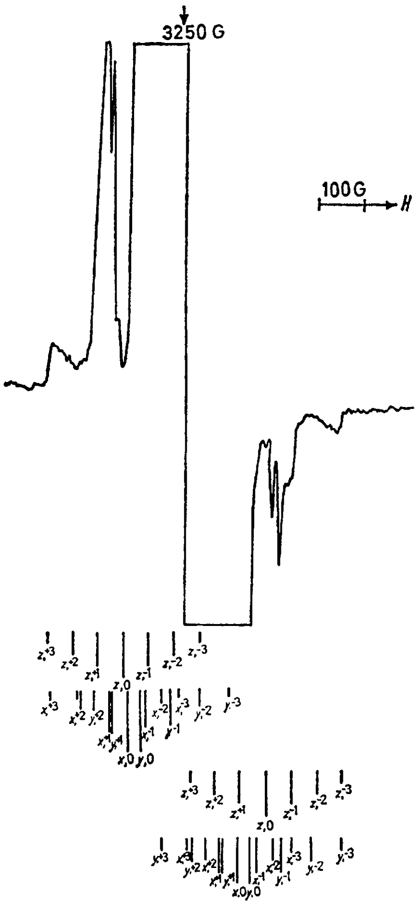

FIGURE 2 As above, but at very high gain, showing the $\pm\frac{1}{2}$ features from radicals containing $^{33}S$. The $\pm\frac{3}{2}$ lines were unfortunately lost in noise

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[8] J. A. Brivati, J. M. Gross, M. C. R. Symons, and D. J. A. Tinling, *J. Chem. Soc.*, 1965, 6504.

[9] Calculated from the data of C. Froese, *J. Chem. Phys.*, 1966, **45**, 1417.

[10] A. Begum and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 2065.

(Figure 2) by assigning the sharply rising initial features to the $^{35}$Cl (+3) $x$ and $z$ lines for the $+\frac{1}{2}$ $^{33}$S line, and to the $^{35}$Cl (−3) $x$ and $z$ lines for the $-\frac{1}{2}$ $^{33}$S line. These $x$ and $z$ lines fortuitously coincide, in contrast with the remainder, thus accounting for the unusual strength of the outermost lines. If this identification and these assignments are accepted, then various structural aspects can be considered.

*The* $^{35}$*Cl Tensor.*—Our results show far too great a complexity of lines in the central region of both $X$- and $Q$-band spectra for the axial symmetry previously assumed.[7] The best fit, indicated for $X$-band in Figure 1 but equally satisfactory at $Q$-band, was derived so as to ensure that the relative intensities of the well resolved $x$-features were properly reproduced. We have previously found that this is an important aid in the interpretation of powder spectra.[11] The $x$ features are regularly spaced indicating no large quadrupole effect. Some quadrupole effect is expected for the $y$ and $z$ lines, but the data derived from the 0 and ±1 components is thought to be satisfactory.

TABLE 1

E.s.r. data assigned to $SO_2Cl_2$ and to related radicals

| | Central atom hyperfine tensor components/G | | | $^{35}$Cl Hyperfine [a] tensor components/G | | | $g$-Tensor components | | |
|---|---|---|---|---|---|---|---|---|---|
| Radical | $x$ | $y$ | $z$ | $x$ | $y$ | $z$ | $x$ | | |
| $SO_2Cl_2^-$ | 51 | 51 | 62 [c] | 64 ± 1 | 35 ± 3 | 40 ± 3 [b] | 2·005 ± 0·001 | 2·017 ± 0·001 | 2·007 ± 0·002 |
| $PO_4^{4-}$ [d] | 1097·5 | 1110 | 1232 | | | | 2·0017 | 2·002 | 2·000 |
| $POCl_3^-$ [e] | | 1359 (iso) | | | 67 (iso) | | | 2·018 (av) | |
| $SeO_4^{3-}$ [f] | 1023 | 1032 | 1193 | | | | 2·031 | 2·002 | 2·000 |

[a] $^{37}$Cl components also detected for many features. [b] This is the experimental tensor; it has been modified as described in the text to give the parameters of Table 2. [c] If our assignment is correct, errors are *ca.* ±3 G. [d] Ref. 4. [e] Ref. 10. [f] Ref. 2.

TABLE 2

Some derived orbital populations (%) for $SO_2Cl_2^-$ and related radicals

| Radical | $a_s^2$ | $a_p^2$ | $a_s^2 + a_p^2$ | $a_p^2/a_s^2$ |
|---|---|---|---|---|
| $SO_2Cl_2^-$($^{33}$S) | 29 | 47 | 76 | 1·6 |
| ($^{35}$Cl) | 2·76 | 22·67 | 25·43 | 8·2 |
| $PO_4^{4-}$ [a] | 31 | 42 | 73 | 1·3 |
| $POCl_3$ [b] | 37 | | | |
| $SeO_4^{3-}$ [c] | 22 | 40 | 62 | 1·7 |

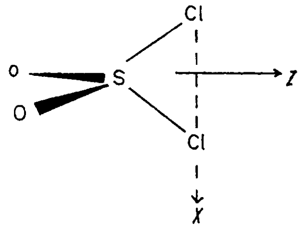
[a] Ref. 4. [b] Ref. 10. [c] Ref. 2.

In deriving the orbital populations in Table 2, we have assumed that all the hyperfine components for $^{35}$Cl and $^{33}$S are positive. Any other sign combination gave impossibly high spin-densities.

*Electronic Structure.*—The orbital populations for sulphur (Table 2) are in fair accord with those found previously for isostructural radicals.[2-4,10] Thus this radical is not anomalous, as previously supposed.[7] However, the results for chlorine, despite their uncertainty, can be taken as proof that there is a relatively high spin-density on these ligands, whilst that on the oxygen ligands must be close to zero. This accords well with expectation,[10] and with the results of theoretical calculations.[12]

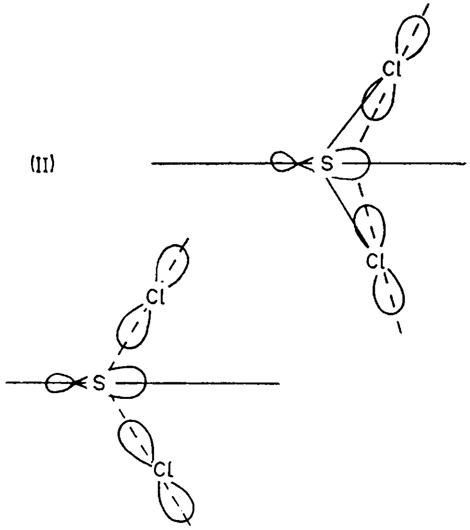
In deriving the spin-density on chlorine, we have assumed that the smallest value (35 G) is the correct perpendicular value, and that their axis ($y$) is normal to the Cl–S–Cl plane (I). Unless θ = 180°, $A_x$ and $A_z$, as measured for the powder spectra, will not be principal values since it is generally found that, for such radicals, powder spectra show strong features only when the two ligand atoms are magnetically equivalent [*i.e.*, for field along $x$ and $z$ in (I)]. If, however, we assume that each $^{35}$Cl tensor has axial symmetry, then the principal values can be calculated from the value for $A_y$. This gives (+69, +35, +35)G for the corrected tensor, which leads to the orbital populations given in Table 2. We estimate that a bond angle of θ = 135·5° would accord properly with this theory. This result depends markedly upon the assumption of axial symmetry, which is not required by the molecular symmetry, so should not be given great significance.

(I)



(II)

(III)



The most striking result for sulphur is that the parallel direction makes an angle of 90° with the apparent chlorine ' parallel ' direction. Thus, as expected, the sulphur

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[11] M. C. R. Symons and J. G. Wilkinson, *J.C.S. Faraday II*, 1972, 1265.

[12] J. Higuchi, *J. Chem. Phys.*, 1969, **50**, 1001.

part of the orbital concerned lies along the $C_{2v}$ axis, bisecting the $\angle$ClSCl angle.

The results clearly rule out the model suggested previously[7] which would require (i) that the orbital on sulphur be pure $3p$ in character, and (ii) that its major axis should be parallel with that for the chlorine hyperfine coupling. However, the data for the two chlorine atoms do confirm the contention that there are some similarities with $Cl_2^-$ radicals, and it might be helpful to think of the structure in terms of overlap between the chlorine $3p$ ($\sigma$) orbitals directed somewhat away from the S–Cl directions with the $3s$–$3p_z$ hybridised sulphur orbital, as depicted in (II). If this were correct, then, of course, our rough estimate of $\theta$ refers to the inter-orbital angle rather than to the bond angle. It is not clear, however, that descriptions of this type have any merit compared with a normal M.O. treatment, and we feel that a model such as that in (III) serves as a satisfactory initial pictorial representation. (It is clear that an earlier suggestion, that spin-polarisation of the $\sigma$-bonding electrons was responsible for the large ligand hyperfine coupling,[10] was in error since the magnitude of the present effect is too large for such a mechanism.)

The $g$-tensor components accord satisfactorily with this description. Thus $g_z > 2{\cdot}0023$ because of spin on chlorine, whilst $g_x > 2{\cdot}0023$ mainly because of spin on sulphur. Then the larger deviation for $g_y$ arises because spin on both sulphur and chlorine is involved in coupling with filled levels.

We conclude that the fairly detailed structural information derived for $SO_2Cl_2^-$ accords well with expectation for such radicals, but sheds no further light on the anomalous results for $ClO_4^{2-}$.

*Mechanism.*—As usual, we envisage an initial ionisation and electron-capture (1).

$$2SO_2Cl_2 \longrightarrow SO_2Cl_2^+ + SO_2Cl_2^- \qquad (1)$$

We have not been able to detect $SO_2Cl_2^+$ radicals, but, since the hyperfine coupling to chlorine is likely to be small,[10] the spectrum could well be concealed beneath the intense central features of $SO_2Cl_2^-$. If these radicals decompose, they might well give sulphur dioxide and $Cl_2^+$, but the chances of our detecting the latter by e.s.r. spectroscopy are small.[13]

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[2/1356 *Received*, 14*th June*, 1972]

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[13] R. S. Eachus, T. P. Sleight, and M. C. R. Symons, *Nature*, 1969, **222**, 769.