

## Formation and Electron Spin Resonance Spectra of Sulphuranyl Radicals of the Type $[\text{CF}_3\text{SSR}_2]\cdot$

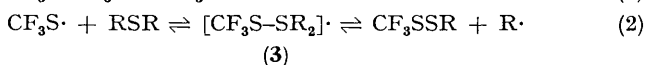
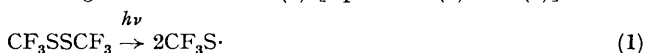
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**Summary** Photochemically generated trifluoromethylthiyl radicals add to dialkyl sulphides to produce sulphuranyl radicals,  $[\text{CF}_3\text{SSR}_2]\cdot$ , the e.s.r. spectra of which are reported.

RADIOLYSIS of organosulphur compounds gives rise to a variety of sulphur-centred radicals which have been studied in rigid matrices by e.s.r. spectroscopy. However, many of these radicals have not been identified with certainty and a number of assignments remain controversial. In particular,  $\gamma$ -radiolysis of thiols and disulphides gives rise to radicals, designated X by Symons,<sup>1</sup> with principal  $g$  values in the region of 2.058, 2.025, and 2.001 ( $g_{\text{average}}$  2.028) which were originally thought to be thiyl radicals,  $\text{RS}\cdot$ . Symons has argued convincingly that this assignment is incorrect and has suggested that species X are either dithiyl radicals ( $\text{RSS}\cdot$ ) (1) or, more likely, sulphuranyl radicals of the type  $[\text{RSSR}_2]\cdot$  (2; R = H or alkyl).<sup>1,2</sup> Other authors<sup>3,4</sup> identify X as the dithiyl radical, and conclude that (2) is not a viable alternative.<sup>3b</sup>

We now report that e.s.r. spectra, which we assign to sulphuranyl radicals related to (2), are observed during photochemical generation of trifluoromethylthiyl radicals in the presence of dialkyl sulphides in fluid solution. Thus, photolysis of a cyclopropane solution containing bis(trifluoromethyl) disulphide and a dialkyl sulphide affords spectra showing well resolved hyperfine splitting and which we assign to the radicals (3) [equations (1) and (2)].



Similar spectra were not detected when  $\text{CH}_3\text{SSCH}_3$  replaced the  $\text{CF}_3\text{SSCF}_3$ , and it appears that the high electronegativity of fluorine results in greater stability of (3), compared with  $[\text{CH}_3\text{SSR}_2]\cdot$ , towards fragmentation.† Attempts to detect radicals of the type (2) in aqueous solution by pulse radiolysis techniques have also failed.<sup>5</sup>

Photolysis of a solution containing dimethyl sulphide, trifluoromethyl iodide, and hexabutylditin (the last two reagents provide a source of  $\text{CF}_3\cdot$ ) gave rise to the spectrum of the trifluoromethyl radical but not to that of any sulphur-centred radical, showing that the signals ascribed to (3) cannot be due to  $\text{CF}_3\text{SR}_2\cdot$  which might be formed by addition of  $\text{CF}_3\cdot$  to  $\text{R}_2\text{S}$ .

The e.s.r. parameters of the sulphuranyl radicals (3) are given in the Table.

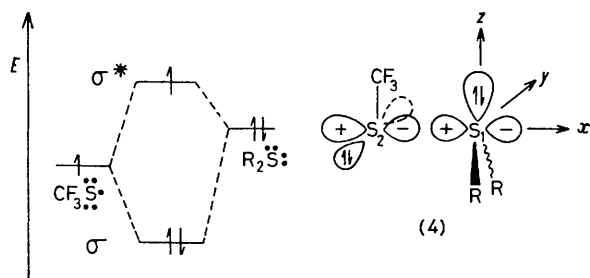
TABLE. E.s.r. parameters for radicals of the type  $[\text{CF}_3\text{SSR}_2]\cdot$  in cyclopropane

| R <sup>1</sup>         | R <sup>2</sup>         | $g$ -Factor<br>at 165 K <sup>a</sup> | Hyperfine splitting (G) at<br>185 K |                          |
|------------------------|------------------------|--------------------------------------|-------------------------------------|--------------------------|
|                        |                        |                                      | $a(3\text{F})$                      | $a(\text{H})^b$          |
| $\text{CH}_3$          | $\text{CH}_3$          | 2.0133                               | 9.2                                 | 4.1 (6)                  |
| $\text{CD}_3$          | $\text{CD}_3$          | 2.0133                               | 9.2                                 | <sup>c</sup>             |
| $\text{Me}_2\text{CH}$ | $\text{Me}_2\text{CH}$ | 2.0130                               | 9.8                                 | 7.1 (2) <sup>d</sup>     |
| $\text{MeCH}_2$        | $\text{Bu}^\dagger$    | 2.1030                               | 10.0                                | ca. 5.3 (2) <sup>e</sup> |
| $\text{Me}_2\text{CH}$ | $\text{Bu}^\dagger$    | 2.0134                               | 10.2                                | 3.8 (1)                  |

<sup>a</sup> The  $g$ -values increase with temperature; for example,  $g = 2.0140$  for  $[\text{CF}_3\text{SS}(\text{Bu}^\dagger)\text{Et}]\cdot$  at 254 K. <sup>b</sup> Number of nuclei coupling is shown in parentheses. <sup>c</sup> Deuterium splitting was not resolved. <sup>d</sup> The lines associated with  $M_I(2\text{H}) = 0$  broaden below 200 K. <sup>e</sup> The methylene protons are diastereotopic in the structure (4), however, magnetic non-equivalence was not detected (line-width ca. 2 G).

† Photolysis of dimethyl disulphide alone or in the presence of a dialkyl sulphide in cyclopropane solution gave rise to solid deposits and to an associated anisotropic e.s.r. signal ( $g$  values 2.054, 2.033, and 2.003) similar to those reported (ref. 1) for species X, but showing no hyperfine structure.

The spectrum of (3; R = CH<sub>3</sub>) exhibits coupling to six equivalent protons, even at low temperatures (146 K), consistent with a structure in which the unpaired electron resides in a  $\sigma^*$  S-S molecular orbital comprised mainly of S-3p orbitals.<sup>1,2</sup> The related cation radicals [R<sub>2</sub>SSR<sub>2</sub>]<sup>†</sup> and [R<sub>2</sub>SeSeR<sub>2</sub>]<sup>†</sup> are thought to have similar electronic structures.<sup>6</sup> The interaction of the unpaired electron in CF<sub>3</sub>S• with a lone pair of electrons on sulphur in R<sub>2</sub>S is illustrated in the Figure.†



FIGURE

The  $M_I(H_\beta) = 0$  lines in the spectrum of [CF<sub>3</sub>SSPr<sub>1</sub>]<sup>•</sup> broaden relative to the remaining lines at low temperatures (<200 K). This is not inconsistent with structure (4)

since it is reasonable that rotation about the Me<sub>2</sub>C(H)-S or S-S bonds, to exchange different environments of the  $\beta$ -protons, should become slow on the e.s.r. time scale at low temperatures.

The  $g$ -factors of (3) are similar to those of the related radical ions [RSSR]<sup>•-</sup> (ca. 2.0133)<sup>7</sup> and [R<sub>2</sub>SSR<sub>2</sub>]<sup>•+</sup> (ca. 2.0103),<sup>8</sup> but larger than those of the radicals [Me<sub>3</sub>SiOSR<sub>2</sub>]<sup>•-</sup> (ca. 2.0076).<sup>9</sup> The  $g$ -factors of (3) increase significantly with temperature, probably as a result of an increase in the average length of the weak S-S bond and the associated decrease in the energy of the  $\sigma^*$ -orbital. More efficient mixing, by spin-orbit coupling, of the half-filled level with orbitals occupied by non-bonding electron pairs on S<sub>1</sub> and/or S<sub>2</sub> would lead to increases in  $g$  along the  $y$ -axis and the direction of the F<sub>3</sub>C-S bond, respectively.

The e.s.r. spectra reported here appear to be the first that can be fairly definitely assigned to radicals of the general type (2). The  $g$ -factors of (3) are appreciably smaller than those of species X, but this does not rule out the possibility that X may also be a radical of type (2) since the replacement of the electronegative CF<sub>3</sub> group by an alkyl group might lead to a substantial increase in  $g$ -factor.

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† The conformation about the S-S bond in (4) is unknown.

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