An Electron Spin Resonance Study of Sulphuranyl Radicals of the Type $R_2S\dot{-}SX$ [X = CF_3 or R′C(O)]

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Photochemically generated trifluoromethyl- or acyl-thiyl radicals add to dialkyl sulphides to form the sulphuranyl radicals $R_2S^1\dot{-}S^2X$ [X = CF_3 or R′C(O)], the e.s.r. spectra of which have been detected. These adducts appear to be non-planar at the three-co-ordinate sulphur and the unpaired electron is thought to occupy an S–S σ^* orbital. The β-hydrogen splittings from the S^1-alkyl groups probably arise mainly through a hyperconjugative mechanism of spin transmission and appear to depend upon the spin density (ρ) in the S^1-$3p_\sigma$ orbital and the dihedral angle (θ) between the S^1CH_β and S^2S^1C planes according to the approximate equation $a(H_\beta) = 25.2\ \rho\cos^2\theta$ G. The *g* factors of the sulphuranyl radicals are markedly dependent upon temperature and the nature of R. At low temperatures, the adducts generally decay by a second-order process, presumably bimolecular self-reaction. Different behaviour is observed when R_2S = $\overline{CH_2(CH_2)_2S}$ or $(Et_2N)_2S$ and rapid ring-opening or S–N cleavage, respectively, occurs even at low temperatures. Temperature-dependent lineshape effects are evident in the spectra of $R_2S\dot{-}SX$, and several different processes appear to be responsible for these effects, including efficient spin–rotation relaxation, conformational interconversion, and the bimolecular sulphide exchange reaction $R_2S + R_2S\dot{-}SX \rightleftharpoons R_2S\dot{-}SX + R_2S$.

BIMOLECULAR homolytic substitution at divalent sulphur is a well established reaction.[1] For example, carbon-centred radicals attack dialkyl or diaryl disulphides to expel an organothiyl radical and give a monosulphide [equation (1)].[2]

$$R^1\cdot + R^2SSR^2 \longrightarrow R^1SR^2 + R^2S\cdot \qquad (1)$$

In principle, reaction (1) could be a concerted or a stepwise process, and in the latter mechanism an intermediate sulphuranyl radical adduct $[R^1(R^2)SSR^2]\cdot$ (1) would be involved. Attempts to detect species of the type (1) in solution have failed when R^1 and R^2 are simple alkyl groups.[3,4] In particular, no e.s.r. signal attributable to (1; $R^1 = R^2 = Me$) was detected when methyl radicals were generated in the presence of dimethyl disulphide or when methylthiyl radicals were generated in the presence of dimethyl sulphide [equation (2)].[4]

$$Me\cdot + MeSSMe \rightleftharpoons [Me_2SSMe]\cdot \rightleftharpoons Me_2S + MeS\cdot \qquad (2)$$

Radiolysis of thiols and disulphides in rigid matrices has been studied extensively by e.s.r. spectroscopy.[5,6] A number of sulphur-centred radical ions and neutral radicals have been detected at low temperatures, including one species with principal *g* values close to 2.058, 2.025, and 2.001 (g_{average} *ca.* 2.028) originally identified as RS·. This assignment has been challenged, and Symons[5] has proposed that the radicals are either perthiyl radicals (RSS·) or sulphuranyl radicals of the type (1). It was concluded that the latter assignment was more likely to be correct, unless both species have very similar properties.[5] Hadley and Gordy,[7] who have shown that these radicals contain two non-equivalent sulphur atoms, prefer the perthiyl structure.

We considered that sulphuranyl radicals of the type (1) would probably be more stable if electron-withdrawing substituents were attached to the two-co-ordinate sulphur atom. For such radicals the contributing structure (2b) would be more important, leading to an increase in the strength of the S–S bond.

$$\underset{(2a)}{R_2S\colon\ \cdot SX} \longleftrightarrow \underset{(2b)}{R_2\overset{+}{S}\cdot\ \colon\overset{-}{S}X}$$

Indeed, preliminary work[4,8] has shown that trifluoromethyl- and acyl-thiyl radicals add to dialkyl sulphides to give sulphuranyl adducts of the type [2; X = CF_3 or R′C(O)] that are readily detectable in fluid solution using e.s.r. spectroscopy. In this paper we report these results in full along with further work in this field.

RESULTS

Cyclopropane solutions containing the disulphide XSSX (*ca.* 0.7M) [X = CF_3, $Bu^tC(O)$, or EtC(O)] and a dialkyl sulphide (1—2M) were irradiated with high intensity u.v. light whilst the sample was in the cavity of the spectrometer.[9] E.s.r. signals, assigned to radicals with the structure (2) on the basis of the spectral parameters, were detected during continuous photolysis.

$$XSSX \xrightarrow{h\nu} 2XS\cdot \qquad (3)$$

$$XS\cdot + R_2S \longrightarrow R_2S\dot{-}SX \qquad (4)$$

(i) *Addition of Trifluoromethylthiyl Radicals*.—The e.s.r. parameters for (2; X = CF_3) and the approximate maximum temperatures at which the radicals could be detected are given in Table 1. The spectra of $Bu^t(Et)S\dot{-}SCF_3$ and $Bu^t(CD_3)S\dot{-}SCF_3$ are shown in Figures 1 and 2, respectively. The assignment to (2; X = CF_3) is strongly supported by the detection of the spectrum ascribed to $Bu^t(Me)S\dot{-}SCF_3$, along with that of the t-butyl radical, during photolysis of di-t-butyl ketone (as a source of $Bu^t\cdot$) in the presence of methyl trifluoromethyl disulphide * in cyclopropane between 140 and 200 K.

Photolysis of bis(trifluoromethyl) disulphide or the dialkyl sulphides (except Me_2S) alone did not give rise to e.s.r. spectra. Photolysis of Me_2S in cyclopropane afforded the e.s.r. signal of the methyl radical. If CF_3SSCF_3 had not been purified by preparative g.l.c., photolysis of the disulphide together with R_2S gave rise [in addition to (2; $X = CF_3$)] to an unidentified spectrum consisting of a binomial septet [a(6F?) 11.3 G, g 2.010 9 at 215 K]. After prolonged photolysis (especially above 200 K) of solutions containing diacyl disulphides (see below) and R_2S a secondary product radical (singlet, ΔB_{p-p} *ca.* 2 G) with a g factor identical to that of the septet was also detected.

TABLE 1

E.s.r. parameters for the sulphuranyl radicals $R^1R^2S\dot{-}SCF_3$ in cyclopropane solution

R^1	R^2	T/K	g Factor [a]	Hyperfine splittings (G) a(3F)	a(Hβ) [b]	Upper limit for detection [c] (K)
CH_3	CH_3	165	2 0133	9.2	4.1 (6)	215
CD_3	CD_3	165	2 0133	9.2		260
$MeCH_2$	$MeCH_2$	163	2 0131	9.2	5.75 (2) [d] 4.05 (2) [d]	210
Me_2CH	Me_2CH	185	2.0132	9.8	7.1 (2) [e]	240
Bu^t	Bu^t	165	2.0140	10.7 [f]		305
Bu^t	CH_3	167	2.0137	9.8 [g]	4.5 (3) [g]	240
Bu^t	CD_3	163	2.0137	9.8 [h]		280
Bu^t	$MeCH_2$	186	2 0135 [i]	10.0	5.3 (2) [j]	280
Bu^t	Me_2CH	196	2.0141	10. 0 [k]	3.5 (1) [l]	285
$CH_2CH_2CH_2$ [m]		156	2.0131	9.3	6.6 (4)	185
$CH_2[CH_2]_2CH_2$		155	2.0128	9.3	6.3 (4)	190

[a] The g factors all increase with temperature; for examples see Figure 4. [b] Number of nuclei coupling is shown in parentheses. [c] Approximate upper temperature limit for detection of the sulphuranyl radical. [d] These splittings are temperature dependent. At 148 K $a(2H_\beta)$ 6.2, $a(2H_{\beta'})$ 4.4 G. [e] The value of $a(2H_\beta)$ is temperature dependent, being 7.3 G at 163 K and 6.4 G at 223 K. The lines associated with $M_I(2H) = 0$ broaden below *ca.* 200 K. [f] The linewidth is at a minimum between 210 and 240 K. [g] Below 150 K an additional splitting was resolved. At 141 K the spectrum is a quartet (9.8 G) of approximately binomial quintets (3.9 G), peak-to-peak linewidth *ca.* 1.5 G. [h] The value of a(F) increases with temperature; at 251 K, $a(F) = 10.5$ G. At 141 K the spectrum contains an additional doublet (3.3 G). The linewidth increases above *ca.* 260 K. [i] The value given in the Table in ref. 4 should read 2.0133 at 165 K. [j] The lines associated with $M_I(2H_\beta) = 0$ are relatively broad showing that the methylene protons are inequivalent. A similar effect appears in 2,2,4-trimethylpentane solution, but in t-butylbenzene solution at 215 K the splittings [5.2 (1H), 6.3 (1H)] are resolved. The $M_1(2H_\beta) \neq 0$ lines broaden above *ca.* 220 K (see Figure 1). [k] The coupling increases with temperature, $a(F) = 10.6$ G at 280 K. [l] The coupling is within the linewidth (*ca.* 6 G) below 145 K. At higher temperatures the coupling decreases and is not resolved above *ca.* 245 K (linewidth is *ca.* 3.5 G at this temperature). [m] Spectrum recorded in 40% (v/v) toluene–cyclopropane.

Those e.s.r. spectra of (2; $X = CF_3$) which were detectable at relatively high temperatures (*ca.* 220 K) and show coupling to protons in the alkyl groups R [namely $Pr^i_2S\dot{-}SCF_3$, $Bu^t(Pr^i)S\dot{-}SCF_3$, and $Bu^t(Et)S\dot{-}SCF_3$], exhibited selective broadening of those lines corresponding to $M_I(H) \neq 0$

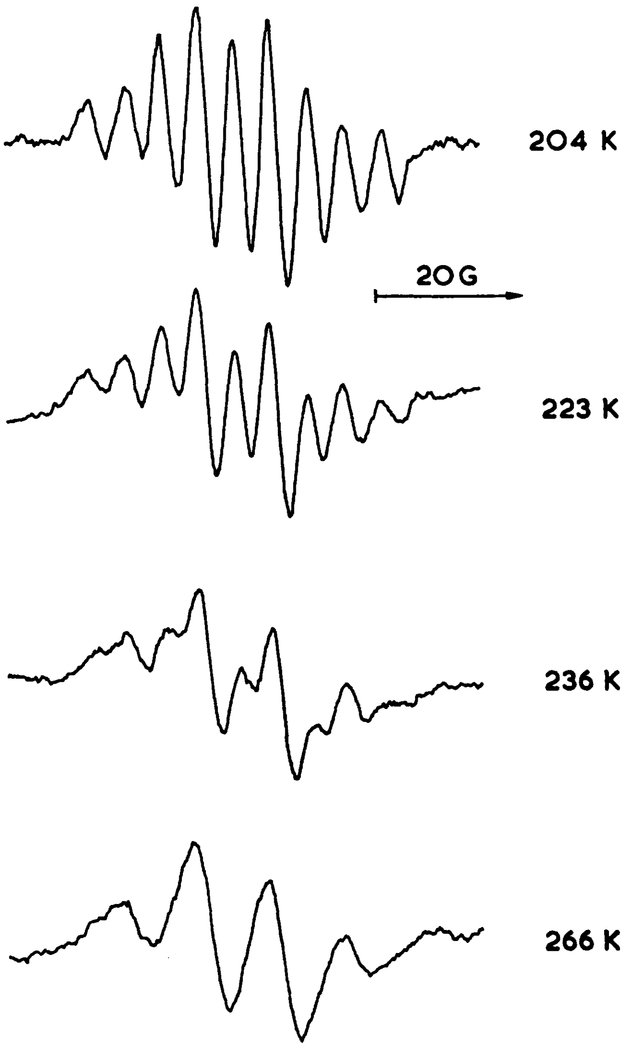

FIGURE 1 Temperature dependence of the e.s.r. spectrum of $Bu^t(Et)S\dot{-}SCF_3$ obtained during photolysis of Bu^tSEt (*ca.* 2M) and CF_3SSCF_3 (*ca.* 0.8M) in cyclopropane

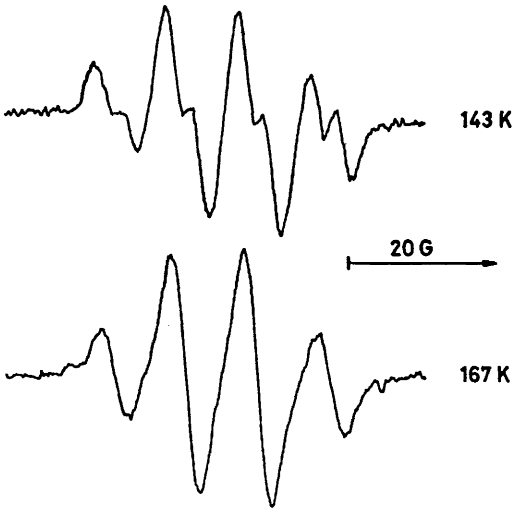

FIGURE 2 E.s.r. spectra of $Bu^t(CD_3)S\dot{-}SCF_3$ in cyclopropane, showing the extra features observed at very low temperatures

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* CH_3SSCF_3 was isolated by preparative g.l.c. after u.v. photolysis of a mixture of CH_3SSCH_3 and CF_3SSCF_3 (1 : 1 v/v) at room temperature. The mass spectrum of the mixed disulphide prepared in this way was as reported previously (N. R. Zack and J. M. Shreeve, *J. Fluorine Chem.*, 1975, **5**, 153).

(see Figure 1). For $Bu^t(Et)S\dot{-}SCF_3$ at a given temperature the extent of this line broadening increased with the concentration of the parent sulphide. For fixed concentrations of Bu^tSEt and CF_3SSCF_3, the degree of broadening at a given temperature (between 215 and 275 K) increased along the solvent series t-butylbenzene < cyclopropane < isooctane, indicating that changes in solvent viscosity are not responsible for the effect. The broadening is probably a result of the sulphide-exchange reaction (5), and an analogous exchange (6) has been identified previously for the related radical cations $(R_2S\dot{-}SR_2)^+$.[10,11]

$$R_2\overset{*}{S} + R_2S\dot{-}SCF_3 \longrightarrow R_2\overset{*}{S}\dot{-}SCF_3 + R_2S \qquad (5)$$

$$R_2\overset{*}{S} + (R_2S\dot{-}SR_2)^+ \longrightarrow (R_2\overset{*}{S}\dot{-}SR_2)^+ + R_2S \qquad (6)$$

The spectrum of the radical $Bu^t{}_2S\dot{-}SCF_3$ shows only fluorine splitting and may be detected at high temperatures (>250 K). In propane solvent, as the temperature was progressively increased above 230 K not only did the stationary-state radical concentration decrease but all the lines progressively broadened. The broadening was also apparent in n-octane solvent, but at significantly higher temperatures. At 238 K the peak–peak linewidths were 2.5 and 1.8 G in propane and octane, respectively, whilst at 297 K these values had increased to 6.1 and 4.0 G. In octane at 297 K the linewidth was independent of the concentration of di-t-butyl sulphide (0.4—1.2M). These observations, particularly the decrease in linewidth in the more viscous solvent, suggest that efficient spin–rotation relaxation is the major cause of line-broadening under these conditions.

Below *ca.* 200 K the lines corresponding to $M_I(2H) = 0$ broaden relative to the other lines in the spectrum of $Pr^i{}_2S\dot{-}SCF_3$. This lineshape effect is probably due to rotation about the $Me_2CH{-}S$ bonds becoming slow on the e.s.r. time scale (see Discussion section).

At very low temperature (<150 K) the spectra of $Bu^t(CH)_3S\dot{-}SCF_3$ and $Bu^t(CD_3)S\dot{-}SCF_3$ showed additional features. At 141 K the spectrum of the protio-radical appeared as a quartet [a(3F) *ca.* 9.8 G] of approximately binomial quintets (spacing *ca.* 3.9 G). This spectrum could result either from the presence of separate signals from approximately equal concentrations of two radicals with different g factors, or from one radical showing an extra splitting of *ca.* 3.3 G from an $I = 1/2$ nucleus. These extra features (doublet separation 3.3 G) are also clearly apparent in the spectrum of $Bu^t(CD_3)S\dot{-}SCF_3$ at 141 K (see Figure 2). Assuming that no species other than (2) is present, it is difficult to see how an extra splitting from an $I = 1/2$ nucleus could arise and therefore we suggest that two slowly interconverting conformations of this radical are present. The spectrum of the protio radical may be simulated if both conformations show a(3H) *ca.* 4.1 G and the g factors are 2.012 3 and 2.014 4.

Decay of (2; $X = CF_3$). Lifetimes of the sulphuranyl radicals (2; $X = CF_3$) do not increase appreciably with the bulk of the *S*-alkyl groups, and steric shielding of the three-co-ordinate sulphur is probably not an important factor governing logevity. At 170 K the radicals $(CH_3)S\dot{-}SCF_3$ and $(CD_3)_2S\dot{-}SCF_3$ decayed with second-order kinetics when photolysis was interrupted.[12,13] The rate constants were similar and close to the diffusion-controlled limit (*ca.* 4×10^9 l mol^{-1} s^{-1} for initial concentrations of *ca.* 1×10^{-7} mol l^{-1}), although the reproducibility was such that an isotope effect ($k_H/k_D < 4$) could have been obscured. At low temperatures the concentrations of $R_2S\dot{-}SCF_3$ (R = CH_3, CD_3, or Bu^t) were proportional to the square-root of the incident light intensity during continuous photolysis, and decay of $Bu^t{}_2S\dot{-}SCF_3$ at 170 K when the light was shuttered was also second order ($2k_t$ 2.0×10^9 l mol^{-1} s^{-1}, initial concentration 3.5×10^{-7} mol l^{-1}).

At higher temperatures (>275 K) decay of $Bu^t{}_2S\dot{-}SCF_3$ became first order [k *ca.* 8.8×10^2 s^{-1} at 295 K], although the e.s.r. spectrum of the t-butyl radical could not be observed. Confirmation that t-butyl radicals could have been detected in the presence of CF_3SSCF_3 was obtained by repeating the experiment with di-t-butyl ketone present as an additional reagent, when the spectra of $Bu^t{}_2S\dot{-}SCF_3$ and $Bu^t\cdot$ were detected simultaneously.

The adduct (3) of $CF_3S\cdot$ to thietan was detectable at very low temperatures, but above 195 K only a spectrum assigned to the alkyl radical (4) [$a(2H_\alpha)$ 22.2, $a(2H_\beta)$ 27.3 G, g 2.002 8 at 218 K] was observed [equation (8)].

$$\overline{CH_2CH_2CH_2S} + CF_3S\cdot \longrightarrow \underset{(3)}{\overline{CH_2CH_2CH_2S}\dot{-}SCF_3} \qquad (7)$$

$$(3) \longrightarrow \underset{(4)}{\cdot CH_2CH_2CH_2SSCF_3} \qquad (8)$$

No sulphuranyl radical could be detected when bis(trifluoromethyl) disulphide was photolysed in the presence of $(Et_2N)_2S$, but the spectrum of $Et_2N\cdot$ was observed and this radical was not detected when the sulphide was photolysed alone. Presumably the sulphuranyl adduct is very unstable with respect to α-scission [equation (9)].

$$(Et_2N)_2S\dot{-}SCF_3 \longrightarrow Et_2N\cdot + Et_2NSSCF_3 \qquad (9)$$

(ii) *Addition of Acylthiyl Radicals.*—Photolysis of dipivaloyl or dipropionyl disulphide in the presence of a series of dialkyl sulphides afforded spectra which are assigned to the sulphuranyl radicals [2; $X = Bu^tC(O)$ or $EtC(O)$]. Diacetyl disulphide was too insoluble in hydrocarbons to yield detectable spectra from [2; $X = MeC(O)$], but photolysis of thiolacetic acid in the presence of dimethyl sulphide did give rise to a signal which we ascribe to $Me_2S\dot{-}SC(O)Me$ [equation (10)].*

$$MeC(O)S\cdot + Me_2S \longrightarrow \underset{(5)}{Me_2S\dot{-}SC(O)Me} \qquad (10)$$

The spectra of the radicals (5) and $Me_2S\dot{-}SC(O)Et$ showed splittings from the *C*-alkyl groups consistent with the proposed structures. The spectroscopic parameters of [2; $X = MeC(O)$, $EtC(O)$, or $Bu^tC(O)$] are gathered in Table 2, and Figure 3 shows the spectrum of $Me_2S\dot{-}SC(O)Bu^t$.

A single-line spectrum (g 2.024 0, $\Delta B_{p\text{-}p}$ *ca.* 2 G) is also apparent in Figure 3 and similar signals were always detected when diacyl disulphides were photolysed with dialkyl sulphides or alone in cyclopropane. We tentatively assign these signals to acylperthiyl radicals (6), probably formed by competing direct photochemical cleavage of a C–S bond in the disulphide [equation (11)].

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* The source of acetylthiyl radicals is unclear. Direct photochemical cleavage of the S–H bond or abstraction of hydrogen from thiolacetic acid by a photogenerated radical [*e.g.* $Me\dot{C}O$ or $Me\cdot$] or photo-excited state are possibilities.

The *g* value of the acylperthiyl radical is close to that reported[14] for Bu^{t}SS· (*g* 2.025) in solution and for other species, which are probably perthiyl radicals (see Discussion section), detected after γ-irradiation of thiols and disulphides in the solid state.[5-7]

$$\underset{(6)}{\mathrm{RC(O)SSC(O)R}} \xrightarrow{h\nu} \mathrm{RC(O)SS\cdot} + \mathrm{R\dot{C}O} \quad (11)$$

The magnitude of $a(\mathrm{H}_\beta)$ * for $\mathrm{R_2S\dot{-}SX}$ and $\mathrm{Bu^t(R)S\dot{-}SX}$ [X = $\mathrm{CF_3}$ or R′C(O)] varies with the nature of R and in most cases, except when R = Me, with temperature (see Tables 1 and 2). The *g* factors of the sulphuranyl radicals [2; X = $\mathrm{CF_3}$ or R′C(O)] increase with temperature and generally, at a given temperature, with the bulk of the *S*-alkyl groups. The variation of *g* with the nature of R in $\mathrm{Bu^t(R)S\dot{-}SCF_3}$ and with temperature for these radicals and for $\mathrm{Bu^t(CD_3)S\dot{-}SC(O)Bu^t}$ and $\mathrm{Bu^t{}_2S\dot{-}SC(O)Bu^t}$ is shown in Figure 4.

TABLE 2

E.s.r. parameters for the sulphuranyl radicals $\mathrm{R^1R^2S\dot{-}SC(O)R^3}$ in cyclopropane solution

R¹	R²	R³	*T*/K	*g* Factor[a]	Hyperfine splitting[b] (G)	Upper limit for detection[c] (K)
$\mathrm{CH_3}$	$\mathrm{CH_3}$	$\mathrm{CH_3}$	159	2.0127	3.7 (6), 1.8 (3)	215
$\mathrm{CD_3}$	$\mathrm{CD_3}$	$\mathrm{CH_3}$	161	2.0127	*d*	220
$\mathrm{CH_3}$	$\mathrm{CH_3}$	$\mathrm{CH_2Me}$	160	2.0129	3.7 (6), 0.9 (2)	215
Bu^t	Bu^t	$\mathrm{CH_2Me}$	168	2.0145[e]	*f*	220
$\mathrm{CH_3}$	$\mathrm{CH_3}$	But	161	2.0140	3.6 (6)	190
$\mathrm{MeCH_2}$	$\mathrm{MeCH_2}$	Bu^t	159	2.0137	3.9 (4)	190
$\mathrm{Me_2CH}$	$\mathrm{Me_2CH}$	Bu^t	159	2.0143	5.8 (2)[g]	210
Bu^t	Bu^t	Bu^t	169	2.0159	*h*	215
Bu^t	$\mathrm{CH_3}$	Bu^t	157	2.0143	3.9 (3)	210
Bu^t	$\mathrm{CD_3}$	Bu^t	158	2.0143	*j*	245
Bu^t	$\mathrm{MeCH_2}$	Bu^t	163	2.0143	4.9 (2)	210
Bu^t	$\mathrm{Me_2CH}$	Bu^t	158	2.0146	4.5 (1)	210
$\mathrm{CH_2CH_2CH_2}$		Bu^t [k]	151	2.0135	5.9 (4)	185
$\mathrm{CH_2[CH_2]_2CH_2}$		Bu^t	158	2.0132	5.5 (4)	220

[a] The *g* factors increase with temperature, for example see Figure 4. [b] Number of β-protons coupling is shown in parentheses. [c] Approximate upper temperature limit for detection of the sulphuranyl radical. [d] No further splitting resolved; $\Delta B_{\mathrm{p-p}}$ *ca.* 3.5 G at 161 K. [e] *g* 2.0154 at 216 K. [f] No further splitting resolved; $\Delta B_{\mathrm{p-p}}$ *ca.* 3.0 G at 168 K. [g] The lines associated with $M_{\mathrm{I}}(2\mathrm{H}) = 0$ broadened below *ca.* 170 K. The coupling decreased with temperature, for example, at 189 K $a\,(2\mathrm{H}\beta) = 5.2$ G. [h] The linewidth passes through a minimum at *ca.* 180 K. At 208 K, $\Delta B_{\mathrm{p-p}}$ is *ca.* 6.5 G. [i] At 144 K the spectrum is an apparent binomial quintet with a line spacing of 3.5 G (see text). [j] Deuterium coupling not resolved, $\Delta B_{\mathrm{p-p}}$ *ca.* 3 G at 158 K. [k] Spectrum recorded in 40% (v/v) toluene–cyclopropane.

Similar lineshape effects to those described above for $\mathrm{Pr^i{}_2S\dot{-}SCF_3}$ were apparent in the spectrum of $\mathrm{Pr^i{}_2S\dot{-}SC(O)Bu^t}$, and at 140 K the central line of the triplet was barely detectable.

The spectrum of $\mathrm{Bu^t(Me)S\dot{-}SC(O)Bu^t}$, like that of $\mathrm{Bu^t(Me)S\dot{-}SCF_3}$ showed extra features at very low temperatures and appeared as an apparent binomial quintet (spacing 3.5 G) at 144 K. A single isomer of this radical could not show an extra proton splitting, and hence [*cf.* $\mathrm{Bu^t(Me)S\dot{-}SCF_3}$] we interpret the spectrum in terms of the presence of similar concentrations of two different conformations of the sulphuranyl radical which interconvert slowly on the e.s.r. time scale at low temperatures. The spectrum may be simulated if these conformations have different *g* factors (2.015 2 and 2.013 1) but similar values of *a*(3H) (*ca.* 3.6 G, $\Delta B_{\mathrm{p-p}}$ 2.0 G). The large linewidth ($\Delta B_{\mathrm{p-p}}$ *ca.* 5 G) would prevent observation of the two species in the spectrum of $\mathrm{Bu^t(CD_3)S\dot{-}SC(O)Bu^t}$ and no splitting was detected even at 140 K.

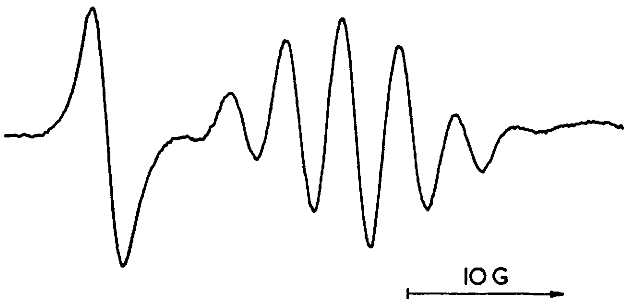

FIGURE 3 E.s.r. spectrum of $\mathrm{Me_2S\dot{-}SC(O)Bu^t}$ obtained during photolysis of $\mathrm{Me_2S}$ and $\mathrm{Bu^tC(O)SSC(O)Bu^t}$ in cyclopropane at 168 K. A singlet (*g* 2.0240) is also apparent at low field (see text)

The decay of [2; X = R′C(O)] was investigated in less detail than that of (2; X = $\mathrm{CF_3}$). Above *ca.* 180 K the spectrum of $\mathrm{Bu^t{}_2S\dot{-}SC(O)Bu^t}$ began to broaden and spin-rotation relaxation may be important in determining linewidth. At 200 K decay of this radical was first order, but

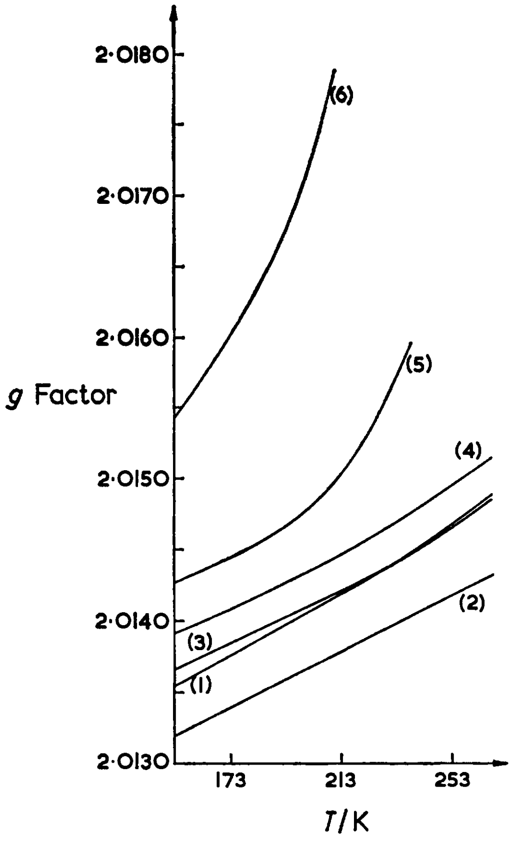

FIGURE 4 Temperature dependence of the *g* factors of $\mathrm{Bu^t(R)S\dot{-}SCF_3}$ [R = $\mathrm{CD_3}$ (1), Et (2), Pr^i (3), and Bu^t (4)] and $\mathrm{Bu^t(R)S\dot{-}SC(O)Bu^t}$ [R = $\mathrm{CD_3}$ (5) and Bu^t (6)]

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* The β-hydrogens of the group R are defined as those attached to the leading carbon atom of R.

at lower temperatures a second-order component was present.

Above about 180 K the adduct of $\mathrm{Bu^tC(O)S\cdot}$ to thietan underwent α-scission (ring-opening) to give the substituted alkyl radical (7) [$a(2\mathrm{H}_\alpha)$ 22.2, $a(2\mathrm{H}_\beta)$ 27.4, $a(2\mathrm{H}_\gamma)$ 0.5 G, g 2.002 8 at 190 K)] [equation (12)]. E.s.r. spectra of both radicals are shown in Figure 5.

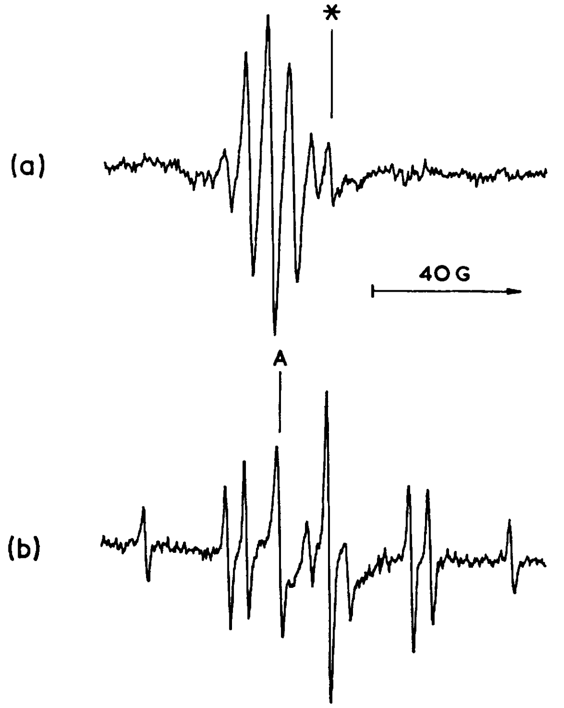
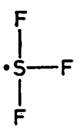


FIGURE 5 E.s.r. spectra obtained during photolysis of thietan and $\mathrm{Bu^tC(O)SSC(O)Bu^t}$ in cyclopropane: (a) at 162 K showing the spectrum of $\overline{\mathrm{CH_2(CH_2)_2S}}\dot{-}\mathrm{SC(O)Bu^t}$ and the central line of (7) marked with an asterisk, (b) at 226 K showing the spectrum of (7) and a singlet (A, g 2.0109) which appeared after prolonged photolysis

$$\overline{\mathrm{CH_2CH_2CH_2S}}\dot{-}\mathrm{SC(O)Bu^t} \longrightarrow \underset{(7)}{\mathrm{\cdot CH_2CH_2CH_2SSC(O)Bu^t}} \quad (12)$$

DISCUSSION

E.s.r. Spectra and Radical Structures.—The e.s.r. spectrum of the trifluorosulphuranyl radical has been detected in a single crystal of $\mathrm{F_3\overset{+}{S}\overset{-}{B}F_4}$ and interpreted in terms of a planar ' T-shaped ' structure (8) with the unpaired electron in an in-plane (σ) orbital and centred mainly on the sulphur atom.[15]



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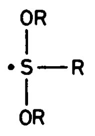

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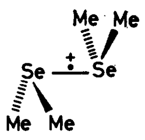
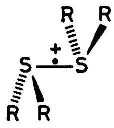


(10)

The sulphuranyl radicals $\mathrm{(CF_3O)_3S\cdot}$,[16] $\mathrm{(RO)_3S\cdot}$,[17] and $\mathrm{R\dot{S}(OR)_2}$ [18] probably adopt similar geometrical structures, with the group R in the last species in an ' equatorial ' site as shown in (9), although whether the unpaired electron in these three radicals is in a σ or π type orbital is not yet known with certainty. In contrast, an e.s.r. study [19] of the radical cation $\mathrm{(Me_2Se\dot{-}SeMe_2)^+}$ trapped in a single crystal of dimethyl selenide has shown that the non-planar structure (10) is adopted and it is very likely that the related cations $\mathrm{(R_2S\dot{-}SR_2)^+}$ have similar structures (11), with a non-planar arrangement of bonds to sulphur.[19] In both (10) and (11) the unpaired electron is essentially confined to an M–M σ* orbital (M = Se or S). It has been proposed that the singly occupied molecular orbital (SOMO) of the sulphuranyl radicals $\mathrm{R_2S\dot{-}Y}$ (Y = Cl,[3,20] Br,[3,20,21] I,[20] or $\mathrm{Me_3SiO}$ [11,22]) is also an S–Y σ* orbital and we have suggested that dialkyl(trimethylsiloxy)sulphuranyl radicals adopt the non-planar structure (12; Y = $\mathrm{Me_3SiO}$).

Related structural differences have been identified for phosphoranyl radicals. For example, $\mathrm{\dot{P}F_4}$ has the ' trigonal bipyramidal ' structure (13) (C_{2v} symmetry) with the unpaired electron located mainly on phosphorus and the apical fluorines in a totally symmetric orbital,[23] whilst $\mathrm{Ph_3\dot{P}Cl}$ has the σ* structure (14) [24] and the phosphine dimer cation radicals $\mathrm{[R_3P\dot{-}PR_3]^+}$ have σ* structures analogous to (10) and (11).[25]



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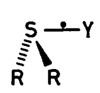

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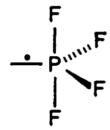

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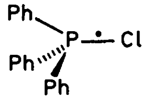

(14)

The *S*-methyl groups of $\mathrm{Me_2S\dot{-}SX}$ [X = $\mathrm{CF_3}$, RC(O)] remain magnetically equivalent even at 140 K, indicating that they are in identical environments. The methylene protons in $\mathrm{Bu^t(CH_3CH_2)S^1\dot{-}S^2CF_3}$ are non-equivalent even at relatively high temperatures * [as they are in $\mathrm{Bu^t(CH_3CH_2)S\dot{-}OSiMe_3}$ [11]]. If this radical is non-planar at $\mathrm{S^1}$, the methylene protons will be diastereotopic and non-equivalent for all rates of rotation about the $\mathrm{CH_2}$–$\mathrm{S^1}$ and $\mathrm{S^1}$–$\mathrm{S^2}$ bonds, whereas if it is planar at $\mathrm{S^1}$ then rotation about one or both of these bonds must be slow on the e.s.r. time scale. Other spectral effects that are best interpreted (see below) in terms of restriction of rotation about C–S and S–S bonds [for $\mathrm{Pr^i{}_2S\dot{-}SX}$ and $\mathrm{Bu^t(Me)S\dot{-}SX}$, respectively] become apparent only at much lower temperatures and hence we believe that the non-equivalence of the methylene protons in $\mathrm{Bu^t(Et)S\dot{-}SX}$ is a consequence of non-planarity at the three-coordinate sulphur. The non-equivalence of pairs of

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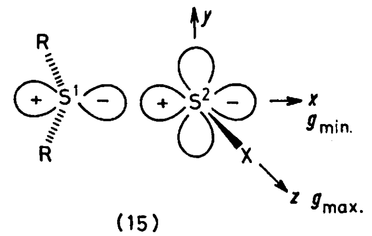
* Different splittings from these two protons were resolved at 215 K in t-butylbenzene solvent. Above this temperature, line broadening obscured the difference.

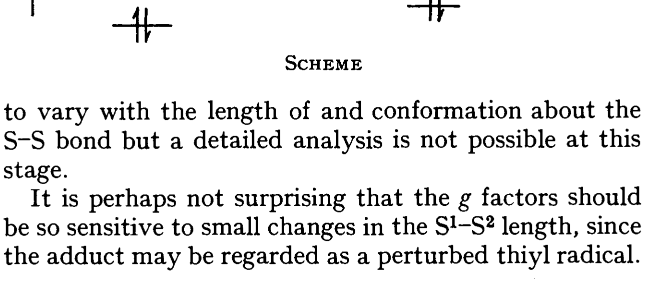
methylene protons in $Et_2S\dot{-}SCF_3$ is probably a result of such non-planarity rather than of the presence of non-equivalent ethyl groups.

We therefore propose that the sulphuranyl adducts [2; X = CF_3 or R'C(O)] possess structures of the type (15), with the unpaired electron in a σ* orbital comprised mainly of S^1 $3p_x$ and S^2 $3p_x$ orbitals (the conformation about the S^1–S^2 bond is unknown). The orbital interactions are indicated in the Scheme.

The *g* factors of [2; X = CF_3 or R'C(O)] are markedly dependent on temperature and the nature of the *S*-alkyl groups (see Figure 4). The isotropic *g* factors ($g_{iso.}$) of (2) are appreciably greater than 2.002 3 and the direction of $g_{max.}$ would be expected to fall along the *z*-axis [see (15)], because of mixing-in by spin–orbit coupling of excited states in which an electron has been promoted from filled π levels on S^1 and S^2, particularly the S^2 $3p_y$ orbital, to the σ* SOMO. The experimentally determined *g* factor ($g_{av.}$) will be a weighted average of $g_{iso.}$ for all the vibrational and conformational states of (2) present in solution at a given temperature. The temperature dependence of $g_{av.}$ probably results from changes in the populations of S–S vibrational levels and/or of conformational levels involving rotation about the S–S or C–S bonds. The S–S bond is weak and its length would be expected to vary significantly with the bulk of the substituents on S^1 and S^2 and the energy difference (Δ*E* in the Scheme) between the HOMO and SOMO will decrease as the bond length increases, leading to an increase in $g_{max.}$. The value of g_y would also be expected to vary with the length of and conformation about the S–S bond but a detailed analysis is not possible at this stage.

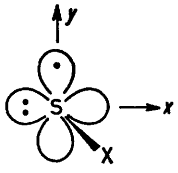


(15)

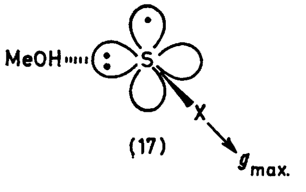


SCHEME

It is perhaps not surprising that the *g* factors should be so sensitive to small changes in the S^1–S^2 length, since the adduct may be regarded as a perturbed thiyl radical. Simple alkylthiyl radicals are only detectable by e.s.r. spectroscopy if medium effects are present which serve to break the degeneracy of the $3p_x$ and $3p_y$ orbitals [see (16)].



(16)

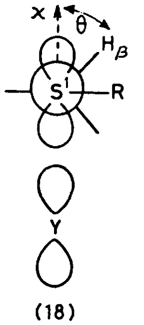


(17)

For example, attempts to detect RS· after γ-radiolysis of thiols in frozen aprotic solvents at 77 K failed, whilst in methanol glasses anisotropic e.s.r. spectra attributed to these species were detected.[5] It was proposed that hydrogen bonding to the alcohol [see (17)] was responsible for breaking the degeneracy of the *p*-orbitals in (16) and quenching the orbital angular momentum about the X–S direction. The extent of quenching and hence the *g* factors for simple thiyl radicals are thus expected to be medium dependent and this is confirmed by experiment.

In contrast with those of (2), the *g* factors of dialkyl(trimethylsiloxy)sulphuranyl radicals $R_2S\dot{-}OSiMe_3$ are essentially independent of temperature.[11] There are probably a number of reasons for this difference, including the smaller spin–orbit coupling constant of oxygen compared with that of sulphur, the lower spin density in the O $2p_x$ orbital in $R_2S\dot{-}OSiMe_3$ compared with that in the S^2 $3p_x$ orbital in (2) (see below), the smaller value of Δ*E* for (2) (see Scheme) compared with the analogous splitting for $R_2S\dot{-}OSiMe_3$, and the higher vibrational frequency of the $S\dot{-}O$ compared with the $S\dot{-}S$ bond.

The β-hydrogen coupling in a σ* radical of the type $R_2S\dot{-}Y$ should arise mainly through a hyperconjugative mechanism of spin transmission and depend upon the dihedral angle θ [see (18)] according to the approximate equation (13), in which ρ is the spin density in the S^1 $3p_x$ orbital.

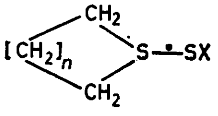


$$a(H_\beta) = \rho B\cos^2\theta \quad (13)$$

(18)

Assuming that there is free rotation about the Me–S bonds ($\cos^2\theta = 0.5$), *B* may be estimated from the value of $a(12H_\beta)$ (6.3 G) [11] for $[Me_2S\dot{-}SMe_2]^+$ in which ρ = 0.5. If this value of *B* (25.2 G) may be applied to the neutral radicals $Me_2S\dot{-}Y$ [Y = Me_3SiO,[11] CF_3S, or RC(O)S] we calculate S^1 $3p_x$ spin densities of 0.61 ($Y = Me_3SiO$), 0.33 (CF_3S), and 0.28 [$Bu^tC(O)S$]. The higher spin density on the three-co-ordinate sulphur when $Y = Me_3SiO$ compared with $Y = XS$ can be attributed to the anti-bonding character of the SOMO and the higher σ inductive effect of the oxygen ligand.

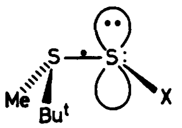
The changes in $a(H_\beta)$ with the nature of the *S*-alkyl groups in [2; $X = CF_3$ or $R'C(O)$] may be associated with the expected conformational preferences about the C–S bonds. The average dihedral angle in the radicals (19; $n = 1$ or 2) derived from thietan or thiolan will be close to 30° and hence $a(4H_\beta)$ would be predicted to be *ca.* 1.5 times $a(6H_\beta)$ in $Me_2S\dot{-}SX$, in good agreement with the observed values (see Tables 1 and 2).



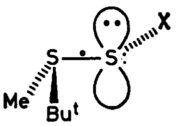
(19)

Models suggest that there is significant congestion at S^1 in the radicals [2; $R = Pr^i$, $X = CF_3$ or $R'C(O)$] and the high value of $a(H_\beta)$ indicates that the average value of θ must be relatively small. The two β-hydrogens are in fact non-equivalent although they exchange rapidly on the e.s.r. time scale at high temperatures. Similar effects have been noted [11] for $Pr^i{}_2S\dot{-}OSiMe_3$ and $[Pr^i{}_2S\dot{-}SPr^i{}_2]^+$ and attributed to interlocking of the two *S*-isopropyl groups and a ' cogwheel ' exchange of the two hydrogens [see structure (17) in ref. 11].

The extra features detected in the spectra of $Bu^t(CH_3)S\dot{-}SX$ at low temperatures appear to arise because exchange between two different conformations of this radical becomes slow on the e.s.r. time scale. We tentatively assign these conformations as (20a and b), although it is surprising that these should be of very similar stability, as is required to account for the appearance of the e.s.r. spectra.



(20a)



(20b)

γ-Radiolysis of alkanethiols and dialkyl disulphides in rigid matrices at low temperatures gives rise to radicals (species X) which contain two non-equivalent sulphur atoms and are characterised by *g* values of *ca.* 2.058, 2.025, and 2.001 ($g_{iso.}$ *ca.* 2.028).[5] E.s.r. spectroscopic data was thought more consistent with assignment of these species as perthiyl radicals (RSS·) without excluding the sulphuranyl structure $R_2S\dot{-}SR$, however, after consideration of chemical evidence the latter structure was favoured. The possibility that both these types of radical have similar spectroscopic parameters could not be excluded.[5]

The e.s.r. spectrum of the t-butylperthiyl radical has recently been reported [14] and *g* is 2.025, close to $g_{iso.}$ for the species X detected in the solid state. The *g* factors of $R_2S\dot{-}SCF_3$ and $R_2S\dot{-}SC(O)R'$ are generally close to 2.014 and decrease with decreasing temperature. This suggests that species X should be identified as a perthiyl radical. However, the S–S bond in $R_2S\dot{-}SX$ (X = alkyl) should be weaker and longer than when $X = CF_3$ or $R'C(O)$ and hence *g* for $R_2S\dot{-}SR$ might be significantly larger than 2.014. Species X, identified as a perthiyl radical, has also been detected after u.v. irradiation of dialkyl sulphides or disulphides in 3-methylpentane glasses.[26]

Decay of [2; $X = CF_3$ *or* $R'C(O)$].—Alkyl radicals readily displace alkylthiyl radicals from dialkyl disulphides, and presumably the adduct $R_2S\dot{-}SR$ is an intermediate in this reaction (see Introduction). The sulphuranyl radicals [2; $X = CF_3$ or $R'C(O)$] are more stable to S–S cleavage, but addition of $CF_3S\cdot$ or $R'C(O)S\cdot$ to R_2S is probably also fairly readily reversible [equation (14)].

$$R_2S^1\dot{-}S^2X \overset{K_{14}}{\rightleftharpoons} R_2S + \cdot SX \qquad (14)$$

This reversibility is probably partially responsible for the loss of the e.s.r. spectra of (2) at high temperature because of an increase in K_{14} and the existence of other possible reactions open to XS·. An increase in the rate of exchange between (2) and XS· (undetected) was considered as a possible cause of the increase in linewidth observed for $Bu^t{}_2S\dot{-}SX$ [$X = CF_3$ or $R'C(O)$] at higher temperatures. However, at a fixed temperature the linewidth for $Bu^t{}_2S\dot{-}SCF_3$ was independent of the concentration of $Bu^t{}_2S$, but decreased with increasing solvent viscosity. This behaviour would not be expected if dissociation is the major cause of line-broadening, but it is that expected if spin-rotation relaxation [27] is predominant in determining linewidth. This mechanism of relaxation can become important for radicals which exhibit large isotropic shifts in *g* factor and the contribution to the linewidth is proportional to $(g_{iso.} - 2.002\,3)^2 T/a^3\eta$, where *a* is the diameter of the radical and η is the viscosity of the solution.[27]

If the R–S bond in (2) is relatively weak the sulphuranyl radical breaks down by cleavage of this bond. For example, [21; $Y = CF_3S$ or $R'C(O)S$] decays by opening of the strained four-membered ring [equation (15)], whilst the analogous adducts with five-membered rings were not observed to fragment in this manner.

$$\underset{(21)}{\overline{CH_2CH_2CH_2S}\dot{-}Y} \longrightarrow \underset{(22)}{\cdot CH_2CH_2CH_2SY} \qquad (15)$$

Thietan reacts with alkoxyl and trimethylsiloxyl radicals to yield (22; $Y = RO$ or Me_3SiO) and presumably an intermediate of the type (21) is involved.[28]

Although decay of $Bu^t{}_2S\dot{-}SCF_3$ is kinetically first order at high temperatures (>275 K), the spectrum of the t-butyl radical was not detected and hence S^1–C cleavage is not occurring rapidly under these conditions. It seems likely that the major decay route involves S–S cleavage [equation (14)] to give Bu^t_2S and $CF_3S\cdot$. At higher temperatures, sulphide, thiyl radical, and (2; $R = Bu^t$, $X = CF_3$) could possibly be in quasi-equilibrium and reactions other than addition to Bu^t_2S (*e.g.* hydrogen abstraction) are probably open to $CF_3S\cdot$. However, at lower temperatures (<250 K) decay is second-order and bimolecular self-reaction is probably involved, although the products are unknown.

EXPERIMENTAL

The techniques employed for the detection of e.s.r. spectra during continuous irradiation of samples in the cavity of the spectrometer have been described previously.[13,29] The kinetics of radical removal were measured by computer-averaging of a large number of signal decay curves produced by positioning a rotating sectored disc in the light path.[12,13] *g* Factors were determined by measurement of the microwave frequency and the magnetic field at the centre of resonance,[11] using the pyrene radical-anion (Na^+ counter-ion) in tetrahydrofuran (*g* 2.002 71) as standard.[30] Temperatures are generally accurate to ±2 K; temperature differences in Figure 4 are ±1 K.

Materials.—The perfluorodimethyl disulphide was a commercial product (P.C.R.) which was purified by preparative g.l.c. (20% MS 200–200 silicone oil on 40—60 mesh Supasorb at 25 °C) before use. Thiolacetic acid and the dialkyl sulphides were redistilled commercial products or were prepared according to literature methods,[11,31] as was bis(diethylamino) sulphide.[32]

The acyl disulphides RC(O)SSC(O)R ($R = Me, Et, Bu^t$) were prepared according to the method of Gladysz [33] by the reaction of the acyl chloride with Li_2S_2 generated *in situ*. *Dipropionyl disulphide* was also prepared by oxidation of EtC(O)SH with $Pb(OAc)_4$ in benzene as described for diacetyl disulphide,[34] and, after distillation (b.p. 63—65 °C at 0.04 Torr), was purified by h.p.l.c. [on silica gel (Partisil 10) with pentane–CH_2Cl_2 (3 : 1 v/v) eluant] (Found: C, 40.5; H, 5.8; S, 35.6. $C_6H_{10}O_2S_2$ requires C, 40.4; H, 5.7; S, 36.0%). *Dipivaloyl disulphide* was purified by distillation, b.p. 75 °C at 0.03 Torr (Found: C, 51.1; H, 7.7; S, 27.6. $C_{10}H_{18}O_2S_2$ requires C, 51.2; H, 7.7; S, 27.4%).

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