An Electron Spin Resonance Study of the Reactions of Oxidising Radicals with Dialkyl Sulphides. Radical Cations derived from Anodic Oxidation of R_2S, $(R_2N)_2S$, and $(R_2N)_2SO$

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Constant current electrochemical oxidation of R_2S, $(R_2N)_2S$, and $(R_2N)_2SO$ gives rise to radical cations which have been detected by e.s.r. spectroscopy. Dialkyl sulphides, except di-t-butyl sulphide which afforded the spectrum of $Bu^t{}_2S^{+\cdot}$, gave the dimer cations $(R_2SSR_2)^{+\cdot}$. Bis(dialkylamino) sulphides or sulphoxides gave monomer cations in which a large fraction of the spin density is on nitrogen. The g factors of $(R_2SSR_2)^{+\cdot}$ increase with the bulk of R, and the g factors of both $(R_2SSR_2)^{+\cdot}$ and $Bu^t{}_2S^{+\cdot}$ are dependent on the temperature, the solvent, and the counter-anion. The sulphide cation radicals have also been generated by photolysis of solutions containing R_2S, Bu^tOOBu^t, and CF_3CO_2H, and formation probably involves oxidation of the sulphide by $Bu^t\overset{\cdot +}{O}H$. The neutral radicals $Bu^tO\cdot$ and $Me_3SiO\cdot$ react with dialkyl sulphides by abstraction of hydrogen from an α-C–H group or by competing addition to sulphur to form a sulphuranyl radical. The e.s.r. spectra of the adducts $R_2\dot{S}OSiMe_3$ have been detected and these radicals appear to be non-planar at sulphur with the unpaired electron probably confined to an S–O σ* orbital.

THE reactions of oxidising radicals with dialkyl sulphides generate both carbon- and sulphur-centred radicals. Pulse radiolytic studies of dialkyl sulphides in aqueous solution have shown that hydroxyl radicals add rapidly [k_i (R = Me) 1.9×10^{10} l mol^{-1} s^{-1} at room temperature] to give sulphuranyl radicals (1), the subsequent transformations of which afford both the dimer cation (2) and the α-alkylthioalkyl radical (3).[1,2]

$$HO\cdot + R_2S \xrightarrow{k_i} \underset{(1)}{R_2\dot{S}OH} \qquad (i)$$

$$R_2\dot{S}OH + R_2S \longrightarrow [(R_2S)_2OH]\cdot \qquad (ii)$$

$$[(R_2S)_2OH]\cdot \longrightarrow \underset{(2)}{(R_2SSR_2)^{+\cdot}} + HO^- \qquad (iii)$$

$$R_2\dot{S}OH \longrightarrow \underset{(3)}{RS\dot{R}(-H)} + H_2O \qquad (iv)$$

$$Bu^tO\cdot + R_2S \longrightarrow Bu^tOH + RS\dot{R}(-H) \qquad (v)$$

$$Bu^tO\cdot + R_2S \longrightarrow R\cdot + RSOBu^t \qquad (vi)$$

$$Bu^tO\cdot + RSOBu^t \longrightarrow R\dot{S}(OBu^t)_2 \qquad (vii)$$

$$Bu^tO\cdot + \overline{CH_2(CH_2)_2S} \longrightarrow Bu^tOSCH_2CH_2CH_2\cdot \qquad (viii)$$

E.s.r. spectra of (2) have been observed in aqueous solution[3] and in the solid state.[4] α-Alkylthioalkyl radicals (3) have been detected by e.s.r. spectroscopy during the reaction of photochemically-generated t-butoxyl radicals with dialkyl sulphides in hydrocarbon solvents.[5-7] Although an intermediate sulphuranyl radical $R_2\dot{S}OBu^t$ has never been detected, secondary product radicals $R\dot{S}(OBu^t)_2$ have been.[8] It appears that formation of $RSOBu^t$ occurs to some extent, probably by alkoxydealkylation of the sulphide [equation (vi)],[8] and with thietan this is the only reaction detected by e.s.r. spectroscopy [equation (viii)].[9]

In a preliminary communication[10] we have reported that e.s.r. spectra of both (3) and the sulphuranyl adduct $R_2\dot{S}OSiMe_3$ (4) are observed simultaneously during the reaction of trimethylsiloxyl radicals with R_2S. However, it was not clear whether formation of (3) and (4) were independent processes or whether (3) was formed by loss of trimethylsilanol from (4) [compare equation (iv)].

The purpose of this work was to investigate the reactions of oxidising radicals with dialkyl sulphides and related organosulphur compounds in non-aqueous media, and to compare the results with those obtained by electrochemical oxidation of the sulphur compounds in the presence of non-nucleophilic counter ions.

RESULTS

(i) *Radical Cations*.—A series of dialkyl sulphides were oxidised using constant-current electrolysis in nitrile or dichloromethane solution with various carrier electrolytes. The anode compartment of the cell was positioned in the cavity of the e.s.r. spectrometer and spectra were recorded during electrolysis.[11] Radical cations were also generated by chemical oxidation techniques. Thus, photolysis of cyclopropane or dichloromethane solutions containing the sulphur compound, di-t-butyl peroxide, and trifluoroacetic acid gave rise to e.s.r. spectra similar to those obtained electrochemically.

All the sulphides, except di-t-butyl sulphide, afforded spectra expected[3] for the dimer cations (2), and the signals from $(Bu^tSEt)_2{}^{+\cdot}$ and $(Bu^tSPr^i)_2{}^{+\cdot}$ were sufficiently intense for the species containing one ^{33}S nucleus (I 3/2) to be detected without isotopic enrichment. The total intensity of the ^{33}S satellites for $(Bu^tSEt)_2{}^{+\cdot}$ was *ca.* 1.3% of that for the radical cation containing only $^{32/34}S$, confirming the presence of two sulphur atoms (the natural abundance of ^{33}S is 0.74%). ^{33}S Satellites were also detected for the product of oxidation of di-t-butyl sulphide, but here the total intensity (0.8%) showed that only one sulphur atom was present in this species, which we identify as the monomer cation radical $Bu^t{}_2S^{+\cdot}$. The dimer cations are formed by union of oxidised and unoxidised sulphide molecules [equations (ix) and (x)].[1-4]

$$R_2S \xrightarrow{-e} R_2S^{+\cdot} \qquad (ix)$$

$$R_2S^{+\cdot} + R_2S \rightleftharpoons (R_2SSR_2)^{+\cdot} \qquad (x)$$

Measured isotopic ratios were extrapolated to zero microwave power to avoid the effects of differential saturation of

TABLE 1

E.s.r. parameters for radical cations derived from R_2S, $(R_2N)_2S$, and $(R_2N)_2SO$

Radical cation	Method of generation [a]	Solvent [b]	Temp. (K)	g Factor	Hyperfine splittings (G)
$(Me_2S)_2^{+\bullet}$	P	C	158 [c]	2.0102	6.3 (12 H)
$(Et_2S)_2^{+\bullet}$	P	C	165	2.0101	6.3 (8 H)
$[CH_2(CH_2)_3S]_2^{+\bullet}$	P	C	178	2.0100	8.6 (8 H)
$(Pr^i{}_2S)_2^{+\bullet}$	P, E	C	273	2.0112	8.9 (4 H) [d]
$(Bu^tSMe)_2^{+\bullet}$	P	C	240	2.0107	8.2 (6 H) [e]
$(Bu^tSEt)_2^{+\bullet}$	P, E	C [f]	220	2.0108	9.8 (4 H),[g] 32.1 (1 S)
$(Bu^tSPr^i)_2^{+\bullet}$	P, E	C [f]	220	2.0122	6.0 (2 H),[h] 31.2 (1 S)
$Bu^t{}_2S^{+\bullet}$	P, E [i]	D	200	2.0130	32.5 (1 S)
$(Me_2N)_2S^{+\bullet}$	P, E [i]	D	218	2.0053 [j]	7.6 (2 N), 7.6 (12 H)
$(Et_2N)_2S^{+\bullet}$	E	D	208	2.0058	7.3 (2 N), 5.0 (8 H)
$[CH_2(CH_2)_3N]_2S^{+\bullet}$	E	B	253	2.0055	7.6 (2 N), 10.3 (8 H)
$(Me_2N)_2\overset{\bullet +}{S}O$	E	D [k]	268	2.0037	13.0 (2 N), 12.4 (12 H)

[a] P = Photochemical method, $CF_3CO_2^-$ counter-ion, E = electrochemical oxidation, BF_4^- counter-ion. When both P and E methods are given, solvent and e.s.r. parameters refer to P unless otherwise stated. [b] C = cyclopropane, D = dichloromethane, B = n-butyronitrile. [c] Exchange broadened above 180 K (see text). [d] Becomes a triplet of triplets [a(2 H) 13.8, a(2 H) 5.8 G at 169 K] below *ca.* 260 K. [e] Linewidth goes through a minimum at *ca.* 210 K. Spectrum of $(Bu^tSCD_3)^{+\bullet}$ was a single line of width *ca.* 6 G. [f] Similar spectra obtained in dichloromethane solvent. [g] Varies from 10.7 G (164 K) to 9.2 G (255 K). [h] Appears as a single line (width *ca.* 6 G) below 195 K. [i] Solvent and e.s.r. parameters refer to electrochemical generation. [j] Varies between 2.0052 (188 K) and 2.0055 (295 K). [k] Similar spectrum obtained in n-butyronitrile solvent.

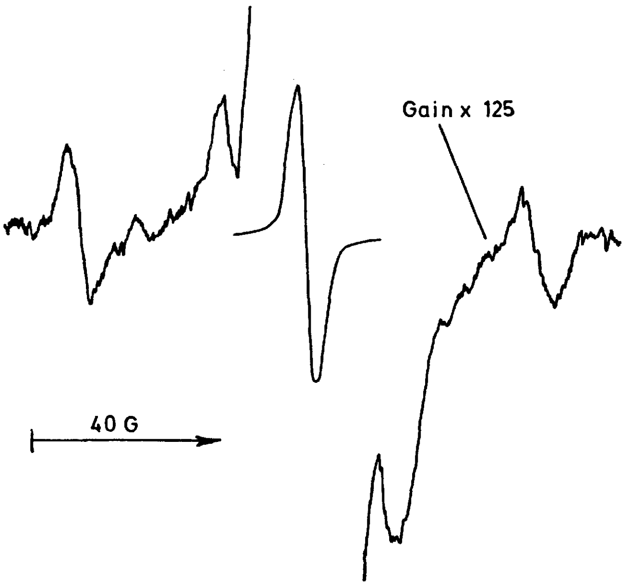


FIGURE 1 E.s.r. spectrum of $Bu^t{}_2S^{+\bullet}$ showing the ^{33}S satellites, obtained by electrolytic oxidation of a solution of $Bu^t{}_2S$ in CH_2Cl_2 containing $Bu^n{}_4NBF_4$. The central signal is partially saturated (nominal power 50 mW)

the main peaks and satellites. Such differential saturation was particularly apparent for $Bu^t{}_2S^{+\bullet}$ (see Figure 1).

Anodic oxidation of $(R_2N)_2S$ and of $(Me_2N)_2SO$ gave rise to e.s.r. spectra which we interpret in terms of coupling to two equivalent nitrogen nuclei and to the α-protons of the

$$(R_2N)_2SX \xrightarrow{-e} \underset{(5)}{[(R_2N)_2SX]^{\dot{+}}} \qquad \text{(xi)}$$

N-alkyl groups. These spectra are ascribed to the radical cation (5; X = lone pair or O).

The shorter-lived radical cations, *e.g.* $(Me_2S)_2^{+\bullet}$, could be generated in detectable concentrations only by using the photochemical method. The e.s.r. parameters are gathered in Table 1.

The linewidth of the spectrum of $(Me_2S)_2^{+\bullet}$ increased with increasing concentration of the parent sulphide.[3] For a given sulphide concentration the linewidth for (2) varied with temperature in different ways depending on the size of the *S*-alkyl groups. When these were small [*e.g.* in $(Me_2S)_2^{+\bullet}$], the linewidth increased with increasing temperature; when bulky alkyl groups were present [*e.g.* in $(Bu^tSPr^i)_2^{+\bullet}$], the linewidth decreased with increasing temperature, whilst for groups of intermediate size [*e.g.* in $(Bu^tSMe)_2^{+\bullet}$] it passed through a minimum as the temperature was increased. The exchange process[3] (xii) will be more rapid at higher temperatures and may lead to an increase in linewidth superimposed upon the normal decrease in linewidth at higher temperatures, because of more rapid tumbling of the radical cation. The rate of exchange appears to decrease as a result of steric effects in the order Me_2S, $CH_2[CH_2]_3S$ > Et_2S > Bu^tSMe > Bu^tSEt, Bu^tSPr^i.

In order to probe the mechanism for generation of (2) by the photochemical method, deuterium labelling studies were carried out. Photolysis of a solution containing Bu^tSCH_3, CF_3CO_2D, and Bu^tOOBu^t gave rise only to the spectrum of $(Bu^tSCH_3)_2^{+\bullet}$ and no incorporation of deuterium into the methyl groups was detected. Similarly, Bu^tSCD_3, CF_3CO_2H, and Bu^tOOBu^t afforded only the spectrum of $(Bu^tSCD_3)_2^{+\bullet}$.

$$R_2S^* + (R_2SSR_2)^{\dot{+}} \rightleftharpoons (R_2S^*SR_2)^{\dot{+}} + R_2S \qquad \text{(xii)}$$

At *ca.* 180 K, the spectrum of $(Pr^i{}_2S)_2^{+\bullet}$ showed splittings from two pairs of equivalent protons, whilst above 260 K splitting from four apparently equivalent protons was detected. At intermediate temperatures differential line-broadening was observed such that only lines 1, 5, and 9 of the low-temperature spectrum remained sharp.

The g factors of the dimer cations (2) are dependent upon temperature, solvent, counter-ion, and size of the alkyl substituents. For a given medium and temperature, the g factor increases with the bulk of the *S*-alkyl groups. The g factors of $Bu^t{}_2S^{+\bullet}$ and $(Bu^tSEt)_2^{+\bullet}$ were measured as a function of temperature for different combinations of solvent

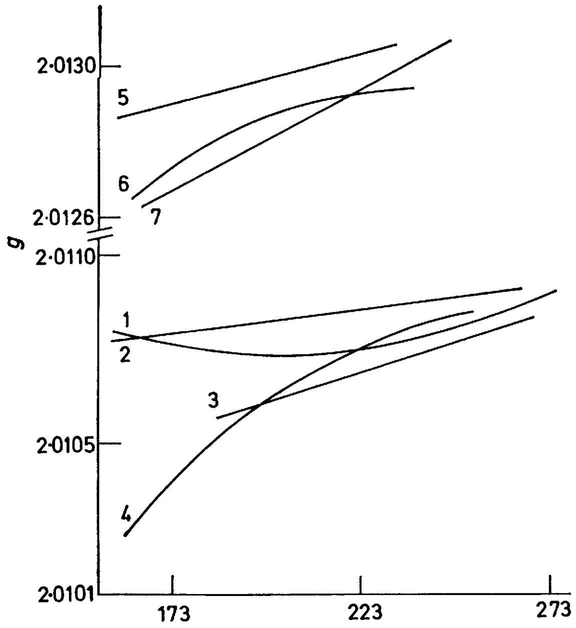


FIGURE 2 Temperature dependence of the g factors of $(\mathrm{Bu^tSEt})_2^{+\bullet}$ (curves 1—4) and $\mathrm{Bu^t{}_2S^{+\bullet}}$ (curves 5—7). Conditions (method of generation, solvent, counter ion, see Table 1 for key): (1) P, C, $\mathrm{CF_3CO_2^-}$; (2) P, D, $\mathrm{CF_3CO_2^-}$ (E, D, $\mathrm{CF_3SO_3^-}$ gave similar results); (3) E, PrCN–MeCN 3 : 2 (v/v), $\mathrm{BF_4^-}$ [E, PrCN–MeCN 3 : 2 (v/v), $\mathrm{ClO_4^-}$ gave similar results]; (4) E, D, $\mathrm{BF_4^-}$; (5) P, C, $\mathrm{CF_3CO_2^-}$; (6) E, D, $\mathrm{CF_3SO_3^-}$; (7) E, D, $\mathrm{BF_4^-}$

and counter-ion. The results are summarised in Figure 2 and, in general, the g factors of both radical cations increased with temperature.

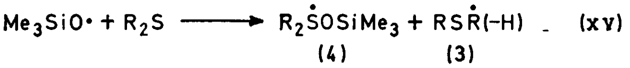
(ii) *Reactions of t-Butoxyl and Trimethylsiloxyl Radicals with Dialkyl Sulphides.*—Photolysis of a cyclopropane solution containing $\mathrm{Bu^tSCH_3}$ and $\mathrm{Bu^tOOBu^t}$ gave rise initially only to the e.s.r. spectrum[6] of $\mathrm{Bu^tS\dot{C}H_2}$ [$a(1\mathrm{H}^1)$ 15.9, $a(1\mathrm{H}^2)$ 17.2 G, g 2.0047 at 198 K] [equation (xiii)].

$$\mathrm{Bu^tO\bullet + Bu^tSCH_3 \longrightarrow Bu^tS\dot{C}H_2 + Bu^tOH} \tag{xiii}$$

Mixtures containing $\mathrm{Bu^tSCH_3}$, $\mathrm{Bu^tSCD_3}$, and $\mathrm{Bu^tOOBu^t}$ were photolysed and the relative concentrations of $\mathrm{Bu^tS\dot{C}H_2}$ and $\mathrm{Bu^tS\dot{C}D_2}$ were monitored during continuous irradiation. Assuming that the rate constants for removal of normal and deuteriated radicals are similar, it can readily be shown that equation (xiv) holds,[12] and at 198 K $(k^{\mathrm{H}}_{\mathrm{xiii}}/k^{\mathrm{D}}_{\mathrm{xiii}})$ was 7.0 ±0.5.

$$(k^{\mathrm{H}}_{\mathrm{xiii}}/k^{\mathrm{D}}_{\mathrm{xiii}}) = [\mathrm{Bu^tS\dot{C}H_2}][\mathrm{Bu^tSCD_3}]/[\mathrm{Bu^tS\dot{C}D_2}][\mathrm{Bu^tSCH_3}] \tag{xiv}$$

Both sulphuranyl radicals (4) and α-alkylthioalkyl radicals (3) were detected as primary products when cyclopropane solutions containing dialkyl sulphides and bis(trimethylsilyl) peroxide were photolysed.



$$\mathrm{Me_3SiO\bullet + R_2S \longrightarrow \underset{(4)}{R_2\dot{S}OSiMe_3} + \underset{(3)}{RS\dot{R}(-H)}} \tag{xv}$$

With $\mathrm{Bu^tSEt}$, the ratio $[\mathrm{Bu^t(Et)\dot{S}OSiMe_3}] : [\mathrm{Bu^tS\dot{C}HMe}]$ was 19 : 1 at 162 K and decreased with increasing temperature. For a peroxide concentration of *ca.* 0.8M, this ratio

TABLE 2

E.s.r. parameters for the sulphuranyl radicals $\mathrm{R^1R^2\dot{S}OSiMe_3}$ in cyclopropane solution

$\mathrm{R^1}$	$\mathrm{R^2}$	Temp. (K)	g Factor	Proton hyperfine splittings[a] (G)
Me	Me	213	2.0076	7.7 (6)[b]
$\mathrm{CD_3}$	$\mathrm{CD_3}$	217	2.0076	1.15 (6)[b,c]
Et	Et	213	2.0074	7.2 (2), 10.0 (2)
$\mathrm{Pr^i}$	$\mathrm{Pr^i}$	213	2.0075	7.4 (2)[d]
Et	$\mathrm{Pr^i}$	193	2.0073	5.6 (1), 8.5 (1), 11.8(1)
$\mathrm{Bu^t}$	Me	213	2.0074	7.7 (3)
$\mathrm{Bu^t}$	Et	213	2.0073	9.7 (1), 11.5 (1)[e]
$\mathrm{Bu^t}$	$\mathrm{Pr^i}$	213	2.0074	5.2 (1)

[a] Numbers of nuclei coupling shown in parentheses. [b] A further splitting into an even number (⩾6) of lines, spacing *ca.* 0.2 G, was detected and is assigned to the nine protons of the $\mathrm{Me_3Si}$ group. [c] Deuterium splitting. [d] Central line broadens relative to the outer lines below 173 K. [e] At low temperatures (<152 K) further fine structure was apparent, indicating freezing out of rotamers about the Et–S bond.

was independent of $[\mathrm{Bu^tSEt}]$ in the range 0.8—2.8M in cyclopropane at 162 K. The ratio (7 : 1) was also independent of the sulphide concentration at 212 K in cyclopentane solvent, when the cyclopentyl radical was also detected, and the ratio $[\mathrm{cyclo\text{-}C_5H_9\bullet}] : [\mathrm{Bu^tS\dot{C}HMe}]$ was proportional to $[\mathrm{cyclo\text{-}C_5H_{10}}] : [\mathrm{Bu^tSEt}]$. These observations strongly support our assumption that (3) and (4) are generated by the reactions of trimethylsiloxyl radicals, rather than photoexcited peroxide,[13] with the sulphides.

The e.s.r. parameters for (4) are summarised in Table 2 and the spectra of $\mathrm{Pr^i{}_2\dot{S}OSiMe_3}$ and $\mathrm{Bu^t(Et)\dot{S}OSiMe_3}$ are shown in Figures 3 and 4. The g factor (2.0073) of $\mathrm{Bu^t(Et)\dot{S}OSiMe_3}$ was invariant in the temperature range 173—243 K. In most experiments the spectrum of an oxymethyl radical, probably $\mathrm{\bullet CH_2OSi(Me_2)OSiMe_3}$, was also detected.[14]

The spectrum of (4; R = Me) exhibited splitting from two equivalent methyl groups (even at 134 K in propane–cyclopropane solvent) and each line was further split into an even number (⩾6) of components *ca.* 0.2 G apart. This small splitting is ascribed to the methyl protons of the $\mathrm{Me_3Si}$ groups, since the spectrum from perdeuteriodimethyl sulphide showed similar fine structure. The spectra ascribed to (4) might possibly be due to the radical (6), formed as shown in equation (xvi) [compare equation (ii)]. We consider this alternative to be much less likely, since

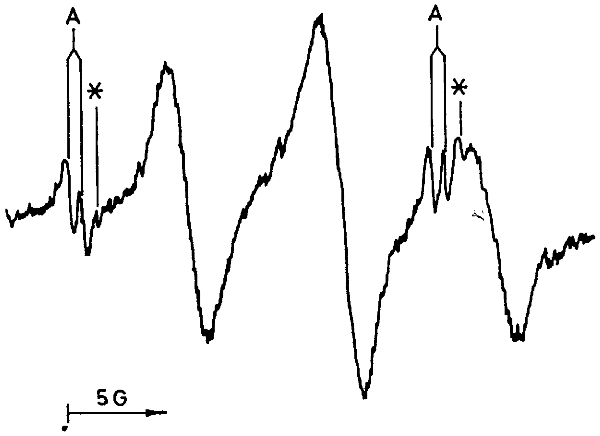


FIGURE 3 E.s.r. spectrum of $\mathrm{Pr^i{}_2\dot{S}OSiMe_3}$ obtained by photolysis of a cyclopropane solution containing $\mathrm{Pr^i{}_2S}$ and $\mathrm{Me_3SiOOSiMe_3}$. A indicates the third and fourth pairs of lines from $\mathrm{Pr^iS\dot{C}Me_2}$ and * indicates lines from $\mathrm{Me_3SiOSi(Me_2)O\dot{C}H_2}$

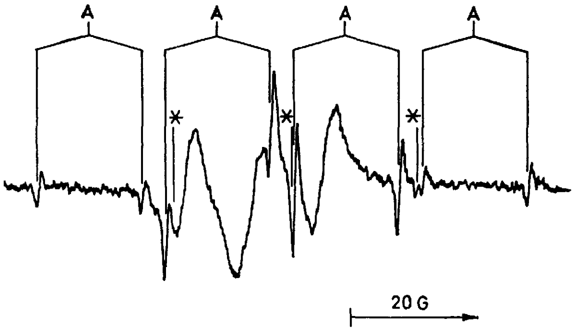


FIGURE 4 E.s.r. spectrum obtained by photolysis of a cyclopropane solution containing Bu^tSEt and $Me_3SiOOSiMe_3$. Lines marked A are due to $Bu^tS\dot{C}HMe$, those marked * are due to $Me_3SiOSi(Me_2)O\dot{C}H_2$

coupling to the protons of the second pair of *S*-alkyl groups in (6) would be expected to exceed 0.2 G.

Mixtures of Bu^tSCH_3 and Bu^tSCD_3 were caused to react with $Me_3SiO\cdot$ and the relative concentrations of $Bu^tS\dot{C}H_2$ and $Bu^tS\dot{C}D_2$ were measured at 198 K. Making the same assumptions as before, we derive a value 3.5 ± 0.5 for (k^H_{xvii}/k^D_{xvii}).

$$R_2\dot{S}OSiMe_3 + R_2S \longrightarrow \underset{(6)}{R_2\dot{S}S(R_2)OSiMe_3} \qquad \text{(xvi)}$$

$$Me_3SiO\cdot + Bu^tSCH_3 \longrightarrow Bu^tS\dot{C}H_2 + Me_3SiOH \qquad \text{(xvii)}$$

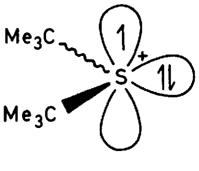
In order to confirm that loss of trimethylsilanol from (4) was not the major source of (3) under our experimental conditions, we investigated the decay of the e.s.r. signals from $Bu^t(Et)\dot{S}OSiMe_3$ and $Bu^tS\dot{C}HMe$ when photolysis was interrupted using the rotating sector technique.[15] In cyclopropane at 175 K the sulphuranyl radical decayed much more slowly than the α-alkylthioalkyl radical; both decays were approximately second order. During the first 8 ms after shuttering the light, $Bu^tS\dot{C}HMe$ decayed to 20% of its original concentration, whilst the concentration of $Bu^t(Et)\dot{S}OSiMe_3$ had dropped by only *ca.* 10%.

Between 150 and 208 K, similar initial concentrations of $Bu^t(CH_3)\dot{S}OSiMe_3$ and $Bu^t(CD_3)\dot{S}OSiMe_3$ decayed at very similar rates, showing that cleavage of a β-C–H bond is not involved in the rate-determining step for removal of the sulphuranyl radical. Decay was approximately second-order in sulphururanyl radical at 170 K for both normal and labelled species, and the first half-life was *ca.* 1×10^{-2} s for an initial concentration of *ca.* 5×10^{-6}M.

DISCUSSION

The equilibrium (x) generally lies well over to the right [1,2] such that only the dimer cation $(R_2SSR_2)^{+\cdot}$ (2) is detected by e.s.r. spectroscopy. Only the spectrum of the monomer cation is observed during oxidation of di-t-butyl sulphide and here steric factors probably prevent dimerisation. Similar conclusions have been reached from pulse radiolytic [2] and solid state e.s.r. studies.[4] The small ^{33}S splitting (corresponding to *ca.* 3% population of the S 3*s* orbital) for $Bu^t{}_2S^{+\cdot}$ suggests that the unpaired electron occupies an S 3*p* orbital perpendicular to the CSC plane as shown in (7). The electronic structure is thus similar to that of the isoelectronic phosphinyl radicals (8).[16]

Similar structures have been suggested previously for the monomeric radical cations derived from diaryl sulphides, and the ring proton splittings are typical of π-electron delocalisation.[17] Extensive delocalisation of the unpaired electron onto nitrogen occurs in the radical cations (5) and contributing structures (9; X = lone pair or O) are important. Such delocalisation is greater in $(Me_2N)_2S^{+\cdot}$ than in the bis(dimethylamino)phosphinyl radical (10) [*a*(P) 70.2, *a*(2N) 4.2, *a*(6H) 2.1 G].[18]



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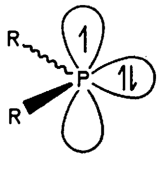

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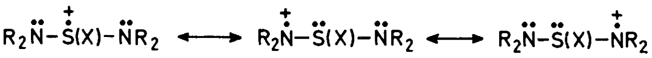
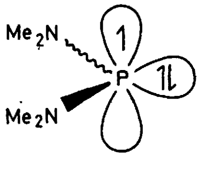


$$R_2\ddot{N}-\overset{+}{\dot{S}}(X)-\ddot{N}R_2 \longleftrightarrow R_2\overset{+}{\dot{N}}-\ddot{S}(X)-\ddot{N}R_2 \longleftrightarrow R_2\ddot{N}-\ddot{S}(X)-\overset{+}{\dot{N}}R_2$$

(9a) (9b) (9c)



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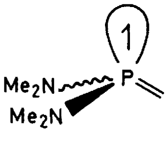

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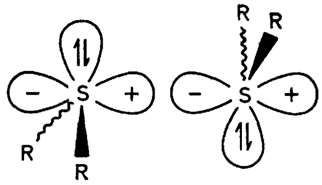

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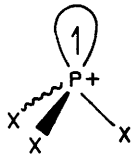

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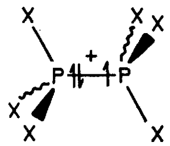

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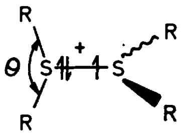

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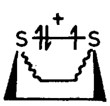


(16)

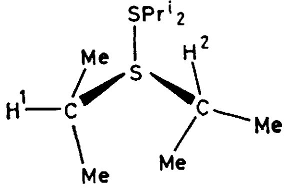
The radical cations $(R_2N)_2\dot{S}\overset{+}{O}$ (5; X = O) are isoelectronic with the bis(dimethylamino)phosphonyl radical (11), which is pyramidal at phosphorus.[19,20] The geometry at sulphur in (5; X = O) is expected to be closer to planar than that at phosphorus in (11). The majority of the spin density is on nitrogen in (5; X = O), and the relative contribution of (9a; X = O) would be expected to be less than that of (9a; X = lone pair) because of the higher electronegativity of sulphur in the former type of radical. For similar reasons, delocalisation onto nitrogen should be less for (10) than for $(Me_2N)_2S^{+\cdot}$. The value of $a(N)/a(H)$ is close to unity for both (5; X = lone pair) and (5; X = O), as it is for $(Me_2NNMe_2)^{+\cdot}$ [a(2N) 13.4, a(12H) 12.7 G] which is probably planar at both nitrogens.[21,22] The g factor of (5; X = O) is lower than that of (5; X = lone pair), in accord with the smaller spin density on sulphur in the former. Delocalisation of the unpaired electron and the positive charge from sulphur would be expected to stabilise $Ar_2S^{+\cdot}$ and (5; X = lone pair or O) relative to the respective dimer cations.

The unpaired electron in (2), and in the related cation radical $(Me_2SeSeMe_2)^{+\cdot}$,[23] appears to occupy a σ^* S–S orbital composed mainly of S $3p$ atomic orbitals as shown in (12).[1,2,4]

The ^{33}S splittings for $(Bu^tSEt)_2^{+\cdot}$ and $(Bu^tSPr^i)_2^{+\cdot}$ indicate that the $3s$ character per sulphur (*ca.* 6%) in the semi-occupied orbital is about twice that for $Bu^t_2S^{+\cdot}$. The CSS angle in (12) is hence greater than 90°, and the sulphur cations thus follow the same structural trend as the related phosphorus cation radicals (13) and (14).[24] The phosphorus atoms in (14) are more pyramidal than in (13), an order which may be rationalised in terms of steric and valence electron repulsive effects.

The α-methylene protons in $(RSCH_2Me)_2^{+\cdot}$ (R = Et or Bu^t) are diastereotopic for the structure (12), because of non-planarity at sulphur. However, the splittings from these protons are the same within the limits imposed by the relatively broad lines ($\geqslant$2 G). An alternative structure, planar at both sulphur atoms, would be (15) (see the discussion of $\cdot SX_3$ radicals below), although it is difficult to reconcile the small size of $a(^{33}S)$ (which requires the angle θ to be close to 180°) with the existence of the species $[\overline{CH_2[CH_2]_nS}]_2^{+\cdot}$ (n = 2 [2] and 3), provided that all the dimer cations have similar structures. Certainly, the intramolecular 'dimer' cation (16) [2] cannot have a structure of the type (15).

Molecular models of (12; R = Pr^i) show considerable congestion and hence the non-equivalence of the α-protons in $(Pr^i_2S)_2^{+\cdot}$ may be understood in terms of conformational rigidity. The most stable conformation about the C–S bonds in (12; R = Pr^i) may be as illustrated in (17). In this conformation H^1 and H^2 are non-equivalent, but could exchange environments by a coupled rotation about the two C–S bonds (cogwheel rotation) to give rise to the observed line-shape effects.



(17)

The deuterium labelling studies eliminate the possibility that photochemical generation of (2) from mixtures of R_2S, Bu^tOOBu^t, and CF_3CO_2H occurs by protonation of an initially formed α-alkylthioalkyl radical [equations (xviii)—(xx)].

Two reasonable alternative pathways [equations (xxi) and (xxii)] for formation of $R_2S^{+\cdot}$ could be competitive, although we favour the direct oxidation of sulphide by a protonated alkoxyl radical.[25]

Interpretation of the changes in g factor of (2) is complicated by the presence of solvation and counter-ion effects. We have shown that the g factors of the sulphuranyl radicals $R_2\dot{S}SCF_3$ in hydrocarbon solvent increase with temperature, and this was attributed to an increase in the average length of the S–S bond at the higher temperatures and the consequent increase in orbital magnetism.[26] For a given solvent, counter-ion, and temperature, the g factors of (2) increase with the bulk of the alkyl substituents. This could be due to steric lengthening of the S–S bond and an associated decrease in the energy separation between the σ^* orbital and the orbitals occupied by non-bonding electrons on sulphur, which would lead to an increase in g factor as described for $R_2\dot{S}SCF_3$.[26] In support of this interpretation, the electronic absorption in the region of 500 nm, which has been assigned to the $\sigma\rightarrow\sigma^*$ transition,[4] shifts to longer wavelengths as the S–S bond length increases.[2,4] However, the present work shows that the g factor of $Bu^t_2S^{+\cdot}$ is also sensitive to medium and temperature changes, and thus solvation and counter-ion effects are also important. The results indicate that variations in the average length of the S–S bond, in cation–anion, and in ion–solvent interactions are probably together responsible for the changes in orbital energies which result in the g factor variations observed for (2).

$$Bu^tO\cdot + Bu^tSCH_3 \longrightarrow Bu^tS\dot{C}H_2 + Bu^tOH \qquad \text{(xviii)}$$

$$(\text{or } Bu^t\overset{\cdot +}{O}H) \qquad\qquad (\text{or } Bu^t\overset{+}{O}H_2)$$

$$Bu^t\dot{S}CH_2 + CF_3CO_2H \longrightarrow Bu^t(CH_3)S^{\dot{+}} + CF_3CO_2^- \qquad \text{(xix)}$$

$$Bu^t(CH_3)S^{\dot{+}} + Bu^tSCH_3 \longrightarrow (Bu^tSCH_3)_2^{\dot{+}} \qquad \text{(xx)}$$

$$Bu^tO\cdot + R_2\overset{+}{S}H \longrightarrow Bu^tOH + R_2S^{\dot{+}} \qquad \text{(xxi)}$$

$$Bu^t\overset{\cdot +}{O}H + R_2S \longrightarrow Bu^tOH + R_2S^{\dot{+}} \qquad \text{(xxii)}$$

$$R_2\underset{\cdot\cdot}{\dot{S}} - X \longleftrightarrow R_2\underset{\cdot\cdot}{\overset{+}{\dot{S}}}\quad :\!\bar{X}$$

(18a) (18b)

Reactions of Alkoxyl and Siloxyl Radicals with Dialkyl Sulphides.—The similarity between a sulphuranyl radical $R_2\dot{S}X$ (18) and the dimer cation (2) is obvious, and an analogous relationship exists between $\cdot PX_4$ and $(X_3PPX_3)^{+\cdot}$.

It has been shown previously that photolysis of solutions containing di-t-butyl peroxide and dialkyl sulphides with α-C–H groups gives rise to spectra of α-alkylthioalkyl radicals (3) [equation (v)].[5-7] It is possible that (3) could be produced mainly by loss of t-butyl alcohol from a short-lived sulphuranyl radical (19) [equation (xxiii)].

$$Bu^tO\cdot + R_2S \longrightarrow \underset{(19)}{R_2\dot{S}OBu^t} \longrightarrow RS\dot{R}(-H) + Bu^tOH \quad (xxiii)$$

The existence of a large kinetic isotope effect for production of $Bu^tS\dot{C}X_2$ ($X = H$ or D) is strong evidence against such a pathway, although it does not preclude the possibility of formation of (19) in a rapid pre-equilibrium followed by rate-determining loss of Bu^tOH. The situation is clearer in the $Me_3SiO\cdot + R_2S$ system, since a sulphuranyl radical adduct can be detected by e.s.r. spectroscopy. Again, there is an appreciable isotope effect for generation of $Bu^tS\dot{C}X_2$ but, in addition, $Bu^t(Et)\dot{S}OSiMe_3$ decays too slowly to be the major source of the shorter lived $Bu^tS\dot{C}HMe$. The conclusion that (3) is not formed mainly by loss of Me_3SiOH from (4) is supported by the observation that decay of $Bu^t(CX_3)\dot{S}OSiMe_3$ ($X = H$ or D) is a second-order process and exhibits no deuterium isotope effect. The actual reaction responsible for decay has not been identified.

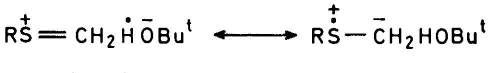
We conclude that the reaction of $Me_3SiO\cdot$ with R_2S involves two independent but competing pathways, abstraction of hydrogen from an α-C–H group to give (3) and addition to sulphur to give (4). Similarly, the reaction of alkoxyl radicals with R_2S in non-polar solvents to give (3) probably involves direct attack at hydrogen. The sulphur atom may, of course, participate in the formation of (3), through the stabilising effect it exerts on the transition state for hydrogen abstraction.[9] This stabilisation can be accounted for in terms of contributions from canonical structures such as (20).

The formation of (3) from the reaction of $HO\cdot$ with R_2S in aqueous solution proceeds *via* an intermediate sulphuranyl adduct,[2] and this mechanistic difference may result from the greater electrophilicity of $HO\cdot$ (compared with $RO\cdot$ or $Me_3SiO\cdot$), and consequent faster addition to the electron rich sulphur, coupled with the nature of the solvent which facilitates loss of water from $R_2\dot{S}OH$. Electrophilicity is expected to increase in the order $RO\cdot < Me_3SiO\cdot < HO\cdot$, $R\overset{+\cdot}{O}H$, in parallel with the yields of products derived by attack at S rather than H.

Various structural alternatives exist for sulphuranyl radicals, $X_3S\cdot$, and these may be planar or pyramidal at sulphur. The unpaired electron in planar T shaped radicals (21) may be in a π or σ orbital, and a non-planar species (22) would probably have a unique 2 centre : 3 electron bond [compare $(R_2SSR_2)^{+\cdot}$].

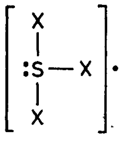
The isotropic e.s.r. spectra of $F_3S\cdot$,[27] $(CF_3O)_3S\cdot$,[28] and $(RO)_3S\cdot$ [29] show that all have two equivalent ligands different from the third. Recently, the anisotropic spectrum of $F_3S\cdot$ in single crystals of $F_3\overset{+}{S}\overset{-}{B}F_4$ has been obtained and interpreted in terms of a planar structure in which the unpaired electron occupies an in-plane (σ) orbital composed of S 3*p* and F 2*p* atomic orbitals.[30] It was thought likely that $(CF_3O)_3S\cdot$, $(RO)_3S\cdot$, and $R\dot{S}(OBu^t)_2$ [8] would also be σ-radicals, although planar π structures have been tentatively suggested for $X\dot{S}(OR)_2$ ($X = R$ or RO).[8,29] It should be noted that the ring proton splittings [*a*(3H) > *a*(2H)] detected for $Ph\dot{S}(OBu^t)_2$ appear to imply delocalisation of the unpaired electron into the π-orbitals of the benzene ring.[8]

The two *S*-methyl groups in $Me_2\dot{S}OSiMe_3$ are apparently equivalent even at 135 K, indicating that they are probably in identical environments. The α-methylene protons in $R(MeCH_2)\dot{S}OSiMe_3$ will be diastereotopic for a non-planar arrangement of bonds to sulphur, as in (23), but (assuming rapid rotation about the S–O bond) not in a planar radical (24).

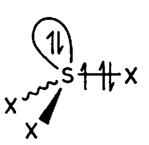


$$R\overset{+}{\dot{S}}{=}CH_2\overset{\cdot}{H}\overset{-}{O}Bu^t \longleftrightarrow R\overset{+}{\dot{S}}{-}\overset{-}{C}H_2HOBu^t$$

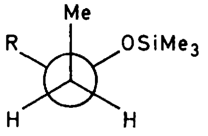
(20a) (20b)



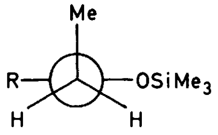
(21)



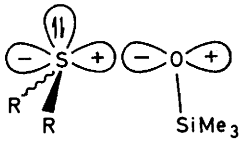
(22)



(23)



(24)



(25)

Whatever the rate of rotation about the CH_2–S bond, the methylene protons in (23) remain magnetically non-equivalent. The spectrum of $Et_2\dot{S}OSiMe_3$ exhibits splitting from two pairs of equivalent protons and even at relatively high temperature (265 K) shows no sign of collapsing to a quintet. This non-equivalence is unlikely to be due to restriction of rotation about the C–S bond, since the spectrum of $Pr^i_2\dot{S}OSiMe_3$ only begins to show the effects of such hindered rotation below *ca.* 173 K (see Table 2). Similar non-equivalence of the methylene protons is shown by the spectrum of $Bu^t(Et)\dot{S}OSiMe_3$ even at 250 K, and only at low temperatures (*ca.* 145 K) were extra lines detected, indicating that interconversion between conformers about the Et–S bond had become slow on the e.s.r. time scale. We conclude that $R_2\dot{S}OSiMe_3$ (4) is non-planar at sulphur and that the unpaired electron probably occupies an S–O σ* orbital composed of S 3*p* and O 2*p* orbitals, as shown in (25).

The structure of (4) is thus similar to those proposed for $(R_2SSR_2)^{+\cdot}$,[2,3] $R_2\dot{S}Br$,[2] and $R_2\dot{S}SCF_3$.[26]

The most stable conformation about the C–S bonds in $Pr^i_2\dot{S}OSiMe_3$ is probably analogous to that suggested for $(Pr^i_2S)_2^{+\cdot}$ [see structure (17) above], thus accounting for the broadening of the central line of the triplet e.s.r. spectrum of this sulphuranyl radical at low temperatures. The *g* factor of (4), unlike those of $(R_2SSR_2)^{+\cdot}$ or $R_2\dot{S}SCF_3$, is essentially independent of temperature. The reason for this difference is not entirely clear and it would be interesting to examine the electronic absorption spectrum of (4).

EXPERIMENTAL

The techniques employed for the detection of e.s.r. spectra during continuous u.v. irradiation [31,32] or constant-current electrolysis [11] of samples in the cavity of the spectrometer have been described previously. 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.[15,31] *g* Factors were determined by measurement of the microwave frequency and the magnetic field at the centre of resonance, using the pyrene radical anion (Na^+ counter-ion) in tetrahydrofuran (*g* 2.002 710) as standard.[33] Average values were used in Figure 2 and these are considered to be precise to ±0.000 05.

In photochemical experiments, cyclopropane or dichloromethane solutions were *ca.* 1.0M in peroxide, *ca.* 1.5M in sulphide, and *ca.* 0.5M in trifluoroacetic acid (when present), and were sealed under vacuum. For the electrochemical experiments, solutions in purified [11] dichloromethane, n-butyronitrile, or acetonitrile were *ca.* 0.4M in sulphide and 0.1M in carrier electrolyte ($Bu^n_4NBF_4$, $Bu^n_4NO_3SCF_3$, $NaClO_4$).

Di-t-butyl peroxide was obtained commercially and purified before use. Bis(trimethylsilyl) peroxide was prepared by a method in the literature.[34] Dialkyl sulphides were purified commercial products or were prepared according to literature methods,[35] as were bis(dialkylamino) sulphides [36,37] and the sulphoxide.[38]

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