Electron Spin Resonance Studies. Part XXXVIII.[1] Evidence for the Formation of Dimeric Radical-cations, $R_2S{\cdot}SR_2^{+\cdot}$, in the One-electron Oxidation of Sulphides

By **Bruce C. Gilbert, Daryl K. C. Hodgeman**, and **Richard O. C. Norman**,* Department of Chemistry, The University of York, Heslington, York YO1 5DD

Evidence is adduced by e.s.r. spectroscopy for the mediation of radical-cations $R_2S{\cdot}SR_2^{+\cdot}$ during oxidation of a sulphide R_2S by the titanium(III)–hydrogen peroxide or –persulphate couple. It is suggested that they arise from a first-formed transient, $R_2S^{+\cdot}$, which is subject to competing reactions of which one is with a further molecule of sulphide. Other reactions, and the variation of their relative importance with structure, are briefly discussed.

We have previously presented evidence that the oxidation of sulphides by the hydroxyl radical gives initially the radical-cation $R^1R^2S^{+\cdot}$ and that this can break down to a neutral radical and a cation in various ways, illustrated in reactions (1)—(3).[1] We now report evidence for a further reaction of the radical-cation, namely its reaction with another molecule of the sulphide to form dimeric radical-cations as in reaction (4).

When a dilute aqueous solution of dimethyl sulphide was oxidised with the titanium(III) ion–hydrogen peroxide couple in a flow system[2] at pH 2·5, the e.s.r. spectrum contained the two singlets (g 2·0018 and 2·0132) which are characteristic of oxy-complexed titanium species[3] and nine equally spaced lines to which a further two lines could be added in the wings under conditions of high spectrometer gain. The relative

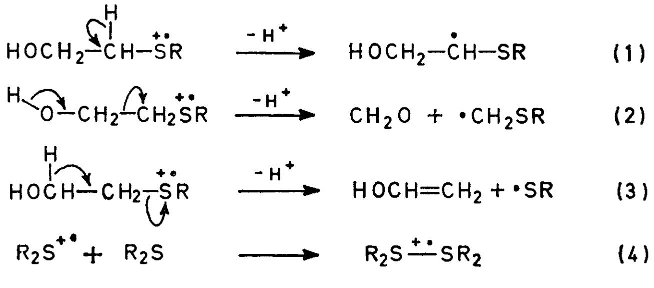
---

[1] Part XXXVII, B. C. Gilbert, J. P. Larkin, and R. O. C. Norman, *J.C.S. Perkin II*, 1973, 272.

[2] R. O. C. Norman and B. C. Gilbert, *Adv. Phys. Org. Chem.*, 1967, **5**, 53.

[3] H. Fischer, *Ber. Bunsengesellschaft Phys. Chem.*, 1967, **71**, 685; R. O. C. Norman and P. R. West, *J. Chem. Soc.* (*B*), 1969, 389.

intensities of the lines correspond closely to those expected if the spin interacts with twelve equivalent protons, the wing lines being lost in the noise; the



$$HOCH_2-CH(H)-\overset{+\bullet}{S}R \xrightarrow{-H^+} HOCH_2-\dot{C}H-SR \quad (1)$$

$$H-O-CH_2-CH_2\overset{+\bullet}{S}R \xrightarrow{-H^+} CH_2O + \bullet CH_2SR \quad (2)$$

$$HOCH(H)-CH_2-\overset{+\bullet}{S}R \xrightarrow{-H^+} HOCH{=}CH_2 + \bullet SR \quad (3)$$

$$R_2S^{+\bullet} + R_2S \longrightarrow R_2S\overset{+\bullet}{-}SR_2 \quad (4)$$

spectrum was satisfactorily simulated on this basis. The high *g* factor (2·0103) and the observation that the signals showed no saturation at microwave powers of 80—100 mW suggest that the unpaired spin is to a large extent accommodated on sulphur, and we assign the spectrum to the species $Me_2S{\cdot}SMe_2^{+\bullet}$.

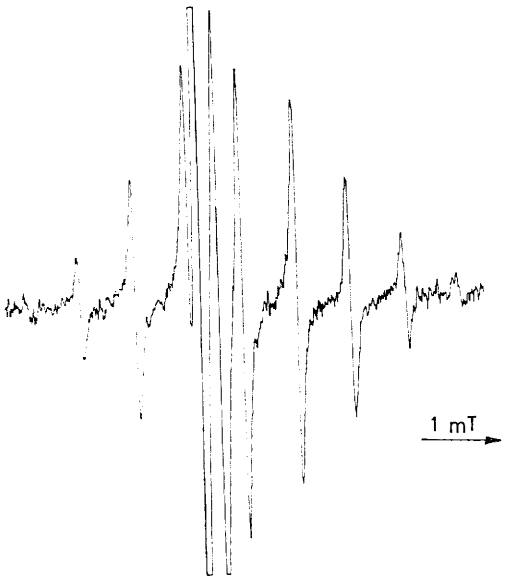


FIGURE 1 E.s.r. spectrum attributed to $Me_2S{\cdot}SMe_2^{+\bullet}$ together with singlets at *g* 2·0118 and 2·0132

The spectrum described above was observed when hydrogen peroxide was mixed either with a solution containing both titanium(III) ions and dimethyl sulphide or with separate solutions of these two materials in a three-stream mixing chamber. The signals were more intense under the latter conditions; moreover, the solution containing both titanium ions and sulphide slowly changed colour, suggesting formation of a complex. In contrast, when the sulphide was contained in the hydrogen peroxide solution, then, depending on the time which elapsed before admixture with titanium ions, the nine-line spectrum was gradually replaced by that of the methyl radical [*a*(3H) 2·29 mT, *g* 2·0025]; evidently under these conditions dimethyl sulphide is oxidised to dimethyl sulphoxide, which is known to yield the methyl radical with the titanium(III) ion–hydrogen peroxide system[4] [*cf.* the behaviour of methionine when treated with hydrogen peroxide and then titanium(III) ion[1,5]]. Subsequent reactions were carried out by mixing separate solutions of the reactants in the three-stream mixing chamber.

When the pH was lowered to 1·0, the nature of the spectrum, and its intensity for a given concentration of the sulphide, were unchanged; the singlet of *g* 2·0118 was now very weak, and there were in addition weak signals from the radical $MeSO_2\cdot$ [*a*(3H) 0·076 mT, *g* 2·0050; *cf.* ref. 6] and the methyl radical which were not removed by distillation of the dimethyl sulphide immediately before use. However, when the pH was raised to 3·6 (with ammonia and EDTA), the spectrum attributed to $Me_2S{\cdot}SMe_2^{+\bullet}$ was no longer observed; it was replaced by one with *a*(2H) 1·65, *a*(3H) 0·36 mT, *g* 2·0049, attributed to the radical $\cdot CH_2SMe$ [*cf.* *a*(1H) 1·67, *a*(1H) 1·75, *a*(3H) 0·31 mT for this radical at —60°, the α-protons interacting non-equivalently in this case because the radical is essentially locked in one conformation at the low temperature used [7]]. This pH dependence suggests that the first-formed transient, $Me_2S^{+\bullet}$, undergoes competing reactions; with dimethyl sulphide it yields $Me_2S{\cdot}SMe_2^{+\bullet}$ and with base (hydroxide ion, ammonia, or EDTA) it undergoes deprotonation.

The reactions of a number of other sulphides with the titanium(III)–peroxide system were studied in like manner. In several cases spectra attributable to dimeric radical-cations were observed, but the resonances were never as intense or as sharp as those ascribed to $Me_2S{\cdot}SMe_2^{+\bullet}$. The results for the predominant radicals are collected in Table 1; in each case the singlets of *g* 2·0118 and 2·0132 were observed at pH 2·5 and the latter at pH 1·0.

Diethyl sulphide reacted at pH 1·0 or 2·5 to give two radicals. The one in smaller concentration was characterised as the radical $\cdot CHMe{\cdot}SEt$ (*cf.* ref. 8). The other gave six lines which, on the assumption that a seventh was obscured by the singlet of *g* 2·0132, analysed satisfactorily for a species in which the spin interacts with eight equivalent protons, the outermost lines being too weak for observation; the spectrum was satisfactorily simulated on this basis and is assigned to the radical-cation $Et_2S{\cdot}SEt_2^{+\bullet}$ At pH 3·6 the latter radical was not detected. The spectrum of the former was accompanied by one with doublet (1·66) and triplet (0·19 mT splittings and *g* factor (2·0047) consistent with the partial structure $-CH_2-S-\dot{C}H-$; a further triplet splitting in the range 0·7—1·3 mT would have been obscured by lines from the other radical, so that a possible structure is $\cdot CH(CH_2OH){\cdot}SEt$, the formation of

---

[4] W. T. Dixon, R. O. C. Norman, and A. L. Buley, *J. Chem. Soc.*, 1964, 3625.

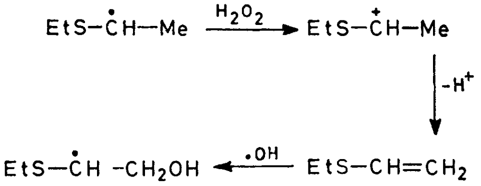
[5] H. Taniguchi, H. Takagi, and H. Hatano, *J. Phys. Chem.*, 1972, **76**, 135.

[6] T. Kawamura, P. J. Krusic, and J. K. Kochi, *Tetrahedron Letters*, 1972, 4075.

[7] I. Biddles, A. Hudson, and J. T. Wiffen, *Tetrahedron*, 1972, **28**, 867.

[8] J. Q. Adams, *J. Amer. Chem. Soc.*, 1970, **92**, 4535.

which can be envisaged as in reaction (5) [*cf.* $a(\alpha\text{-H})$ 1·64, $a(CH_2)$ 1·01 mT for [1] $\cdot CH(CH_2OH)\cdot SBu^t$].



(5)

The oxidation of di-isopropyl sulphide at pH 1·0 gave a strong spectrum assigned to the radical $\cdot CMe_2\cdot SCHMe_2$; there were in addition weak signals which are provisionally assigned to the radicals $Me_2CH\cdot SO_2\cdot$ [$a(6H)$ 0·23 mT, g 2·0053; *cf.* evidence that $a(\beta\text{-H}) > a(\alpha\text{-H})$ in radicals of this type [9]] and $\cdot CMe(CH_2OH)\cdot SCHMe_2$ [$a(3H)$ 1·95 mT, $a(CH_2)$ not observed but would have been masked if in the range 1·0—1·2 mT, g 2·0042; *cf.* the preceding paragraph]. No resonance was observed which could be attributed to the radical-cation $Me_2CHS\cdot SCHMe_2^{+\cdot}$.

TABLE 1

E.s.r. parameters for the major radicals from sulphides in acid solution

Sulphide	pH	Radical	Relative concentration	Splitting constants (mT)	g
Me_2S	2·5 [a]	$Me_2S\cdot SMe_2^{+\cdot}$		0·68 (12H) [b]	2·0103
	3·6	$\cdot CH_2\cdot SMe$		1·65 (2H), 0·36 (3H)	2·0049
Et_2S	2·5 [a]	$Et_2S\cdot SEt_2^{+\cdot}$	3	0·67 (8H) [b]	2·0103
		$\cdot CHMe\cdot SEt$	1	1·70 (1H), 2·10 (3H), 0·15 (2H)	2·0044
	3·6	$\cdot CHMe\cdot SEt$			
$Pr^i{}_2S$	1·0	$\cdot CMe_2\cdot SCHMe_2$		2·04 (6H)	2·0038
$[CH_2]_4S$ [c]	2·5	$[CH_2]_4S\cdot S[CH_2]_4^{+\cdot}$		0·93 (8H)	2·0102
	3·6	$\cdot CHCH_2SCH_2CH_2$		2·12 (1H), 3·28 (4H)	2·0027
$MeSCH_2CH_2OH$	1·0	$(HOCH_2CH_2SMe)_2^{+\cdot}$	1	0·66 (10H) [b]	2·0102
		$\cdot CH_2\cdot SCH_2CH_2OH$	1·5	1·65 (2H), 0·19 (2H)	2·0048
	2·5	$\cdot CH_2\cdot SCH_2CH_2OH$			
$MeS[CH_2]_3SMe$	2·5 [a]	$\cdot CH(SMe)\cdot [CH_2]_2SMe$		1·68 (3H), [d] 0·27 (3H)	2·0046
		$\cdot CH_2S[CH_2]_3SMe$		1·64 (2H), 0·21 (2H)	2·0048

[a] The same results were obtained at pH 1·0. [b] Not all the resonances were observed; see text. [c] Tetrahydrothiophen. [d] Fortuitous equality of $a(\alpha\text{-H})$ and $a(\beta\text{-H})$.

The oxidation of tetrahydrothiophen at pH 2·5 gave only one species, identified as the dimeric radical-cation by interaction of the spin with eight equivalent protons (all nine lines were seen in this instance) and the high g factor. At pH 3·6 the only radical observed was identified as the 3-tetrahydrothiophenyl radical on the basis of its hydrocarbon-like g factor and the large splitting from four β-protons, which occupy conformationally suitable positions for strong interaction in this species, as well as the typical value of $a(\alpha\text{-H})$. The 2-tetrahydrothiophenyl radical could not be detected either by increasing the power or by reducing the concentration of hydrogen peroxide.

2-Methylthioethanol at pH 1·0 gave both the radical $\cdot CH_2SCH_2CH_2OH$ [1] and a species which we believe to be the dimeric radical-cation [the seven most intense lines of the eleven expected for this species if $a(Me) = a(CH_2)$ were observed]; only the former radical was detected at pH 2·5. 1,3-Bis(methylthio)propane at pH 2·5 gave the radicals $\cdot CH_2\cdot S[CH_2]_3SMe$ and $\cdot CH(SMe)\cdot [CH_2]_2SMe$, but neither at this pH nor at pH 1·0 were there resonances which could be unambiguously attributed to either a dimeric radical-cation or the possible cyclic radical-cation. No signal could be detected on oxidation of the following compounds, possibly because of their low solubility in water: dibutyl sulphide, di-t-butyl sulphide, and 1,3,5-trithian.

We also examined the use of the titanium(III)–persulphate couple, in which the reactive entity is considered to be the sulphate radical-anion,[10] for the oxidation of dimethyl and diethyl sulphide at pH 2·2. The same spectra were recorded as with the titanium(III)–peroxide system at pH 2·5, but their intensities were less by a factor of *ca.* 10.

If the spectra described above are indeed from dimeric radical-cations, then oxidation of a mixture of two sulphides should give three such species. We tested this by oxidising a mixture of dimethyl sulphide and tetrahydrothiophen at pH 2·5. When the reactants were in equimolar proportion, the spectrum showed essentially only the presence of the dimeric radical-cation from tetrahydrothiophen; however, with three times as much dimethyl sulphide as tetrahydrothiophen, not only were signals from $Me_2S\cdot SMe_2^{+\cdot}$ and $[CH_2]_4S\cdot S[CH_2]_4^{+\cdot}$ observed but also there were five resonances which were consistent with their being from a radical with $a(6H)$ 0·68, $a(4H)$ 0·99 mT, g 2·0103; the lines were simulated satisfactorily by these parameters, and it was shown that the remaining lines would have been masked by those from the other two radical-cations. These parameters are in the ranges expected for the species $[CH_2]_4S\cdot SMe_2^{+\cdot}$ by comparison with the values for the corresponding two symmetrical radical-cations. The relative concentrations of the three radical-cations were $Me_2S\cdot SMe_2^{+\cdot} : [CH_2]_4S\cdot SMe_2^{+\cdot} : [CH_2]_4S\cdot S[CH_2]_4^{+\cdot} =$ 1·0 : 2·1 : 1·2.

---

[9] A. G. Davies, B. P. Roberts, and B. R. Sanderson, Abstracts, The Autumn Meeting of the Chemical Society, Nottingham, 1972, p. G8.

[10] R. O. C. Norman, P. M. Storey, and P. R. West, *J. Chem. Soc.* (*B*), 1970, 1087.

Intensity and Linewidth of the Spectrum of $Me_2S{\cdot}SMe_2^{+\cdot}$.—The intensity of the spectrum of the radical-cation $Me_2S{\cdot}SMe_2^{+\cdot}$ (measured as the product of the square of the peak-to-peak linewidth of the first derivative, ΔH, and the height of a suitable resonance, Y, for lines of the same shape) varied with the concentration of dimethyl sulphide as shown in Figure 2. The levelling off of the concentration of the radical-cation at higher concentrations of the sulphide is probably due to the essentially complete scavenging of hydroxyl radicals. It is perhaps significant that the radical concentration varies linearly with $[Me_2S]^2$ when $[Me_2S]$ is fairly small, whereas we have found that the concentration of, *e.g.*, $\cdot CH_2OH$ from methanol under the same conditions varies linearly with [MeOH].

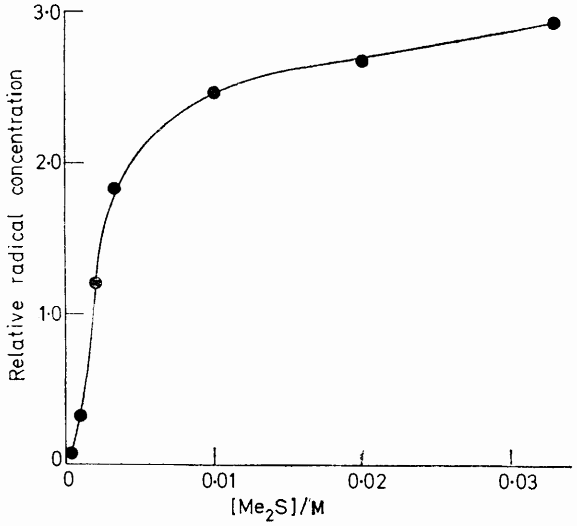


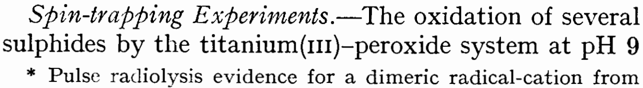
FIGURE 2 Variation of concentration of $Me_2S{\cdot}SMe_2^{+\cdot}$ with $[Me_2S]$

The linewidth varied with the concentration of dimethyl sulphide as shown in Table 2. The linear relationship between these quantities suggests the occurrence of the exchange process shown in reaction (6); thus, as the concentration increases, the average life time of the dimeric radical-cation decreases and the lines broaden. The rate constant for reaction (6) calculated from the variation in linewidth is $1{\cdot}5 \times 10^8$ l mol^{-1} s^{-1} at 11 °C.

TABLE 2

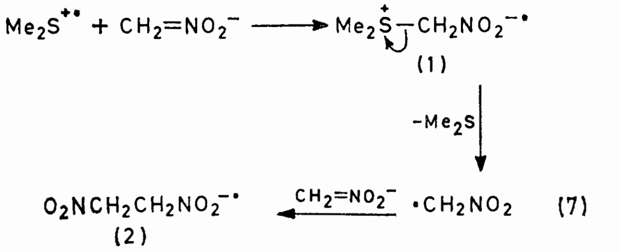
Variation of linewidth with concentration of dimethyl sulphide

Concentration/mol l^{-1}	0·002	0·010	0·020	0·033	0·050
Linewidth/μT	63	78	94	112	146



(6)

Spin-trapping Experiments.—The oxidation of several sulphides by the titanium(III)–peroxide system at pH 9 was carried out in the presence of the nitromethane *aci*-anion, $CH_2{:}NO_2^-$, which is an efficient trap for radicals.[11,12] When dimethyl sulphide was oxidised, three species were detected spectroscopically: $CH_3NO_2^{-\cdot}$, $CH_2OH{\cdot}NO_2^{-\cdot}$, and[12,13] $O_2N{\cdot}CH_2CH_2{\cdot}NO_2^{-\cdot}$. The first two were also detected when the sulphide was omitted, and the formation of the third is a characteristic of systems in which there is a radical present with a high electron affinity, such as the sulphate radical-anion[10] or[12] Br· (possibly as $BrOH^{-\cdot}$ or $Br_2^{-\cdot}$). Its formation in this case is consistent with the presence of the radical-cation $Me_2S^{+\cdot}$ and reaction (7), although electron-transfer from the *aci*-anion to this radical-cation may occur within a looser association of the reactants than the adduct (1).



(7)

The following three compounds behaved in the same way as dimethyl sulphide: tetrahydrothiophen, 2-methyl-1,3-dithiolan, and 2,2-dimethyl-1,3-dithiolan. However, in other cases the sulphide gave rise not only to the radical-anion (2) but also to species resulting from the trapping of a carbon- or sulphur-centred radical; the data are in Table 3, the assignments of the spectra following the principles described previously.[1]

Conclusions.—Although a complete spectrum attributable to a species of the type $R_2S{\cdot}SR_2^{+\cdot}$ was observed only for tetrahydrothiophen, the splitting patterns and g factors observed in three other cases, and evidence for a ' crossed ' dimeric species from tetrahydrothiophen and dimethyl sulphide, leave no doubt that such species are formed by a range of sulphides.* They represent a new class of radicals for which, since each sulphur atom is formally associated with 8·5 valence electrons, d orbital participation must be invoked to account for the bonding. The detailed electronic structure is not clear, but the following is notable. The ratio of the proton hyperfine splittings in the species $[CH_2]_4S{\cdot}S[CH_2]_4^{+\cdot}$ from tetrahydrothiophen and $Me_2S{\cdot}SMe_2^{+\cdot}$ from dimethyl sulphide is close to 3 : 2, and this is what would be expected, by analogy with carbon radicals, if the spin on sulphur is in an orbital perpendicular to the plane of the carbon and sulphur atoms [*e.g.* (3)] and interaction with protons is by a mechanism of hyperconjugative type with a $\cos^2\theta$ dependence.[2]

In the absence of kinetic data, no definitive statement about the relative ease with which a particular species

---

* Pulse radiolysis evidence for a dimeric radical-cation from dimethyl sulphide also exists (G. Meissner, A. Henglein, and G. Beck, *Z. Naturforsch.*, 1967, **22b**, 13).

[11] B. C. Gilbert, J. P. Larkin, and R. O. C. Norman, *J.C.S. Perkin II*, 1972, 1272.

[12] D. Behar and R. W. Fessenden, *J. Phys. Chem.*, 1972, **76**, 1710.

[13] D. J. Edge, R. O. C. Norman, and P. M. Storey, *J. Chem. Soc.* (*B*), 1970, 1096.

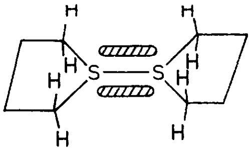
Table 3

E.s.r. parameters for radicals formed with $CH_2{:}NO_2^-$

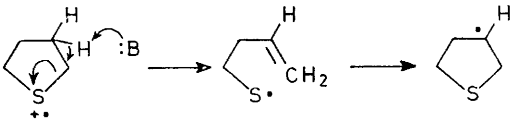
Sulphide	Radical	Splitting constants (mT) a(N)	a(β-CH_2)	a(other)	g
Et_2S	$EtS{\cdot}CH_2NO_2^{-\cdot}$	2·44	0·63	0·07 (2δ-H)	2·0055
	$EtS{\cdot}CHMe{\cdot}CH_2NO_2^{-\cdot}$	2·52	1·97 [a]	0·06 (1γ-H)	2·0050
Pr_2S	$PrS{\cdot}CH_2NO_2^{-\cdot}$	2·45	0·64	0·08 (2δ-H)	2·0055
$Bu^tSCH_2CH_2CH_2OH$	$HO[CH_2]_3S{\cdot}CH_2NO_2^{-\cdot}$	2·45	0·63	0·08 (2δ-H)	2·0056
	$Bu^tS{\cdot}CH_2NO_2^{-\cdot}$ [b]	2·51	0·88		2·0054

[a] The sum of the splittings for the two inequivalent β-protons; the inner two lines of the β-proton pattern were too broad for accurate measurement (*cf.* ref. 11). [b] *cf.* Ref. 1.

$R_2S^{+\cdot}$ forms $R_2S{\cdot}SR_2^{+\cdot}$ or undergoes other reactions can be made, but the following interpretation is consistent with the results so far. Along the series Me_2S, Et_2S, $Pr^i{}_2S$, the ratio of the observed concentrations of the dimeric radical-cation to the carbon-centred radical at pH 1 decreases. Now, evidence from our earlier study[1] indicated that the hydrogen atom in $(RS{\cdot}CHR^1R^2)^{+\cdot}$ is lost, as a proton, with decreasing ease as R^1, R^2 are varied from H to Me, so that the present results suggest that the ease of reaction of $R_2S^{+\cdot}$ with R_2S falls off sharply in the order $R = Me > Et > Pr^i$. It is notable, too, that the oxidation of dimethyl sulphide and tetrahydrothiophen in the presence of $CH_2{:}NO_2^-$ gives only the species (2) whereas that of diethyl sulphide and 2-methylthioethanol results in the trapping of carbon- and sulphur-centred radicals [as well as the species (2) in the former case]. This suggests that the radical-cations from the first two are more reactive than those from the other two towards $CH_2{:}NO_2^-$, just as the results in strongly acid solution for formation of the dimeric sulphur radical-cations suggest that they are more reactive towards the corresponding sulphide. Both trends are consistent with steric hindrance to the reaction of a species $R_2S^{+\cdot}$ with nucleophiles.


(3)

Finally, it is surprising that the oxidation of tetrahydrothiophen at pH 3·6 gives the radical (6), since the acyclic sulphides we have studied here and previously[1] yield radicals derived, formally, by loss of a hydrogen atom from C–H next to sulphur but not further removed. Possibly the radical-cation (4) undergoes elimination as in reaction (8) in preference to the loss of an α-proton owing to the relief of conformational strain, the resulting radical (5) then closing to give (6).



(4) (5) (6) (8)

EXPERIMENTAL

Materials.—3-t-Butylthiopropan-1-ol was prepared from t-butyl mercaptan and 3-chloropropan-1-ol by adapting the method for 2-t-butylthioethanol.[14] 2-Methyl- and 2,2-dimethyl-dithiolan were prepared from ethane-1,2-dithiol with acetaldehyde and acetone, respectively.[15] 1,3-Bis-methylthiopropane was prepared from propane-1,3-dithiol with sodium methoxide and methyl iodide.[16] All other materials were commercial samples.

Methods.—E.s.r. spectra were determined on a Varian E-3 spectrometer with an X band klystron and 100 kHz modulation. Splitting constants were measured to within ±0·01 mT and g factors to within ±0·0001 by comparison with Fremy's salt [a(N) 1·3091 mT,[17] g 2·0055 [18]]. Spectrum simulation was carried out with a programme kindly supplied by Dr M. F. Chiu and was used to confirm splitting constants and relative concentrations of radicals. pH Measurements were made to within ±0·01 unit with a Beckman model 72 pH meter.

Mixing chambers which allowed simultaneous mixing of either two or three solutions just before passage into the spectrometer cavity were employed; the total flow-rate was *ca.* 100 ml min^{-1}.

For reactions in the three-stream mixing chamber at pH 2·5, the first solution contained titanium(III) chloride (0·012M), the second hydrogen peroxide (0·036M), and the third the sulphide (usually 0·01—0·015M or saturated if the solubility was low). For reactions at pH 1·0 the titanium(III) and hydrogen peroxide solutions were acidified with sulphuric acid to give a pH of 1·0 after mixing. For reactions at pH 3·6 EDTA (6 g l^{-1}) was added to the titanium(III) solution and the pH of this solution adjusted to 4·7 with ammonia; with equal flow rates this gave a final pH of 3·6. For spin-trapping experiments the titanium(III) solution was prepared as for experiments at pH 3·6 except that the pH was adjusted to 9·0 with ammonia. The third solution contained both the sulphide (*ca.* 0·01M) and nitromethane (0·019M) and the pH was adjusted to 9·0 with ammonia. For reactions with persulphate, the hydrogen peroxide solution was replaced by a sodium persulphate solution (0·015M).

The support of this work by the S.R.C. is gratefully acknowledged.

[3/770 *Received*, 11*th April*, 1973]

---

[14] C. D. Hurd and K. Wilkinson, *J. Amer. Chem. Soc.*, 1949, **71**, 3429.

[15] H. Fuhrer and H. H. Günthard, *Helv. Chim. Acta*, 1962, **45**, 2036.

[16] K. S. Boustany and A. Jacot-Guillarmod, *Chimia*, 1969, **23**, 331.

[17] R. J. Faber and G. K. Fraenkel, *J. Chem. Phys.*, 1967, **47**, 2462.

[18] J. Q. Adams, S. W. Nicksic, and J. R. Thomas, *J. Chem. Phys.*, 1966, **45**, 654.