Electron Spin Resonance Studies. Part XXXVII.[1] Oxidation of β-Hydroxy-sulphides by the Hydroxyl Radical and Structural Features of Sulphur-conjugated Radicals

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E.s.r. spectroscopy in conjunction with a rapid-flow system has been used to show that both carbon radicals and thiyl radicals mediate in the oxidation of some β-hydroxy-sulphides with the hydroxyl radical in aqueous solution; the carbon radicals are detected directly and the thiyl radicals by way of their adducts with a spin trap. It is suggested that both types of radical are formed following the abstraction of an electron from sulphur; thus, the sulphur radical cation can undergo loss of a proton from an adjacent carbon atom or heterolysis of an adjacent C–C bond, to yield a carbon radical, or heterolysis of a C–S bond, to yield a thiyl radical. The structures of the carbon radicals are discussed in the light of the trends shown in their e.s.r. parameters.

SEVERAL studies of the e.s.r. spectra of sulphur-containing free radicals in solution have been reported recently. For example, β-thioalkyl radicals have been generated by the one-electron oxidation of thiols in the presence of an olefin to trap the thiyl radical,[2,3] and α-thioalkyl radicals have been obtained by the one-electron oxidation of sulphides,[2,4,5] alkyl disulphides,[4] and β-thiocarboxylate ions.[6] Our interest in the structural features and fragmentation reactions of radicals of the type $\cdot CH(OR)\cdot CH_2X$ ($R = H$ or alkyl; $X =$ an electronegative substituent), as revealed by their e.s.r. spectra,[7,8] led us to study the one-electron oxidation of some β-hydroxy-sulphides in the hope of obtaining the e.s.r. spectra, and studying the behaviour, of radicals of the types $\cdot CH(SR)\cdot CH_2OH$ and $\cdot CH(OH)\cdot CH_2SR$. The results both throw light on the mechanisms of oxidation of organic sulphides and yield information about the structure of sulphur-conjugated carbon radicals.

Radicals were generated from sulphides by oxidation with the titanium(III)–hydrogen peroxide system,[9] usually at pH 4·5. The spectra are reported in the Table together with their assignments, and, where two or more radicals are observed, their concentrations relative to one of them; one spectrum is illustrated in the Figure. Except in a few cases, which are discussed in detail below, the assignments were straightforward; they are based on the hyperfine splitting constants and are also in accord with the fact that the *g*-factors are in all cases significantly higher than those of not only hydrocarbon-like radicals but also hydroxy-conjugated radicals,[9] consistent with there being a sulphur atom attached to the tervalent carbon atom. The assignments of the spectra from β-isopropylthioethanol are illustrative. The spectrum with a(6H) 2·01, a(2H) 0·08 mT is attributed to the radical $\cdot CMe_2\cdot SCH_2CH_2OH$, for which a large splitting from the methyl protons would be expected and for which a γ-proton splitting of 0·08 mT is reasonable. The spectrum with a(2H) 1·63, a(1H) 0·20 mT cannot be ascribed to a species formed from the sulphide only by the loss of a hydrogen atom; the *g*-factor suggests sulphur-conjugation, and the two splittings are consistent with the presence of two α-protons and one γ-proton (compare, especially, the parameters for the radical $\cdot CH_2\cdot SCH_2CH_2OH$, formed from β-methylthioethanol), so that the spectrum is assigned to the radical $\cdot CH_2\cdot SCHMe_2$, which is derived, formally, by the loss of the group CH_2OH. In addition to the spectra of these two radicals, there were four lines (in two closely separated pairs) which cannot be attributed with certainty; however, a reasonable interpretation is that they were the lines of relative intensity two in the spectrum of the radical $\cdot CH(CH_2OH)\cdot SCHMe_2$, for on this basis the measured spacings of the four lines yield single-proton splittings (1·66 and 0·16 mT) which are in the ranges expected for the α- and γ-protons in this radical, and the lines of relative intensity one would be masked by resonances for other radicals, given that a(β-H) is in the anticipated range [*ca.* 1 mT; *cf.* the radicals $\cdot CH(CH_2OH)\cdot SR$ ($R = Bu^t$ or CH_2CH_2OH)].

Some of the expected resonances were masked in one other case. Only three of the nine lines expected for the radical $\cdot CH_2\cdot SCH_2Me$ from β-ethylthioethanol could be discerned, corresponding to lines 3, 7, and 8 (read from low to high field; relative intensities 1, 1, 2) of the triplet of triplets expected for this species; however, these lines yielded splitting constants for the α- and γ-protons in the ranges typical for these protons in radicals of this type (*cf.* the data for $\cdot CH_2\cdot SCH_2CH_2OH$), leaving little doubt about the validity of the assignment.

In the spectrum of the radical $\cdot CH(SMe)\cdot CH_2CH(NH_3^+)CO_2^-$ from methionine, the central line(s) expected from interaction with the two β-protons could not be discerned. These protons are likely to have slightly different splittings as the result of the presence of an

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[1] Part XXXVI, A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J.C.S. Perkin II*, 1972, 2053.

[2] P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, 1971, **93**, 846.

[3] T. Kawamura, M. Ushio, T. Fujimoto, and T. Yonezawa, *J. Amer. Chem. Soc.*, 1971, **93**, 908.

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

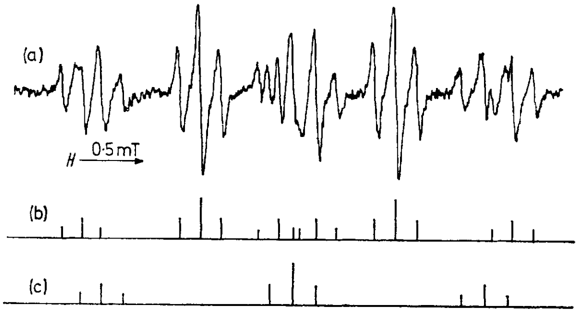
[5] I. Biddles, A. Hudson, and J. T. Wiffen, *Tetrahedron*, 1972, **28**, 867.

[6] P. Neta and R. W. Fessenden, *J. Phys. Chem.*, 1971, **75**, 2277.

[7] A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J.C.S Perkin II*, 1972, 786.

[8] B. C. Gilbert, J. P. Larkin, and R. O. C. Norman, *J.C.S. Perkin II*, 1972, 794.

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



E.s.r. spectrum, (a), observed during the oxidation of thiodiglycol, together with stick-reconstructions for the spectrum of (b) $\cdot CH(CH_2OH)\cdot SCH_2CH_2OH$ and (c) $\cdot CH_2SCH_2CH_2OH$

adjacent chiral carbon atom,[10] and we infer that the inner two resonances of the expected four are broadened beyond detection owing to restricted rotation and possibly also because the effect of the chiral carbon itself fluctuates owing to rapid exchange processes of its polar substituents. It is, incidentally, notable that the oxidation of methionine under our conditions gives radicals derived, formally, by the abstraction of a hydrogen atom, whereas when methionine is allowed to stand with hydrogen peroxide before reaction with titanium(III) ion, the radicals detected are fragmentation products from its sulphoxide.[11]

E.s.r. spectra and their assignments

Reactant	Radical	Relative concentration	Splitting constants (mT) [a] $a(\alpha\text{-H})$	$a(\beta\text{-H})$	$a(\gamma\text{-H})$	g	ΔH/ mT
$MeSCH_2CH_2OH$	$\cdot CH_2SCH_2CH_2OH$		1·64 (2H)		0·19 (2H)	2·0048	0·045
$EtSCH_2CH_2OH$	$\cdot CH_2SCH_2Me$ [b]	1	1·625 (2H)		0·22 (2H)	2·0049	0·045
	$\cdot CHMeSCH_2CH_2OH$	3	1·70 (1H)	2·09 (3H)	0·14 (2H)	2·0044	0·035
$PrSCH_2CH_2OH$	$\cdot CH_2SCH_2Et$	1	1·63 (2H)		0·23 (2H)	2·0049	0·045
	$\cdot CH(CH_2Me)SCH_2CH_2OH$	3	1·66 (1H)	1·89 (2H)	0·13 (2H)	2·0043	0·04
$Me_2CHSCH_2CH_2OH$	$\cdot CH_2SCHMe_2$	1	1·63 (2H)		0·20 (1H)	2·0048	0·045
	$\cdot CMe_2SCH_2CH_2OH$	0·6		2·01 (6H)	0·08 (2H)	2·0037	0·03
	$\cdot CH(CH_2OH)SCHMe_2$	0·25	1·66 (1H)	c	0·16 (1H)	2·0045	0·045
$Bu^tSCH_2CH_2OH$	$\cdot CH_2SBu^t$	1	1·61 (2H)			2·0049	0·045
	$\cdot CH(CH_2OH)SBu^t$	0·25	1·64 (1H)	1·01 (2H)		2·0045	0·045
$S(CH_2CH_2OH)_2$	$\cdot CH_2SCH_2CH_2OH$	1	1·64 (2H)		0·19 (2H)	2·0048	0·045
	$\cdot CH(CH_2OH)SCH_2CH_2OH$	2	1·67 (1H)	1·00 (2H)	0·175 (2H)	2·0045	0·045
$S(CH_2CMe_2OH)_2$	$\cdot CH_2SCH_2CMe_2OH$		1·64 (2H)		0·21 (2H)	2·0048	0·045
$MeSCH_2CH_2CH(CO_2H)NH_2$	$\cdot CH_2SCH_2CH_2CH(NH_3^+)CO_2^-$	1	1·64 (2H)		0·21 (2H)	2·0048	0·045
	$\cdot CH(SMe)CH_2CH(NH_3^+)CO_2^-$	1·5	1·68 (1H)	2·97 (2H) [d]	0·29 (3H)	2·0046	0·045

[a] α, β, γ refer, respectively, to protons at the tervalent carbon atom and successive atoms. [b] Only three lines were observed; see text. [c] Not observed; see text. [d] The sum of the values for the two β-protons; see text.

In the case of four of the thio-compounds, we sought evidence for the mediation of radicals other than those detected directly; for this purpose we carried out oxidations at pH 9 in the presence of the *aci*-anion of nitromethane, since this is an efficient trap for many reactive radicals and yields relatively long-lived species.[10] When β-methylthioethanol was oxidised in this way, the radical observed had a(N) 2·55, a(2H) 0·96, a(2H) 0·06 mT, g 2·0050; we infer that it is the species $CH_2(OH)\cdot CH_2SCH_2CH_2NO_2^{-\cdot}$, formed from the radical $\cdot CH_2\cdot SCH_2CH_2OH$, the larger and smaller proton splittings being due to the β- and γ-methylene protons, respectively (relative to the nitro-function). Thiodiglycol gave both this radical and one with splitting constants identical with those of the radical obtained by oxidising β-mercaptoethanol in the presence of the trap [a(N) 2·42, a(2H) 0·59, a(2H) 0·08 mT, g 2·0055] (relative concentrations 2·5 : 1); we infer that the species is $CH_2(OH)\cdot CH_2SCH_2NO_2^{-\cdot}$, formed from the radical $\cdot SCH_2CH_2OH$, the larger and smaller proton splittings being due to the β- and δ-protons, respectively. The oxidation of β-t-butylthioethanol gave three radicals: the spectrum of one was identical with that from β-mercaptoethanol, indicating mediation of the radical $\cdot SCH_2CH_2OH$; the spectrum of the second was identical with that from the oxidation of 1,1-dimethylethanethiol in the presence of the trap [a(N) 2·51, a(2H) 0·88 mT, g 2·0054], from which we infer mediation of the radical $\cdot SBu^t$ and thence $Bu^tSCH_2NO_2^{-\cdot}$; the spectrum of the third [a(N) 2·55, a(2H) 0·96, a(2H) 0·06 mT, g 2·0050] we attribute to the radical $Bu^tSCH_2CH_2NO_2^{-\cdot}$, formed from $\cdot CH_2\cdot SBu^t$; the relative concentrations of the three were *ca.* 3 : 1 : 6. The oxidation of the compound $S(CH_2CMe_2\cdot OH)_2$ gave a spectrum with a(N) 2·42, a(2H) 0·58, a(2H) 0·08 mT, g 2·0056, attributed to the radical $Me_2C(OH)\cdot CH_2SCH_2NO_2^{-\cdot}$ [*cf.* the parameters for the radical $CH_2(OH)\cdot CH_2SCH_2NO_2^{-\cdot}$]; other resonances corresponded to a radical with g 2·0050, presumably $Me_2C(OH)\cdot CH_2SCH_2CH_2NO_2^{-\cdot}$, but the spectrum was too complex for firm attribution. (In this series of radical anions, those of type $RSCH_2NO_2^-$ have significantly higher g-factors than those of type $RSCH_2CH_2NO_2^{-\cdot}$, doubtless reflecting the acquisition of some of the spin by sulphur in the former case.)

Modes of Formation of Radicals.—It is notable that, except for β-methylthioethanol, each of the β-hydroxysulphides yielded a radical by the fragmentation, in a formal sense, of the group CH_2OH. We considered three possible ways in which this might occur.

(*a*) A compound of the type $CHR'(OH)\cdot CH_2SR$ would be expected to react with the hydroxyl radical by loss of

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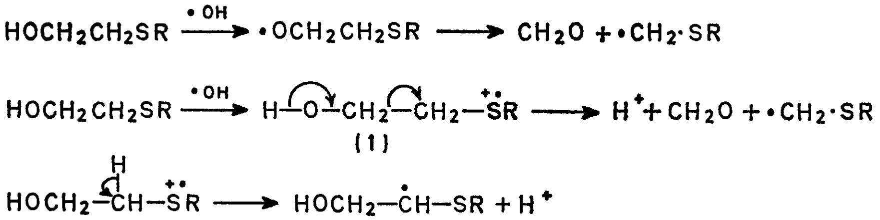
[10] B. C. Gilbert, J. P. Larkin, and R. O. C. Norman, *J.C.S. Perkin II*, 1972, 1272.

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

a hydrogen atom from the hydroxyl-bearing carbon atom to give the radical $\cdot CR'(OH)\cdot CH_2SR$; this might fragment to the radical $\cdot CH_2SR$ and the aldehyde R'CHO. However, this possibility was ruled out by our finding that the compound $S(CH_2CMe_2OH)_2$, which does not possess such an abstractable hydrogen atom, nevertheless yields the radical $\cdot CH_2SCH_2CMe_2OH$ by, formally, the loss of CMe_2OH, and acetone was detected as a product.

(*b*) Abstraction of a hydrogen atom from the hydroxyl group and fragmentation could yield the species $\cdot CH_2SR$ [reaction (1)]. Now, alcoholic hydroxy-groups are relatively inert towards the hydroxyl radical (although not towards the sulphate radical-anion [12]), but possibly in this case the abstraction and fragmentation could be concerted, driving force being provided in part by the development of the strong stabilisation energy of sulphur-conjugated radicals.[13]

(*c*) Reaction with the hydroxyl radical might occur at sulphur, to yield the radical-cation (1); this reaction, which would be expected to take place more readily with a sulphide than with an ether, could be followed by fragmentation as in reaction (2). This process bears some similarity to the reaction of phenethyl alcohol with the hydroxyl radical in which in essence, by way of adducts formed by addition of the radical to aromatic carbon, the radical abstracts one electron from the aromatic ring, with fragmentation of the side-chain to yield the benzyl radical; [14] reaction (2) could likewise occur by way of addition of the hydroxyl radical, in this case at sulphur (*cf.* ref. 15). We note also that the other carbon radicals detected could be formed from the radical cation (1), by the loss of a proton from either carbon atom attached to sulphur [*e.g.* reaction (3)], as could the thiyl radicals (see later).

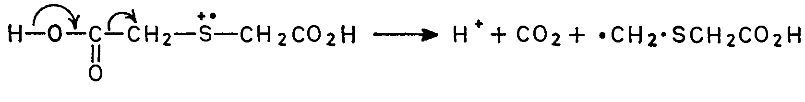


$$HOCH_2CH_2SR \xrightarrow{\bullet OH} \bullet OCH_2CH_2SR \longrightarrow CH_2O + \bullet CH_2\cdot SR \qquad (1)$$

$$HOCH_2CH_2SR \xrightarrow{\bullet OH} \underset{(1)}{H{-}O{-}CH_2{-}CH_2{-}\overset{+\bullet}{S}R} \longrightarrow H^+ + CH_2O + \bullet CH_2\cdot SR \qquad (2)$$

$$HOCH_2{-}\overset{H}{C}H{-}\overset{+\bullet}{S}R \longrightarrow HOCH_2{-}\overset{\bullet}{C}H{-}SR + H^+ \qquad (3)$$

Apart from the fact that formation of the sulphur radical-cation provides a path for the generation of all the detected radicals, we believe that mechanism (*c*) is more probable than mechanism (*b*) for the following reason. Under the same reaction conditions, not only does the ratio of the observed concentrations of the radicals $\cdot CH_2\cdot SCHR^1R^2$ and $\cdot CR^1R^2\cdot SCH_2CH_2OH$ from the sulphide $CH_2(OH)\cdot CH_2SCHR^1R^2$ increase with the degree of alkylation (0 for $R^1 = R^2 = H$; 0·33 for $R^1 = H$, $R^2 = Me$; 1·6 for $R^1 = R^2 = Me$), but also the actual concentration of the former radical was found to increase in this order; the relative values, for the examples quoted above, were 0, 10, and 30, and, for $\cdot CH_2\cdot SBu^t$ from β-t-butylthioethanol, 60. Now, there is no reason to expect that the natures of R^1 and R^2 will significantly affect the rates of formation or destruction of this type of radical, and thus its observed concentration, if it is formed as in reaction (1). However, the results are in accord with mechanism (*c*) provided that reaction of the hydroxyl radical at sulphur becomes faster as the extent of alkylation at an adjacent carbon atom is increased (as we should expect, at least by consideration of ionisation potentials in the gas phase [16]); moreover, the trend in the ratio of the observed concentrations of the pairs of radicals referred to above could be due in part to a reduction in the ease with which a proton is lost from the group CHR^1R^2, to give the radical $\cdot CR^1R^2\cdot SCH_2CH_2OH$, as methyl groups are successively introduced (*cf.* the behaviour of nitrogen radical cations [17]). In addition, it is notable that the mediation of sulphur radical-cations could underlie the formation of the radical $\cdot CH_2\cdot SCH_2CO_2H$ and its conjugate base from, respectively, thiodiglycollic acid and the titanium(III)–peroxide system [11] and thiodiglycollate anion on pulse radiolysis [6] [*e.g.* reaction (4)].



$$H{-}O{-}\underset{\underset{O}{\|}}{C}{-}CH_2{-}\overset{+\bullet}{S}{-}CH_2CO_2H \longrightarrow H^+ + CO_2 + \bullet CH_2\cdot SCH_2CO_2H \qquad (4)$$

One of two possible paths is likely to be responsible for the formation of the thiyl radicals: either abstraction of a hydrogen atom from the hydroxyl-bearing carbon atom is followed by homolysis [*e.g.* reaction (5)]; or formation of the sulphur radical-cation is followed by heterolysis [*e.g.* reaction (6)]. Reaction (5), with the t-butoxyl radical in place of hydroxyl, has been suggested to account for the formation of acetone from (2; R = R' = Me),[18] but reaction *via* the sulphur radical-cation is also

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[12] A. Ledwith, P. J. Russell, and L. H. Sutcliffe, *Chem. Comm.*, 1971, 964.

[13] A. Ohno and Y. Ohnishi, *Tetrahedron Letters*, 1969, 4405.

[14] R. O. C. Norman and R. J. Pritchett, *J. Chem. Soc.* (*B*), 1967, 926.

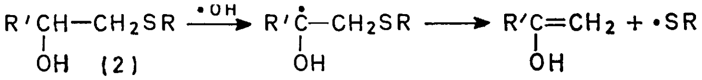
[15] R. N. Haszeldine, B. Higginbottom, R. B. Rigby, and A. E. Tipping, *J.C.S. Perkin I*, 1972, 155.

[16] H. Bock and G. Wagner, *Angew. Chem. Internat. Edn.*, 1972, **11**, 150.

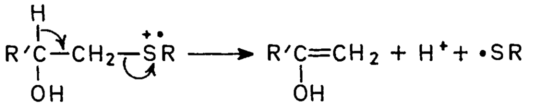
[17] C. A. Audeh and J. R. Lindsay Smith, *J. Chem. Soc.* (*B*), 1970, 1280; M. Masui and H. Sayo, *ibid.*, 1971, 1593.

[18] E. S. Huyser and R. M. Kellogg, *J. Org. Chem.*, 1966, **31**, 3366.

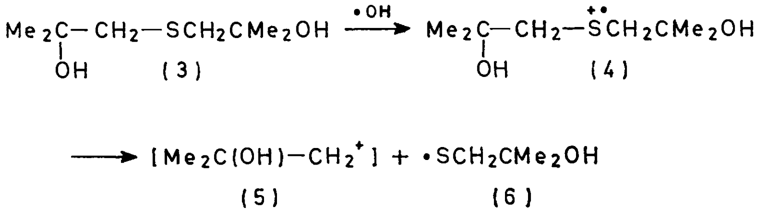
consistent with the available evidence.[18] However, the compound (3), which cannot react to give a thiyl radical by the former mechanism, nevertheless yields such a radical, (6), as shown by the trapping experiment above, so that in this case at least we infer the mediation of the sulphur radical-cation (4). [Methyl ethyl ketone, the formation of which might have accompanied the heterolysis of the radical-cation (4) (*cf.* the pinacol rearrangement) could not be detected; however, acetone was obtained, in accord with the occurrence of reaction (8) and detection of the radical $\cdot CH_2SCH_2CMe_2OH$.]



$$\underset{\text{OH}\ \ (2)}{\text{R}'\text{CH}}\text{—CH}_2\text{SR} \xrightarrow{\cdot\text{OH}} \underset{\text{OH}}{\text{R}'\dot{\text{C}}}\text{—CH}_2\text{SR} \longrightarrow \underset{\text{OH}}{\text{R}'\text{C}}\text{=CH}_2 + \cdot\text{SR} \qquad (5)$$

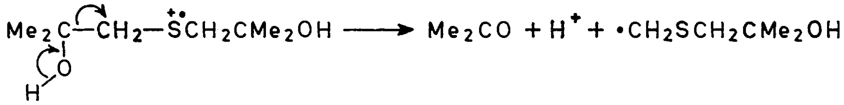


$$\underset{\text{OH}}{\overset{\text{H}}{\text{R}'\text{C}}}\text{—CH}_2\text{—}\overset{+\bullet}{\text{S}}\text{R} \longrightarrow \underset{\text{OH}}{\text{R}'\text{C}}\text{=CH}_2 + \text{H}^+ + \cdot\text{SR} \qquad (6)$$



$$\underset{\text{OH}\qquad (3)}{\text{Me}_2\text{C}}\text{—CH}_2\text{—SCH}_2\text{CMe}_2\text{OH} \xrightarrow{\cdot\text{OH}} \underset{\text{OH}\qquad (4)}{\text{Me}_2\text{C}}\text{—CH}_2\text{—}\overset{+\bullet}{\text{S}}\text{CH}_2\text{CMe}_2\text{OH}$$

$$\longrightarrow \underset{(5)}{[\text{Me}_2\text{C(OH)—CH}_2^{\ +}]} + \underset{(6)}{\cdot\text{SCH}_2\text{CMe}_2\text{OH}} \qquad (7)$$



$$\underset{\text{O—H}}{\text{Me}_2\text{C}}\text{—CH}_2\text{—}\overset{+\bullet}{\text{S}}\text{CH}_2\text{CMe}_2\text{OH} \longrightarrow \text{Me}_2\text{CO} + \text{H}^+ + \cdot\text{CH}_2\text{SCH}_2\text{CMe}_2\text{OH} \qquad (8)$$

It is apparent that competing reactions are involved in the formation, from β-hydroxy-sulphides, of carbon radicals and thiyl radicals; we have suggested that the competition could occur after the formation of a sulphur radical-cation. Now, the thiyl radicals, although efficiently trapped, were not detected directly, whereas the carbon radicals were. However, this does not imply that formation of carbon radicals is the more rapid process, since not only are the relative rates of destruction of the two types of radical unknown but also the thiyl radicals could have escaped direct detection because their spectra are likely to have large linewidths owing to a marked anisotropy in g,[19] so that a concentration many times that of the carbon radicals would not necessarily have been observed. Indeed, in two cases there are indications that the formation of thiyl radicals is the preferred path. First, compound (2; R = R′ = Me) with the t-butoxyl radical gives acetone essentially quantitatively.[18] Secondly, from the oxidation of thiodiglycol (thiodiethanol) we obtained acetaldehyde but not formaldehyde, implying that the processes summarised by reaction (9) are more important than those summarised by reaction (10).

$$CH_2(OH)\cdot CH_2SCH_2CH_2OH \xrightarrow{\cdot OH} \cdot SCH_2CH_2OH + CH_3CHO + H_2O \qquad (9)$$

$$CH_2(OH)\cdot CH_2SCH_2CH_2OH \xrightarrow{\cdot OH} \cdot CH_2SCH_2CH_2OH + HCHO + H_2O \qquad (10)$$

Structural Features of Sulphur-conjugated Radicals.—Evidence has previously been adduced that a substituent SR at tervalent carbon is less effective than OR or OH at inducing deformation of the bonds at that carbon atom from coplanar towards pyramidal but more effective at delocalising the unpaired electron.[5,7,20] For example, the larger value of a(β-Me) for the radical ·CHMe·OEt (2·23 mT [7]) than for its sulphur analogue ·CHMe·SEt (1·98 mT [7]) indicates that there is a smaller spin density at the tervalent carbon atom in the latter and so shows that sulphur has a greater capacity than oxygen for removing spin, whereas the lower value of a(α-H) for the former radical (1·40 and 1·68 mT, respectively) has been interpreted as resulting from a more ' bent ' structure in the case of the oxygen-conjugated radical;[7] further, the ratio of a(β-Me) : a(α-H), which, we have argued, is a useful criterion for estimating whether a carbon radical is significantly ' bent ' or not,[7,21] is in the range of those for radicals which are believed to be coplanar at the tervalent carbon atom (*ca.* |1·2|), in the case of ·CHMe·SEt (|1·18|), unlike its oxygen analogue (|1·55|). Of the radicals reported in this paper, only one, $\cdot CHMe\cdot SCH_2CH_2OH$, possesses both α-H and β-Me; for this species, the value of a(β-Me)/a(α-H), |1·23|, is

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[19] P. B. Ayscough, ' Electron Spin Resonance in Chemistry,' Methuen, London, 1967, p. 350.

[20] A. Hudson and K. D. J. Root, *J. Chem. Soc.* (*B*), 1970, 656.

[21] A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Soc.* (*A*), 1971, 124.

also in the range expected for planar radicals. Our results, whilst in accord with this interpretation, give information about other structural features of sulphur-conjugated radicals and their dependence upon the nature of other substituents. Three features in particular are notable.

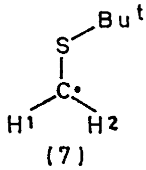
First, the introduction of a methyl group into the radical $\cdot CH_2 \cdot SCH_2CH_2OH$ in place of one of the α-hydrogen atoms results in a small increase in *a*(α-H) for the remaining α-proton (1·64 to 1·70 mT). Now, introduction of an alkyl group in place of α-H in other carbon radicals causes a significant decrease in *a*(α-H), whether the radicals are coplanar at the tervalent carbon atom or not; in the former case, the decrease [*e.g.*, *a*(α-H) 2·16 and 2·02 mT for $\cdot CH_2 \cdot CO_2H$ and $\cdot CHMe \cdot CO_2H$, respectively [22]] reflects the capacity of the methyl group to acquire *ca.* 8% of the spin [23,24] from the tervalent carbon atom and, in the latter, the decrease doubtless reflects both delocalisation and the effect of the methyl group on shape.[7,21]

Secondly, the value for the spin-withdrawing parameter for the substituent SCH_2CH_2OH is appreciably larger when it is estimated [24] from *a*(β-Me) for $\cdot CHMe \cdot SCH_2CH_2OH$ (0·224) compared with $\cdot CMe_2 \cdot SCH_2CH_2OH$ (0·188).

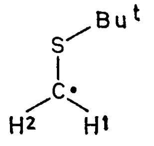
Thirdly, in the series $\cdot CH_2 \cdot SR$, $\cdot CHMe \cdot SR$, and $\cdot CMe_2 \cdot SR$ ($R = CH_2CH_2OH$), both the *g*-factor and *a*(γ-H) fall as the degree of alkylation is increased:

	$\cdot CH_2 \cdot SR$	$\cdot CHMe \cdot SR$	$\cdot CMe_2 \cdot SR$
g	2·0048	2·0044	2·0037
a(γ-H)/mT	0·19	0·14	0·08

One factor to be considered in interpreting these observations is that the radicals could exist in two conformations with a coplanar arrangement of the bonds to sulphur and the tervalent carbon atom which, when the latter contains two different substituents (apart from the sulphur group), would be expected to have different energies. Hudson *et al.* have found that, at low temperature, different splittings are resolved for the two α-protons in the radical $\cdot CH_2 \cdot SBu^t$ (1·62 and 1·75 mT), consistent with the occurrence of the planar conformations (7) and (8) in which H^1 and H^2 are magnetically inequivalent and which interconvert relatively slowly.[5] Thus, the higher value of *a*(α-H) for $\cdot CHMe \cdot SCH_2CH_2OH$ than for $\cdot CH_2 \cdot SCH_2CH_2OH$ could result if introduction of the methyl substituent into the latter led to a preference for that coplanar conformation in which the remaining α-proton adopted the position associated with the larger interaction with the spin. However, this is unlikely to be the only factor involved. First, on this basis *a*(α-H) would be expected to increase at the most (*i.e.* assuming 100% population of one conformer) by the difference between the smaller value for the two α-protons and their mean; as judged by the data for $\cdot CH_2 \cdot SBu^t$, this is likely to be only *ca.* 0·07 mT, *i.e.* less than the decrease in *a*(α-H) to be expected from delocalisation on to the methyl substituent (*ca.* 8% of 1·64, *i.e.* 0·13 mT). Secondly, these considerations do not account for the disparate values of the spin-withdrawing parameters for SCH_2CH_2OH or for the trends in *g* or *a*(γ-H) which have been referred to.



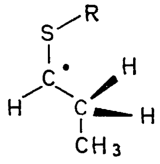
(7)



(8)

We suggest that another factor is important, namely, that the successive introduction of methyl groups in place of hydrogen at the tervalent carbon in the radicals $\cdot CH_2SR$ results in an increase in the compressional forces in the coplanar conformations relative to those noncoplanar ones which arise by rotation about the bond between sulphur and the tervalent carbon atom. The relatively higher population of the latter would result in less effective conjugation between the tervalent carbon atom and sulphur, and so in a reduction of the spin density at sulphur; in turn, the spin-withdrawing parameter for the sulphur substituent would fall, the *g*-factor would be reduced (tending ultimately to the value for a hydrocarbon-like radical), *a*(γ-H) would fall, and *a*(α-H) would rise (since there would be a higher spin density at the α-carbon atom). These trends correspond to those observed.

Similar trends in the e.s.r. parameters are apparent when the group CH_2OH replaces hydrogen at the tervalent carbon atom [*cf.* the *g*-factor and *a*(α-H) for $\cdot CH_2SBu^t$ and $\cdot CH(CH_2OH) \cdot SBu^t$, and these parameters and *a*(γ-H) for $\cdot CH_2SPr^i$ and $\cdot CH(CH_2OH) \cdot SPr^i$]. In contrast, the further changes which occur when one alkyl group is replaced by a larger one are small or insignificant; thus, in the series $\cdot CHR \cdot SCH_2CH_2OH$ the *g*-factor is only slightly smaller for R = Et than for R = Me, and in the series $\cdot CH(CH_2OH) \cdot SR$ the *g*-factors are the same, and *a*(α-H) is little different, for $R = Pr^i$ and Bu^t. That there should be little effect in the former series when Et replaces Me is not exceptional, for the methyl group in the former substituent can adopt positions in which it does not increase the steric compression as compared with that in the methyl-substituted radical [*e.g.* conformation (9)]; however, it is evident that an additional



(9)

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factor is operative in determining a(α-H) for the ethyl-substituted radical, since the value is ***smaller*** for ·CHEt·SCH_2CH_2OH than for ·CHMe·SCH_2CH_2OH.

Finally, a(β-H) for the methylene protons in the radicals ·CH(CH_2OH)·SR (R = Bu^t or CH_2CH_2OH) is unusually [7] low, as it is in other radicals which possess a $+M$ substituent at the α-carbon atom and a hydroxy-substituent at the β-carbon.[7]

EXPERIMENTAL

Materials.—Thiodiglycol (thiodiethanol), β-methylthioethanol, and methionine were obtained commercially. β-t-Butylthioethanol was prepared by the method of Hurd and Wilkinson,[25] and β-ethyl-, β-propyl-, and β-isopropylthioethanol were prepared from β-mercaptoethanol and the appropriate bromide or chloride in the presence of sodium ethoxide in ethanol.[26] *Bis-(2-hydroxy-2-methylpropyl) sulphide* was obtained from isobutylene chlorohydrin and sodium sulphide by the method described for the synthesis of thiodiglycol [27] and was obtained as a colourless, viscous oil, b.p. 106° at 0·2 mmHg, which solidified on long standing (m.p. 32—34°); $\nu_{max.}$ (liquid film) 3360 cm^{-1} (broad); τ ($CDCl_3$) 6·7 (2H, s), 7·19 (4H, s), and 8·62 (12H, s) (Found: C, 54·0; H, 10·1. $C_8H_{18}O_2S$ requires C, 53·9; H, 10·2%).

E.s.r. Studies.—A Varian E-3 e.s.r. spectrometer with 100 kHz modulation and an X-band klystron was used. 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,[28] g 2·0055 [29]]. Spectrum simulation, with a programme kindly supplied by Dr. M. F. Chiu, was used to confirm splitting constants and to determine relative concentrations of radicals. pH Measurements were made to within ±0·1 unit with an Electronic Instruments model 23A pH meter.

A mixing chamber which allowed the simultaneous mixing of three reactants was employed. All solutions were degassed by the passage of nitrogen. For reactions at pH 4·5, the first solution contained 0·008M-titanium(III) chloride, ethylenediaminetetra-acetic acid (6 g l^{-1}), and ammonia to give the required pH, the second contained 0·033M-hydrogen peroxide, and the third was a *ca.* 0·07M-solution of the sulphide. The trapping experiments were carried out by adding nitromethane (0·01M) to the third solution, both this and the first solution being treated with ammonia to give pH 9. There was no difference in the spectrum from the oxidation of the compound $S(CH_2CMe_2OH)_2$ in the presence of the nitromethane *aci*-anion when the solution of the sulphide under nitrogen was set aside for 1·5 h before oxidation instead of for only a few minutes, showing that the sulphur radical which was trapped was not formed from the possible hydrolysis product, $Me_2C(OH)\cdot CH_2SH$.

Product Studies.—Titanium(III) chloride solution (12·5%; 30 ml) in water (20 ml) and hydrogen peroxide solution (100 vol; 6 ml) in water (44 ml) were added simultaneously from burettes to a stirred solution of bis-(2-hydroxy-2-methylpropyl) sulphide (2 g) in water (50 ml). When addition was complete, the solution was stirred for a further 5 min and then a solution of 2,4-dinitrophenylhydrazine (0·4 g) in methanol (10 ml) containing concentrated sulphuric acid (1 drop) was added. After 5 min, the solution was extracted with chloroform and the extract was dried (Na_2SO_4). T.l.c.[30] [silica gel G; solvent 1: light petroleum (b.p. 40—60°) and diethyl ether (1 : 1); solvent 2: carbon tetrachloride, light petroleum (b.p. 60—80°), and ethyl acetate (20 : 5 : 7)] showed that the 2,4-dinitrophenylhydrazone of acetone was the major component; that of methyl ethyl ketone could not be detected.

The oxidation of thiodiglycol was carried out in the same way. The 2,4-dinitrophenylhydrazone of acetaldehyde was observed but that of formaldehyde was not detectable.

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