Electron Spin Resonance Studies. Part XLVII.[1] Sulphinyl- and Sulphonyl-Substituted Aliphatic Radicals

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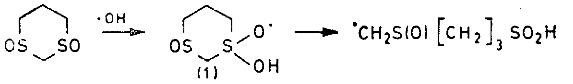
E.s.r. spectroscopy has been employed to characterise sulphinyl- [$\cdot CR^1R^2S(O)R^3$] and sulphonyl-conjugated [$\cdot CR^1R^2S(O_2)R^3$] carbon radicals. The former group are generated during the reaction between 1,3-bis-sulphoxides and the hydroxyl radical and from sulphoxides with the phenyl radical; the latter are formed from sulphones with either phenyl or hydroxyl (the reactivities and selectivities of which are compared). There is evidence that both groups of radicals are coplanar at the tervalent carbon atom, that the sulphinyl group withdraws *ca.* 6% of the spin from that carbon atom, and that the sulphonyl group has no capacity for spin-delocalisation. Evidence is also presented that acyclic radicals which possess a β-sulphinyl or β-sulphonyl substituent readily fragment to the corresponding alkene and a radical $RSO\cdot$ or $RSO_2\cdot$.

SULPHINYL- and sulphonyl-conjugated carbon radicals have been invoked as intermediates in a number of photochemical,[2] radiochemical,[3,4] and chemical[5] reactions of sulphoxides and sulphones. We now report their detection by the e.s.r. method, and discuss the structural features revealed by their e.s.r. parameters; we also note some mechanistic features. In all cases the radicals were highly transient and were generated for e.s.r. detection by a flow-system technique.

E.s.r. Spectra and their Assignments.—(i) *Sulphinyl-substituted radicals.* (a) *Reaction of* 1,3-*bis-sulphoxides with the hydroxyl radical.* There is evidence from our previous studies that sulphoxides react with the hydroxyl radical as in reaction (1);[6,7] no other process competes effectively with the first step in this sequence, which is essentially diffusion-controlled.[8]

$$R_2SO \xrightarrow{\cdot OH} R_2S(O\cdot)OH \rightarrow R\cdot + RSO_2H \qquad (1)$$



(2)

It therefore seemed likely that a 1,3-bis-sulphoxide would react with the hydroxyl radical to yield a sulphinyl-conjugated radical [*e.g.* reaction (2)], and we investigated this possibility with four cyclic bis-sulphoxides.

The 1,3-bis-sulphoxides were prepared in aqueous solution from[9] the corresponding disulphides and hydrogen peroxide at 0°. They were not isolated before use and were oxidised in aqueous acid by admixture with titanium(III) ion and hydrogen peroxide. A high conversion into the bis-sulphoxide was evident because, although sulphides and sulphoxides are of comparable reactivity towards the hydroxyl radical,[8] a radical from an incompletely oxidised disulphide was detected in only one case. Moreover, there was no spectroscopic indication of further oxidation to the sulphone (the spectra of radicals derived from sulphones are described later).

1,3-Dithian 1,3-dioxide gave two radicals in approximately equal concentration. We assign one [a(2H) 2.00 mT, g 2.0025] the structure $\cdot CH_2S(O)[CH_2]_3SO_2H$, formed as in reaction (2), with splitting from the protons on the tervalent carbon atom; support for this assignment is described later. Some further splitting of the hyperfine lines was evident, but we were unable to reduce the linewidth (*ca.* 0.1 mT) by an amount sufficient to achieve complete resolution. The second radical had hyperfine splittings [a(2H) 1.63, a(2H) 0.20 mT] and g factor (2.0048) compatible with its being a sulphur-conjugated radical,[10] and we believe it to be $\cdot CH_2S[CH_2]_3SO_2H$, formed from the monosulphoxide.

The other three cyclic 1,3-bis-sulphoxides, those from 1,3-dithiolan and its 2-methyl and 2,2-dimethyl-derivatives, gave only one radical each; they are assigned as α-sulphinyl-substituted radicals on the basis of their splitting constants (Table 1) and g factor (2.0025).

(b) *Reaction of sulphoxides with the phenyl radical.* Although the hydroxyl radical reacts with sulphoxides preferentially at sulphur, it appeared possible that another radical might display a relatively greater propensity for abstracting a hydrogen atom from a C–H bond adjacent to the sulphinyl group. This proved to be so for the phenyl radical.

We chose as the source of the phenyl radical the reaction between benzenediazonium ion and titanium(III) in basic solution. Although the radical when generated in this way has not been detected directly by the e.s.r. method, its relatively rapid formation has been inferred from the observation of the e.s.r spectra of a variety of adducts formed with unsaturated compounds.[11]

The admixture of benzenediazonium tetrafluoroborate, titanium(III) ion, and dimethyl sulphoxide at pH *ca.* 8

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[1] Part XLVI, B. C. Gilbert, H. A. H. Laue, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1975, 892.

[2] A. M. Koulkes-Pujo, F. Barat, J. C. Mialocq, and J. Sutton, *J. Photochem.*, 1973—1974, **2**, 439.

[3] R. Bensasson and E. J. Land, *Chem. Phys. Letters*, 1972, **15**, 195.

[4] P. B. Ayscough, K. J. Ivin, and J. H. O'Donnell, *Trans. Faraday Soc.*, 1965, **61**, 1110.

[5] C. Walling, G. M. El-Taliawi, and R. A. Johnson, *J. Amer. Chem. Soc.*, 1974, **96**, 133.

[6] B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1975, 303.

[7] B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1975, 308.

[8] G. Meissner, A. Henglein, and G. Beck, *Z. Naturforsch.*, 1967, **22b**, 13.

[9] D. S. Tarbell and C. Weaver, *J. Amer. Chem. Soc.*, 1941, **63**, 2939.

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

[11] A. L. J. Beckwith and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1969, 403.

gave a spectrum with the same g factor and hyperfine splitting as for other radicals considered to have the structure $\cdot CH_2S(O)R$ (Table 1), and it is attributed to the radical $\cdot CH_2S(O)Me$. Likewise, diethyl sulphoxide gave a spectrum attributed to $\cdot CHMe{\cdot}S(O)Et$.

Further confirmation of these assignments was obtained by observation of the spectrum we have attributed to the radical $\cdot CH_2S(O)Me$ when the titanium(III)–hydrogen peroxide reaction was carried out in the presence of hypophosphorous acid and bromomethyl methyl sulphoxide. This is consistent with the formation of the radical-anion $HPO_2^{\cdot-}$ from hypophosphorous acid and hydroxyl radical [12] and the expected [13] removal of the bromine atom from the bromo-compound by this species [reaction (3)].

$$MeS(O)CH_2Br \xrightarrow{HPO_2^{\cdot-}} MeS(O)CH_2\cdot \qquad (3)$$

The hyperfine splitting constants for the sulphinyl-conjugated radicals are collected in Table 1; each had g 2.0025.

TABLE 1

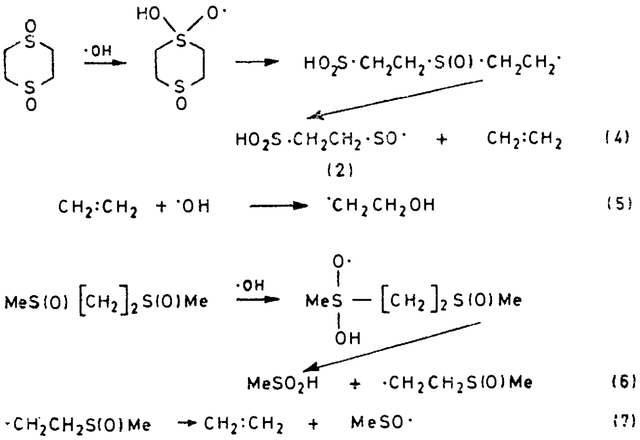
Sulphinyl-conjugated radicals

Radical	Origin	Hyperfine splittings/mT
$\cdot CH_2S(O)[CH_2]_3SO_2H$	*a*	2.00 (2 H)
$\cdot CH_2S(O)[CH_2]_2SO_2H$	*a*	2.00 (2 H)
$\cdot CHMeS(O)[CH_2]_2SO_2H$	*a*	2.01 (1 H), 2.52 (3 H)
$\cdot CMe_2S(O)[CH_2]_2SO_2H$	*a*	2.33 (6 H)
$\cdot CH_2S(O)Me$	*b,c*	2.00 (2 H)
$\cdot CHMeS(O)Et$	*d*	2.02 (1 H), 2.53 (3 H)

[a] The cyclic 1,3-bis-sulphoxide + $\cdot OH$. [b] $Me_2SO + Ph\cdot$. [c] $MeS(O)CH_2Br + HPO_2^{\cdot-}$. [d] $Et_2SO + Ph\cdot$.

(c) *Reactions of* 1,4-*bis-sulphoxides with the hydroxyl radical*. Just as the reaction of the hydroxyl radical with a 1,3-bis-sulphoxide gives an α-sulphinyl-substituted carbon radical, so its reaction with a 1,4-bis-sulphoxide would be expected to give a β-sulphinyl-substituted radical. We obtained evidence that this process occurs, but could not detect the sulphinyl-containing radicals by e.s.r. spectroscopy owing, we believe, to their rapid fragmentation.

The reaction of 1,4-dithian 1,4-dioxide with the Ti^{III}–H_2O_2 couple gave two radicals. One [a(2H) 0.95 mT, g 2.0105] had a g factor typical of alkylsulphinyl radicals [1] and hyperfine splitting expected for a radical of the type [1] $RCH_2SO\cdot$; we infer that it is species (2). The other was characterised by its g factor (2.0050) as an alkylsulphonyl radical; [1,7] its resonances were consistent with its being of the type [7] $RCH_2CH_2SO_2\cdot$ [a(2H) *ca.* 0.4, a(2H) *ca.* 0.2 mT, with some of the hyperfine lines obscured by those from the other radical]. Such a species would be expected to be formed by hydrogen atom abstraction from a sulphinic acid [7] derived from radical (2). When a higher concentration of hydrogen peroxide was employed in this experiment a third signal was detected which we assign to the radical $\cdot CH_2CH_2OH$ on the basis of its g factor (2.0025) and hyperfine splittings [a(2H) 2.78, a(2H) 2.22 mT].[14] These observations are consistent with the occurrence of reactions (4) and (5), although the second and third steps in the former may be concerted.*



Under these conditions, the 1,4-bis-sulphoxide $MeS(O)[CH_2]_2S(O)Me$ gave the spectrum of the radical $\cdot CH_2CH_2OH$ and a partially resolved quartet [a(3H) *ca.* 0.1 mT, g 2.0049] which is attributed [6] to the radical $MeSO_2\cdot$. No resonances were present which could be attributed to the radical $MeSO\cdot$. We infer the occurrence of reactions (6), (7), and (5), and attribute the failure to detect the radical $MeSO\cdot$ to its spectrum having excessively broad lines owing to its small rotational correlation time (*cf.* ref. 1).

(ii) *Sulphonyl-substituted radicals*. (a) *Reactions of sulphones with the phenyl radical*. Dimethyl sulphone (0.24M),† diethyl sulphone (0.09M), and sulpholan (0.05M) reacted with the phenyl radical (generated from benzenediazonium ion and Ti^{III} at pH *ca.* 8) to give the spectrum of one radical in each case which can be assigned, on the basis of their hyperfine splitting patterns, to the sulphonyl-conjugated carbon radicals $\cdot CH_2S(O_2)Me$, $\cdot CHMeS(O_2)Et$, and (3), respectively; the larger triplet splitting in (3) is assigned to the β-protons, its magnitude reflecting the relatively small dihedral angle made by the β-C–H bonds and the singly occupied carbon p-orbital. Our results for the radical $\cdot CH_2S(O_2)Me$ support the tentative assignment previously given to a weak triplet signal observed during the γ-radiolysis of the sulphone.[4] E.s.r. parameters are collected in Table 2.

(b) *Reactions with the hydroxyl radical*. Dimethyl and diethyl sulphone were found to be of low reactivity towards the hydroxyl radical, consistent with the findings of Lagercrantz and Forshult who were unable to trap radicals from these reactions.[15] For example, the inclusion of 0.12M-dimethyl sulphone with the

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* Under these conditions, the concentration of bis-sulphoxide was insufficient to scavenge all the hydroxyl radicals; reaction of $\cdot OH$ with a reactive molecular product such as ethylene is therefore to be expected.

† Concentrations are those after mixing, except where stated.

[12] B. C. Gilbert, J. P. Larkin, R. O. C. Norman, and P. M. Storey, *J.C.S. Perkin II*, 1972, 1508.

[13] A. L. J. Beckwith, *Austral. J. Chem.*, 1972, **25**, 1887.

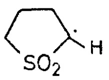
[14] A. L. J. Beckwith and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1969, 400.

[15] C. Lagercrantz and S. Forshult, *Acta Chem. Scand.*, 1968, **23**, 811.

$\mathrm{Ti^{III}{-}H_2O_2}$ couple gave only the two singlets which are derived from titanium–peroxide complexes.[16] Commercial (95—99%) diethyl sulphone (0.09M) gave only a weak spectrum of the radical $\cdot\mathrm{CHMeS(O_2)Et}$, together with the spectra of the radicals $\cdot\mathrm{CH_2CH_2OH}$, $\mathrm{Et}\cdot$, $\mathrm{EtSO_2}\cdot$, and one of the singlets from titanium–peroxide complexes (*g* 2.0132), from which we infer that scavenging of the hydroxyl radical is incomplete. We suggest that the radicals $\cdot\mathrm{CH_2CH_2OH}$ and $\mathrm{EtSO_2}\cdot$ are formed from $\cdot\mathrm{CH_2CH_2S(O_2)Et}$ as in reaction (8). The ethyl radical is likely to arise from traces of diethyl sulphoxide, which is known to yield this species with the hydroxyl radical at a rate close to the diffusion-controlled limit.[7]

$$\cdot\mathrm{CH_2CH_2S(O_2)Et} \xrightarrow{-\mathrm{EtSO_2}\cdot} \mathrm{CH_2{:}CH_2} \xrightarrow{\cdot\mathrm{OH}} \cdot\mathrm{CH_2CH_2OH} \qquad (8)$$

Sulpholan proved to be significantly more reactive; a 0.05M solution gave a strong spectrum which is assigned to radical (4); as expected [*cf.* radical (3)], there are large splittings from the two sets of methylene protons. A weaker spectrum of the isomeric radical (3) was also detected.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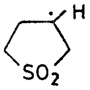
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Dipropyl sulphone (0.045M) gave the spectra of two radicals in about equal concentration. One is assigned to the species $\cdot\mathrm{CH_2CH_2CH_2S(O_2)Pr}$ on the basis of the pattern and magnitude of its hyperfine splittings; the splitting of 2.19 mT is within the range expected for the α-protons (*cf.*, *e.g.*, $\cdot\mathrm{CH_2Me}$ in Table 3), and the largest and smallest splittings are assigned to the β- and γ-protons, respectively. The *g* factor (2.0050) and hyperfine splitting [*a*(2H) 0.27, *a*(5H) 0.075 mT] of the second radical characterise it as an alkylsulphonyl radical;[7] we suggest that it is $\mathrm{PrSO_2}\cdot$, with $a(\beta\text{-H}) > a(\alpha\text{-H}) = a(\gamma\text{-H})$,[*] formed as in reaction (9). Di-t-butyl sulphone gave only the radical[7] $\mathrm{Bu^tSO_2}\cdot$ [*a*(9H) 0.255 mT, *g* 2.0054]; this could not have been formed from sulphoxide impurity, since $\mathrm{Bu^t{}_2SO}$ gave, as expected,[7] the t-butyl radical, and we infer the occurrence of reaction (10).

$$\mathrm{Pr_2SO_2} \xrightarrow{\cdot\mathrm{OH}} \mathrm{Me\dot{C}HCH_2S(O_2)Pr} \longrightarrow \mathrm{MeCH{:}CH_2} + \mathrm{PrSO_2}\cdot \qquad (9)$$

$$\mathrm{Bu^t{}_2SO_2} \xrightarrow{\cdot\mathrm{OH}} \cdot\mathrm{CH_2CMe_2S(O_2)Bu^t} \longrightarrow \mathrm{Me_2C{:}CH_2} + \mathrm{Bu^tSO_2}\cdot \qquad (10)$$

1,2-Oxathiolan 2,2-dioxide gave the spectra of two radicals. One, with two large triplet-splittings in addition to a doublet, is clearly assigned to the radical (5). The other (*g* 2.0030), which was present in about twice the concentration of the first, might be that of the radical (6) or the isomeric sulphonyl-conjugated radical; we believe it to be the former, for the latter would be expected to have a lower *g* factor and a much larger splitting constant for its single (α) proton [*cf. e.g.*, $\cdot\mathrm{CHMeS(O_2)Et}$ and (see later) $\cdot\mathrm{CHMeS(O_2)O^-}$], whereas both these parameters are reasonable for a carbon radical adjacent to an oxygen substituent.[17] Finally, the spectra from the ethanesulphonate ion are assigned to the species $\cdot\mathrm{CHMe{\cdot}SO_3^-}$ and $\cdot\mathrm{CH_2CH_2SO_3^-}$, the triplet splitting of 2.22 mT in the latter being attributed to the α-protons [*cf., e.g.,* $\cdot\mathrm{CH_2Me}$ and $\cdot\mathrm{CH_2CH_2CH_2S(O_2)Pr}$]. The radicals were present in approximately equal concentrations.

TABLE 2

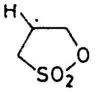
Sulphonyl-substituted radicals

Radical	Origin	Hyperfine splittings/mT	*g*
$\cdot\mathrm{CH_2S(O_2)Me}$	*a*	2.23 (2 H), 0.21 (3 H)	2.0025
$\cdot\mathrm{CHMeS(O_2)Et}$	*a,b*	2.16 (1 H), 2.73 (3 H), 0.21 (2 H)	2.0025
(3)	*a,b*	2.10 (1 H), 3.88 (2 H), 0.18 (2 H)	2.0025
(4)	*b*	2.21 (1 H), 3.275 (2 H), 3.475 (2 H), 0.08 (2H)	2.0029
$\cdot\mathrm{CH_2CH_2CH_2S(O_2)Pr}$	*b*	2.19 (2 H), 2.68 (2 H), 0.05 (2 H)	2.0026
(5)	*c*	2.18 (1 H), 3.36 (2 H), 3.52 (2 H)	2.0028
(6)	*c*	1.60 (1 H), 2.98 (2 H), 0.09 (2 H)	2.0030
$\cdot\mathrm{CHMeS(O_2)O^-}$	*d*	2.17 (1 H), 2.59 (3 H)	2 0025
$\cdot\mathrm{CH_2CH_2S(O_2)O^-}$	*d*	2.22 (2 H), 1.85 (2 H)	2.0027

[a] Sulphone + Ph·. [b] Sulphone + ·OH. [c] 1,2-Oxathiolan 2,2-dioxide + ·OH. [d] $\mathrm{EtSO_3^-}$ + ·OH.

Structural Features in Sulphinyl- and Sulphonyl-substituted Radicals.—Table 3 summarises the e.s.r. parameters for some sulphinyl- and sulphonyl-conjugated radicals and some related species. Several features are of note.

First, radicals of the type ·CHMeX which have a planar geometry at the tervalent carbon atom are characterised by ratios of *a*(β-H) : *a*(α-H) of *ca.* 1.2:1 whereas for non-planar species the ratios are substantially higher.[17] We infer from the ratios for the radicals $\cdot\mathrm{CHMeS(O)Et}$, $\cdot\mathrm{CHMeS(O_2)Et}$, and $\cdot\mathrm{CHMeS(O_2)O^-}$ (1.25, 1.26, and 1.19, respectively) that each is essentially planar at the tervalent carbon.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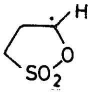
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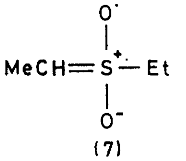
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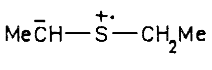
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Secondly, as estimated from *a*(β-H) by Fischer's

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[*] Slightly different values have been reported for this radical in a non-aqueous solvent at −40° (A. G. Davies, B. P. Roberts, and B. R. Sanderson, *J.C.S. Perkin II*, 1973, 626; *cf.* ref. 7).

[16] H. Fischer, *Ber. Bunsengesellschaft Phys. Chem.*, 1967, **71**, 685.

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

method,[18] which is appropriate at least for planar radicals,[19] we conclude that the sulphinyl substituent in $\cdot CHMeS(O)Et$ removes only *ca.* 6% of the unpaired spin from the tervalent carbon atom, and that the sulphonyl substituent in $\cdot CHMeS(O_2)Et$ *is wholly ineffective at removing spin* [although canonical structures such as (7) would suggest otherwise]. The latter conclusion can also be reached directly from the values of a(β-H) for $\cdot CHMeS(O_2)Et$ and $\cdot CH_2Me$, which, within the experimental error, are identical. Moreover, whereas a(α-H) is smaller for $\cdot CH_2S(O)Me$ than for $\cdot CH_3$, reflecting delocalisation on to the sulphinyl group, it is essentially the same for $\cdot CH_2S(O_2)Me$ as for $\cdot CH_3$. The results for the radical $\cdot CHMeS(O_2)O^-$ suggest that the sulphonate substituent has little spin-delocalising effect. In contrast to the results for these sulphur-containing substituents, the carbonyl group removes *ca.* 16% of the spin from an adjacent tervalent carbon,[18] and the ethylthio group in $\cdot CHMeSEt$ [20] removes *ca.* 22%.

TABLE 3

Isotropic e.s.r. parameters for some radicals containing sulphur substituents, and related species, in aqueous solution at ambient temperature

	Hyperfine splittings/mT [a]			
Radical	a(α-H)	a(β-H)	a(γ-H)	g
$Me\dot{C}H_2$ [b]	2.22	2.71		2.0025
$Me\dot{C}HS(O_2)Et$	2.16	2.73	0.21	2.0025
$Me\dot{C}HS(O_2)O^-$	2.17	2.59		2.0025
$Me\dot{C}HS(O)Et$	2.02	2.53		2.0025
$Me\dot{C}HSEt$ [c]	1.70	2.10	0.15	2.0044
$\cdot CH_3$ [b]	2.29			2.0025
$\cdot CH_2S(O_2)Me$	2.23		0.21	2.0025
$\cdot CH_2S(O)Me$	2.00			2.0025
$\cdot CH_2SMe$ [c]	1.65		0.36	2.0049

[a] α, β, γ refer to protons attached to the tervalent carbon atom and successive atoms. [b] Ref. 14. [c] Ref. 20.

Thirdly, whereas, as expected, a(α-H) is smaller for $\cdot CHMeS(O_2)Et$ than for $\cdot CH_2S(O_2)Me$, reflecting spin delocalisation onto the methyl group in the former, the values for $\cdot CHMeS(O)Et$ and $\cdot CH_2S(O)Me$ are essentially the same. It has been noted previously [10] that a(α-H) is *larger* for radicals of the type $\cdot CHMeSR$ than for $\cdot CH_2SR$, and it was suggested that the methyl substituent may serve to increase the compressional forces in the coplanar conformations of the $>\dot{C}{-}S<$ fragment, thereby reducing the effectiveness of the conjugation between the tervalent carbon atom and sulphur and therefore the spin-delocalising effect of the sulphur atom; trends in a(γ-H) and g are in accord with this interpretation.[10] It is probable that an analogous explanation applies to the radicals $\cdot CHMeS(O)Et$ and $\cdot CH_2S(O)Me$.

Fourthly, the absence of detectable splitting from the γ-protons in the radicals $\cdot CHMeS(O)Et$ and $\cdot CH_2S(O)Me$ (the line-width was 0.12 mT; any splitting must be significantly less than 0.1 mT) is in contrast to the substantial splitting in the RS- and $RS(O_2)$-conjugated radicals. It suggests that the γ-splitting in the RS-conjugated radicals reflects mainly hyperconjugative interaction with the spin on sulphur [*cf.* structure (8) and the high g factor] and is of positive sign, that in the $RS(O)_2$-conjugated radicals arises from spin polarisation and is of negative sign, and there is an approximate cancelling of these contributions in the RS(O)-conjugated radicals.

The g factors of both the sulphinyl- and sulphonyl-conjugated radicals are little greater than the free-spin value and the same as for hydrocarbon radicals such as ethyl. In contrast, the g factors of radicals containing β-$S(O_2)R$, β-$S(O)_2OR$, and β-$S(O_2)O^-$ substituents [(4), (5), and $\cdot CH_2CH_2S(O_2)O^-$, respectively] are somewhat higher.

Mechanistic Features.—No sulphinyl-containing radicals can be detected when the methyl radical is generated in the presence of dimethyl sulphoxide [6] or another alkyl radical is generated in the presence of the corresponding sulphoxide.[7] Further, we found that the spectrum of the methyl radical is unquenched, and that of $\cdot CH_2S(O_2)Me$ is not detectable, when the methyl radical is generated from dimethyl sulphoxide with the Ti^{III}–H_2O_2 couple in the presence of an excess of dimethyl sulphone. Thus, the results of our reactions with the phenyl radical are in keeping with the view that this species is more reactive than alkyl radicals.[21] Although we were unable to determine rate constants for reactions with the phenyl radical, we can set a lower limit for that with dimethyl sulphoxide, as follows. In the absence of dimethyl sulphoxide, the phenyl radical is not present in detectable concentration, so that its life-time must be $<10^{-4}$ s; detection of the radical $\cdot CH_2S(O)Me$ in the presence of 0.15M-sulphoxide then implies that $k[Me_2SO]$ is $>10^4$ s^{-1}, where k is the rate constant for ($Ph\cdot + Me_2SO$), so that $k > 6 \times 10^4$ l mol^{-1} s^{-1}.

Our results show that the phenyl and hydroxyl radicals differ not only in their behaviour towards sulphoxides, the former preferentially abstracting a hydrogen atom and the latter reacting at sulphur, but also in their selectivity in hydrogen atom abstraction from sulphones. Thus, the phenyl radical gave only the sulphonyl-conjugated radicals (3) from sulpholan and $\cdot CHMeS(O_2)Et$ from diethyl sulphone, whereas hydroxyl gave a higher concentration of the non-conjugated radical (4), compared with (3), from sulpholan and [as judged by the formation of $\cdot CH_2CH_2OH$ and $EtSO_2\cdot$ as in reaction (8)] $\cdot CH_2CH_2S(O_2)Et$ as well as $\cdot CHMeS(O_2)Et$ from diethyl sulphone. This doubtless reflects, at least in part, the differing electronegativities of the two radicals; for example, the electrophilic hydroxyl radical is relatively more reactive towards the methylene group in sulpholan which is the further of the two from the electron-withdrawing sulphonyl group, as compared with the less electrophilic phenyl radical. Indeed, the deactivating effect of the sulphonyl group on abstraction by

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hydroxyl from adjacent C–H is well illustrated by the failure of dimethyl sulphone to yield a detectable concentration of $\cdot\mathrm{CH_2S(O_2)Me}$ in this way. We can infer that the rate of abstraction is less than that at which hydroxyl radicals are removed by reduction by titanium(III) ion, from which it follows that, given $k(\cdot\mathrm{OH} + \mathrm{Ti^{III}}) =$ *ca.*[22] $3 \times 10^9\ \mathrm{l\ mol^{-1}\ s^{-1}}$ and $[\mathrm{Ti^{III}}]$ in the e.s.r. cavity was $\leqslant 2$mM, $k(\cdot\mathrm{OH} + \mathrm{Me_2SO_2})$ is $< 6 \times 10^6\ \mathrm{l\ mol^{-1}\ s^{-1}}$; this can be compared with, *e.g.*, $k =$ *ca.* $10^8\ \mathrm{l\ mol^{-1}\ s^{-1}}$ for $(\cdot\mathrm{OH} + \mathrm{Me_2CO})$.[23]

Two types of radical fragmentation are notable. First, the radical (1) appears to fragment to give the sulphinyl-conjugated radical $\cdot\mathrm{CH_2S(O)[CH_2]_3SO_2H}$ in preference to the non-conjugated isomer, $\cdot\mathrm{CH_2CH_2CH_2S(O)CH_2SO_2H}$ (there was no evidence for the latter or for a radical derived from it); the five-membered cyclic analogue behaves analogously. Secondly, there is evidence that radicals of the type $\mathrm{RS(O)CH_2CH_2}\cdot$ and $\mathrm{RS(O_2)CH_2CH_2}\cdot$ fragment to ethylene and sulphinyl or sulphonyl radicals, respectively. However, it is interesting that the cyclic radicals (4) and (5) were detected, although they might have been expected to fragment. A possible explanation for their reduced tendency to fragment is that less entropy is gained than when an acyclic analogue cleaves, but another possibility is that they are stereoelectronically unsuited to fragmentation; that is, in contrast to the situation in the acyclic radicals, there can be no significant overlap between the half-filled orbital in the cyclic radicals and the C–S bond which is to be broken (*cf.* ref. 24).

EXPERIMENTAL

The e.s.r. spectrometer and flow system have been described in detail;[25] a three-stream simultaneous-mixing chamber was used in all experiments. Hyperfine splitting constants were determined to within ± 0.01 mT and g factors to within ± 0.0001 by comparison with an aqueous solution of Fremy's salt [a(N) 1.309 mT,[26] g[27] 2.0055].

Materials were usually commercial samples. Other materials were prepared as follows. Diethyl sulphoxide was made by the method of Leonard and Johnson.[28] 1,3-Bis-sulphoxides were prepared in aqueous solution by[9] stirring the appropriate 1,3-disulphide with the calculated amount of 30% hydrogen peroxide at 0°. Bromomethyl methyl sulphoxide was prepared from dimethyl sulphoxide and bromine.[29] 1,4-Disulphoxides were prepared following the method of Bell and Bennett.[30] Di-t-butyl sulphone was prepared following Bordwell and McKellin.[31] Diazonium salts were prepared as described previously.[11]

Reactions.—(i) *With titanium*(III)*-hydrogen peroxide.* The three reagent streams contained 6mM-titanium(III) chloride, 15mM-hydrogen peroxide, and the organic compound (0.12—0.3M), respectively. The pH was adjusted to *ca.* 1.5 by the addition of concentrated sulphuric acid to the titanium(III) solution.

For the reaction involving $\mathrm{HPO_2}^{-\cdot}$, 16mM-hypophosphorous acid was included in the titanium(III) solution and the concentration of bromomethyl methyl sulphoxide was 5mM.

(ii) *With titanium*(III)*-benzenediazonium fluoroborate.* The three reagent streams contained 8 mM-titanium(III) chloride together with EDTA (6 g $\mathrm{l^{-1}}$), 8mM-benzenediazonium fluoroborate, and the sulphoxide or sulphone (0.12—0.72M), respectively. The pH of the titanium(III) solution was adjusted to pH 8 by the addition of potassium carbonate solution, and one drop of concentrated sulphuric acid was added to the solution of the diazonium salt.

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