Electron Spin Resonance. Part 67.[1] Oxidation of Aliphatic Sulphides and Sulphoxides by the Sulphate Radical Anion ($SO_4^{-\cdot}$) and of Aliphatic Radicals by the Peroxydisulphate Anion ($S_2O_8^{2-}$)

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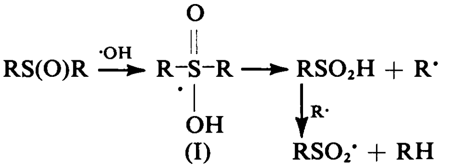
E.s.r. experiments employing *in situ* photolytic decomposition of the peroxydisulphate anion ($S_2O_8^{2-}$) have been carried out to study the reaction of $SO_4^{-\cdot}$ with aliphatic sulphides and sulphoxides. For the former, ' dimer ' radical cations ($R_2SSR_2^{+\cdot}$) are detected; these are evidently generated *via* direct one-electron oxidation of the sulphide (to give firstly $R_2S^{+\cdot}$). The more complex behaviour of the latter [involving, for example, the reaction of $Me_2S(O)$ to give $^{\cdot}CH_2S(O)Me$ (at low pH), $Me^{\cdot}$, and $MeSO_2^{\cdot}$] is interpreted in terms of the initial formation of an (undetected) radical cation $R_2S(O)^{+\cdot}$, subsequent competing reactions of which include deprotonation and hydration (followed by fragmentation).

Flow-system studies of the generation of radicals with $^{\cdot}OH$ (from Ti^{III}/H_2O_2) in the presence of $S_2O_8^{2-}$ provide evidence that the latter is an effective oxidant for both unsubstituted and α-oxygen-substituted alkyl radicals. The rate of oxidation is increased by α-Me and α-OH or -OR groups [*e.g.* for $Me^{\cdot}$ the rate constant is 3.3×10^4 dm^3 mol^{-1} s^{-1}; for $^{\cdot}CH_2OH$, the value is 1.3×10^5 dm^3 mol^{-1} s^{-1}].

It has been shown[2] by e.s.r. spectroscopy that the reaction of $^{\cdot}OH$ with simple dialkyl sulphides leads to the formation of both carbon-centred radicals and ' dimer ' radical cations [*e.g.* from dimethyl sulphide $^{\cdot}CH_2SMe$ and $Me_2SSMe_2^{+\cdot}$ (for which a σ*-structure is proposed[3])]. Complementary pulse-radiolysis investigations[4-6] have established that the rapidly formed adducts $R_2S(OH)^{\cdot}$ react both by loss of water (to give carbon-centred radicals) and by acid-catalysed loss of hydroxide to give $R_2SSR_2^{+\cdot}$, at least in part *via* the monomeric radical cation $R_2S^{+\cdot}$ and subsequent reaction with R_2S; a further route to the carbon-centred radicals involves deprotonation of $R_2S^{+\cdot}$.

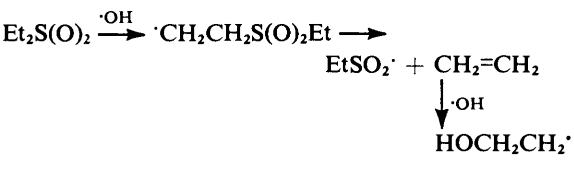
Hydroxyl radicals have also been shown[7] to be particularly reactive towards aliphatic sulphoxides, which in most cases yield alkyl and alkylsulphonyl radicals detectable by e.s.r. (see also ref. 8): the mechanism evidently involves fragmentation of the adduct (I) and subsequent reaction of the alkyl radical and sulphinic acid so produced [reaction (1)].



$$\mathrm{RS(O)R} \xrightarrow{\cdot\mathrm{OH}} \underset{\text{(I)}}{\mathrm{R{-}\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{\dot{S}}}{-}R}} \longrightarrow \mathrm{RSO_2H} + \mathrm{R}^{\cdot} \qquad (1)$$
$$\mathrm{RSO_2H} \xrightarrow{\mathrm{R}^{\cdot}} \mathrm{RSO_2^{\cdot}} + \mathrm{RH}$$

Reactions of $NH_3^{+\cdot}$ and $Bu^tO^{\cdot}$ with both sulphides and sulphoxides are believed to follow essentially similar routes (see refs. 9 and 10, respectively). On the other hand the more nucleophilic phenyl radical reacts differently, to give sulphur-conjugated radicals directly, as in reaction (2).[11] With sulphones $Ph^{\cdot}$ again reacts *via* α-hydrogen abstraction whereas the electrophilic hydroxyl radical largely reacts at sites more remote from the sulphonyl group, giving, for example, sulphonyl and β-hydroxyalkyl radicals *via* attack at the β-position [reaction (3)].

$$C_6H_5^{\cdot} + Me_2S(O) \longrightarrow C_6H_6 + {}^{\cdot}CH_2S(O)Me \qquad (2)$$



$$\mathrm{Et_2S(O)_2} \xrightarrow{\cdot\mathrm{OH}} {}^{\cdot}\mathrm{CH_2CH_2S(O)_2Et} \longrightarrow \mathrm{EtSO_2^{\cdot}} + \mathrm{CH_2{=}CH_2} \qquad (3)$$
$$\mathrm{CH_2{=}CH_2} \xrightarrow{\cdot\mathrm{OH}} \mathrm{HOCH_2CH_2^{\cdot}}$$

We report here the results of an investigation of the reactions of these substrates with the sulphate radical anion ($SO_4^{-\cdot}$) which is thought to be the key intermediate in the photochemical, thermal, and transition-metal-catalysed decompositions of peroxydisulphate (see *e.g.* ref. 12). It is known that $SO_4^{-\cdot}$ is a very electrophilic radical which can undergo hydrogen-atom abstraction[13] and addition[14] reactions and which, with many substrates (*e.g.* carboxylates,[15] electron-rich alkenes,[14] aromatic compounds[16]) behaves as an effective one-electron oxidant. Comparison of the ionisation potentials[17] (which should be at least a guide to the ease of removal of an electron from substrates in aqueous solution) of Me_2S (8.69 eV) and $Me_2S(O)$ (8.85 eV) with that of benzene (9.245 eV) suggests that the first two, like the last,[16] may be susceptible to one-electron oxidation by $SO_4^{-\cdot}$. Our investigation was also prompted by the recent report[18] that γ-irradiation of solid samples of $Me_2S(O)$ at 77 K gives e.s.r. signals attributed to $Me_2S(O)^{+\cdot}$ and $[Me_2S(O)]_2^{+\cdot}$ (*cf.* the better known sulphide analogues) and the suggestion[19] that $R_2S(O)_2^{+\cdot}$ is formed during the radiolysis of sulphones at room temperature. Our experiments were designed to establish whether such cation radical intermediates are formed in the reaction between $SO_4^{-\cdot}$ and sulphides, sulphoxides, and sulphones in fluid solution.

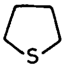
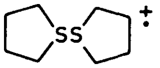
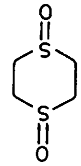
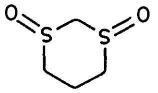
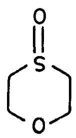
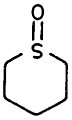
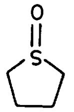
Results and Discussion

Two approaches were employed in order to generate $SO_4^{-\cdot}$ in the cavity of the e.s.r. spectrometer. In the first, three reactant solutions containing Ti^{III} (*ca.* 0.01 mol dm^{-3}), $S_2O_8^{2-}$ (*ca.* 0.025 mol dm^{-3}), and the substrate (*ca.* 0.01—0.1 mol dm^{-3}), respectively, were mixed *ca.* 50 ms before the combined solution flowed through the cavity: $SO_4^{-\cdot}$ is formed *via* reaction (4). In the second, aqueous solutions of the substrate

$$Ti^{III} + S_2O_8^{2-} \xrightarrow{k_4} Ti^{IV} + SO_4^{-\cdot} + SO_4^{2-} \qquad (4)$$

(typically 0.05 mol dm^{-3}) and peroxydisulphate (0.05 mol dm^{-3}) were irradiated, as they flowed slowly through the cavity, by the unfiltered radiation from an Hanovia 977B-1 1 kW mercury-xenon lamp; in many cases improved signals could be obtained by using acetone–water as the solvent (addition of acetone not only aids substrate solubility in many cases but also appears to assist photodecomposition of peroxydisulphate, presumably *via* energy transfer from a photo-

Table 1. E.s.r. parameters of radicals detected in the oxidation of sulphides and sulphoxides with $SO_4^{-\cdot}$

Substrate	Radical	Hyperfine splittings (mT)[a]			
		a(α-H)	a(β-H)	a(γ-H)	g[b]
Me_2S	$Me_2SSMe_2^{+\cdot}$		0.66(12)		2.0104
Et_2S	$Et_2SSEt_2^{+\cdot}$		0.66(8)		2.0103
			0.93(8)		2.0102
$Me_2S(O)$	$Me^{\cdot}$	2.28(3)			2.0026
	$MeSO_2^{\cdot}$		0.094(3)		2.0049
	$^{\cdot}CH_2S(O)Me$	1.99(2)			2.0025
$Et_2S(O)$	$Et^{\cdot}$	2.18(2)	2.69(3)		2.0026
	$EtSO_2^{\cdot}$		0.10(2)	0.21(3)	2.0053
	$^{\cdot}CHMeS(O)Et$	2.02(1)	2.53(3)		2.0025
$Pr^iS(O)$	$Pr^iSO_2^{\cdot}$		*c*	0.23(6)	2.0053
$Bu^tS(O)Me$	$MeSO_2^{\cdot}$				
$MeS(O)CH_2CH_2CH(NH_3^+)CO_2^-$	$MeSO_2^{\cdot}$				
	$^{\cdot}CH[S(O)Me]CH_2CH(NH_3^+)CO_2^-$	2.15(1)	1.99(2)		2.0025
$(HOCH_2CH_2)_2S(O)$	$HOCH_2CH_2SO_2^{\cdot}$		*c*	0.385(2)	2.0051
$(HO_2CCH_2CH_2)_2S(O)$	$HO_2CCH_2CH_2SO_2^{\cdot}$		0.13(2)	0.26(2)	2.0050
	[d] $RCH_2CH_2SO_2^{\cdot}$		0.06(2)	0.235(2)	2.0050
	$SO_3^{-\cdot}$				2.0031
	[e] $RCH_2CH_2SO_2^{\cdot}$		0.06	0.235(2)	2.0050
	$SO_3^{-\cdot}$				
	[e] $ROCH_2CH_2SO_2^{\cdot}$		*c*	0.375(2)	2.0051
	$SO_3^{-\cdot}$				
	[e] $RCH_2CH_2SO_2^{\cdot}$		*c*	0.225(2)	2.0051
	$SO_3^{-\cdot}$				
	[e] $RCH_2CH_2SO_2^{\cdot}$		*c*	0.30(2)	2.0050
	$SO_3^{-\cdot}$				

[a] Typically ±0.005 mT. [b] ±0.0001. [c] Further hyperfine splitting incompletely resolved. [d] The structure of the alkyl chain is not determined, but is probably $CH_3CH_2CH_2CH_2$– (see Scheme 2). [e] The complete structure of the chain is not determined but is likely to be that which results by the operation of oxidation, fragmentation, and intramolecular abstraction as outlined for tetrahydrothiophene *S*-oxide in Scheme 2.

excited state [20,21]). All experiments were carried out with deoxygenated solutions at ambient temperature (*ca.* 20 °C) at a series of pH values in the range 0.5—9.

(a) *Reactions of Sulphides with* $SO_4^{-\cdot}$.—When dimethyl sulphide and diethyl sulphide reacted with $SO_4^{-\cdot}$ generated by the Ti^{III}–$S_2O_8^{2-}$ couple in a flow system in the pH range 0.5—9, weak signals from $Me_2SSMe_2^{+\cdot}$ and $Et_2SSEt_2^{+\cdot}$, respectively, were detected, as noted before [2] (e.s.r. parameters are given in Table 1). Much better signals from the same species were obtained *via* the photolytic decomposition of peroxydisulphate, particularly when acetone was also a cosolvent. The corresponding dimer cation radical was also detected from tetrahydrothiophene, but no signals could be discerned in experiments with di-isopropyl or higher sulphides or 1,4-dithiane (where formation of an intramolecularly bonded S–S cation radical might have been expected [5]).

Unlike findings in the corresponding hydroxyl-radical oxidation of related substrates, where signals from $R_2SSR_2^{+\cdot}$ were strongly pH-dependent and where signals from sulphur-

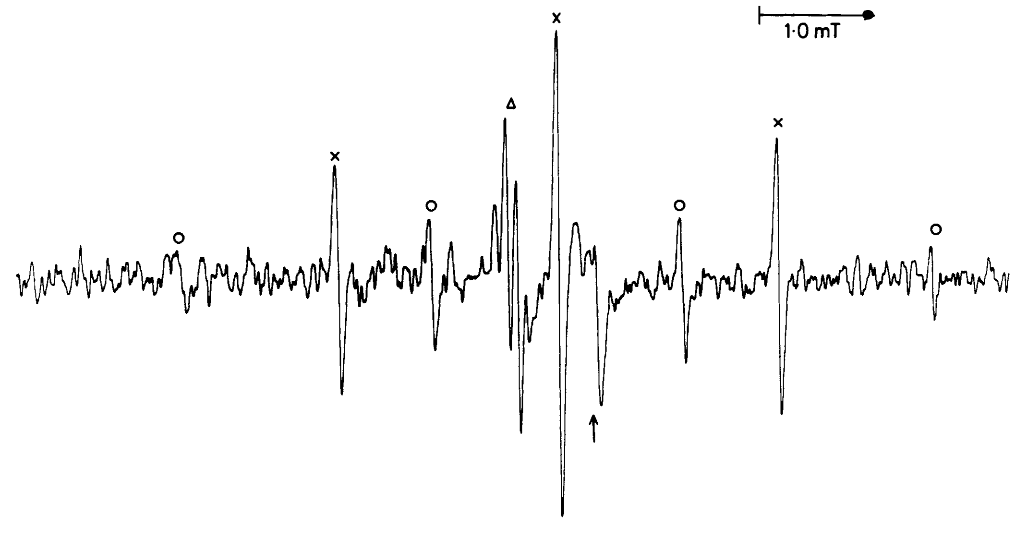


Figure 1. E.s.r. spectra obtained from reaction of $Me_2S(O)$ with $SO_4^{-\cdot}$ (generated by photolysis of peroxydisulphate in aqueous acetone) at pH 1.5: O $Me^\cdot$; x $^\cdot CH_2S(O)Me$; Δ $MeSO_2^\cdot$; the arrowed absorption is from a paramagnetic impurity in the glass cell

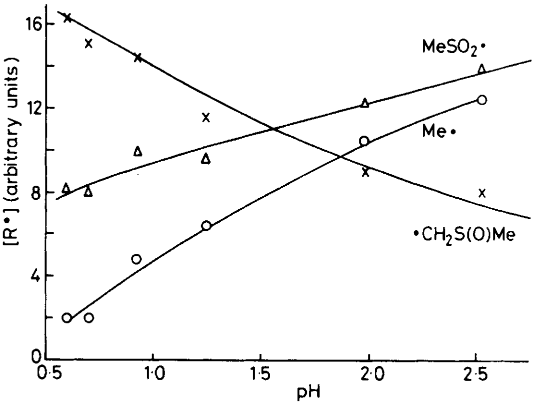


Figure 2. Variation with pH of the concentrations of radicals obtained from $Me_2S(O)$ with $SO_4^{-\cdot}$

conjugated radicals were characterized at higher pH values, no such species were detected in these experiments, and $[R_2SSR_2^{+\cdot}]$ was not sensitive to pH. Although it is possible that sulphur-conjugated radicals are formed (*e.g.* by direct hydrogen abstraction by $SO_4^{-\cdot}$ or fragmentation of $R_2S^{+\cdot}$) and subsequently oxidised by $S_2O_8^{2-}$ (see later), it seems likely that the dominant processes occurring are reactions (5) and (6).

$$R_2S + SO_4^{-\cdot} \longrightarrow R_2S^{+\cdot} + SO_4^{2-} \qquad (5)$$

$$R_2S^{+\cdot} + R_2S \longrightarrow R_2SSR_2^{+\cdot} \qquad (6)$$

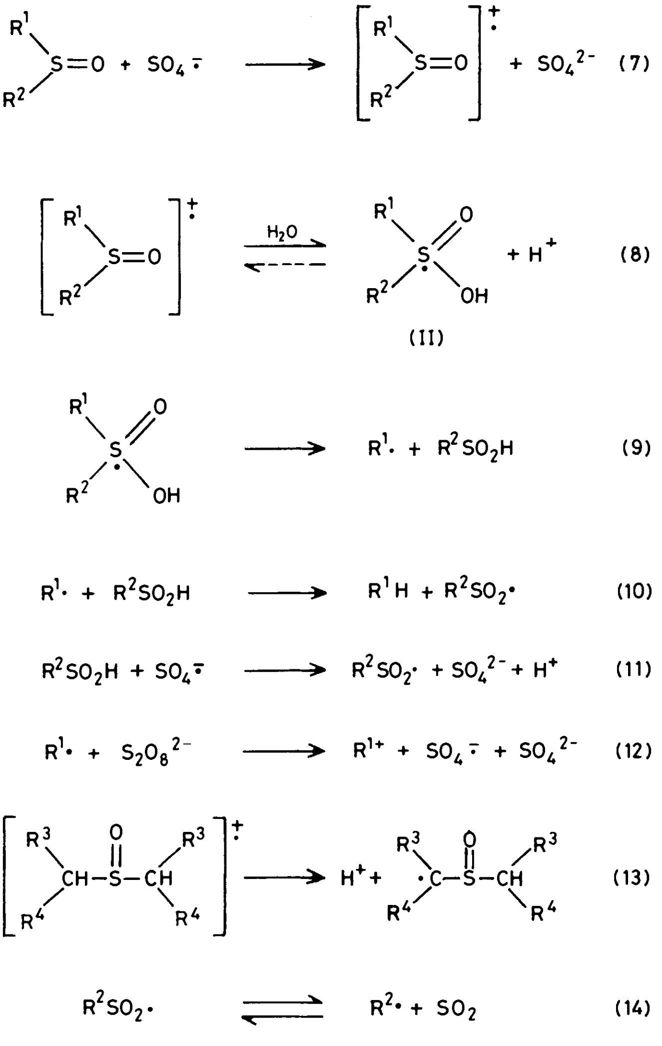
(b) *Reaction of Sulphoxides with* $SO_4^{-\cdot}$.—(i) *E.s.r. spectra detected.* As with sulphides, employment of direct photolysis as a means of generating $SO_4^{-\cdot}$ for subsequent reaction led to the detection of considerably stronger signals than with the flow system: the former technique was hence the method of choice.

Reaction between $SO_4^{-\cdot}$ and dimethyl sulphoxide led to the detection of three radicals (see Figure 1), the relative proportions of which were pH dependent (see Table 1 and Figure 2). At low pH (<0.5) a strong signal attributed to[11] $^\cdot CH_2S(O)Me$ was accompanied by a weak spectrum from $MeSO_2^\cdot$ (see ref. 7). As the pH was raised, the signals from the latter grew in intensity, to be accompanied by the spectrum of the methyl radical, and the intensity of the lines from $^\cdot CH_2S(O)Me$ steadily decreased. Analogous behaviour was observed for the radicals $^\cdot CHMeS(O)Et$, $EtSO_2^\cdot$, and $Et^\cdot$ in the corresponding reaction of $Et_2S(O)$.

Reactions of $SO_4^{-\cdot}$ with other symmetric acyclic sulphoxides $R_2S(O)$ led to the detection of the appropriate sulphonyl radicals (but not alkyl or sulphinyl-conjugated radicals) for $R = Pr^i$, CH_2CH_2OH, and $CH_2CH_2CO_2H$; reaction of $Bu^tS(O)Me$ led to the detection of $MeSO_2^\cdot$ alone, whereas methionine *S*-oxide gave both this radical and $^\cdot CH[S(O)Me]CH_2CH(NH_3^+)CO_2^-$ (see Table 1). For a series of cyclic mono- and di-sulphoxides signals were observed in each case from (ring-opened) sulphonyl radicals (*cf.* characterization[7] of identical species from the same substrates with $^\cdot OH$) and $SO_3^{-\cdot}$ (a singlet with[22] *g* 2.0031).

(ii) *Mechanistic considerations.* The results for $SO_4^{-\cdot}$ bear a general resemblance to those obtained for $\cdot OH$ and the same set of substrates, in which reaction evidently proceeds *via* an initially formed adduct (I) followed by fragmentation and a subsequent hydrogen-atom abstraction reaction (intramolecular for cyclic substrates) from the sulphinic acid produced. This suggests that the mechanisms may have some features in common. However, some important differences should also be noted, including the detection in the $SO_4^{-\cdot}$ system not only of radicals which appear to result from hydrogen-atom abstraction from the parent sulphoxides [*e.g.* for $Me_2S(O)$ and $Et_2S(O)$] but also of generally higher concentrations of $RSO_2^\cdot$, coupled with *lower* concentrations of $R^\cdot$ from $Me_2S(O)$ and $Et_2S(O)$]: in particular, for other substrates the appropriate alkyl radicals, if formed, were not detected with $SO_4^{-\cdot}$, in contrast to the reaction with $^\cdot OH$.

The similarities between the results for $^\cdot OH$ and $SO_4^{-\cdot}$, at least above pH *ca.* 2, can be accounted for if the reactions have an intermediate adduct (II) in common (see Scheme 1). Now such an intermediate could most reasonably be formed in the persulphate system *via* rapid hydration of a first-formed radical cation (whose formation *might* itself involve an adduct), as indicated [reactions (7) and (8)]; such a process, the initial stage of which would not be unexpected in terms of the ionisation potentials of the substrates, has close parallels in the rapid hydration demonstrated for radical cations formed from, *e.g.* vinyl ethers,[23] furans, and thiophenes[24] in their reactions with, *e.g.* $SO_4^{-\cdot}$ and $^\cdot OH$ at low pH. The higher concentrations



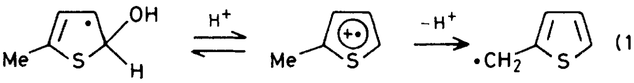
Scheme 1.

of $RSO_2\cdot$ and lower relative concentrations of alkyl radicals in the sulphoxide–$SO_4^{-\cdot}$ oxidations could then be accounted for on the not unreasonable hypothesis that $SO_4^{-\cdot}$ itself is an effective oxidant for the sulphinic acid (or at higher pH the corresponding sulphinate anion) produced in reaction (9) [*e.g.* reaction (11)] * and that $S_2O_8^{2-}$ is responsible, at least in part, for the removal of alkyl radicals [*via* reaction (12), in addition to (10) *cf. e.g.* ref. 12]. It is perhaps significant that, although $Me\cdot$ and $Et\cdot$ *can* be detected in the presence of $S_2O_8^{2-}$, there was no trace of the radical $Pr^{i\cdot}$ in the oxidation of $Pr^i_2S(O)$ or of $Bu^{t\cdot}$ in the reaction of $Bu^tS(O)Me$ [identification of $MeSO_2\cdot$, as in the reaction of $\cdot OH$, suggests that fragmentation of the adduct proceeds in the direction which gives the most stable radical ($Bu^{t\cdot}$), *i.e.* reaction (9; $R^1 = Bu^t$, $R^2 = Me$)]. Such a contrast would be understandable in terms of the expected readier oxidation of the secondary and tertiary radicals. Experiments which confirm this suggestion are described in the last part of this paper.

If this mechanism does indeed play an important part in the reaction sequence then it remains to be explained how radicals formed by hydrogen-abstraction from the parent compounds arise from $Me_2S(O)$ and $Et_2S(O)$ at pH < *ca.* 2. The first possibility is that $SO_4^{-\cdot}$ can bring about direct α-H abstraction (*cf.* its reaction with alcohols and ethers[13]), though its apparent failure to do so above pH 2 argues strongly against this {we attempted to gain information on the possible occurrence of this by studying the reaction of $(C^2H_3)_2S(O)$ under similar circumstances (both in separate experiments and in competition with its protonated counterpart): though $\cdot C^2H_2S(O)C^2H_3$ [$a(^2H)$ 0.325 mT, *g* 2.0025], $\cdot C^2H_3$ [$a(^2H)$ 0.35 mT, *g* 2.0026], and $C^2H_3SO_2\cdot$ (singlet) were observed in experiments with the deuteriated substrate, the relatively poor signal-to-noise ratio for the first two radicals (which results from the multiplicity of deuterium splittings) prevented a meaningful interpretation in terms of a possible kinetic isotope effect}.

The second possibility is that the reactive species at low pH is different from that at pH *ca.* 2, *e.g.* $HSO_4\cdot$. However, although the pK_a value of this radical appears not to have been reported, we would expect it to be considerably less than *ca.* 2 [HSO_4^- has pK_a 2.0,[25] but it is expected that the corresponding radical would have a significantly lower value (compare *e.g.* pK_a values of 7.1 and 12.18 for $H_2PO_4^-$ and HPO_4^{2-}, respectively,[25] with those of 5.7 and 8.9 for the corresponding radicals[26] $H_2PO_4\cdot$ and $HPO_4^{-\cdot}$]. A third and more attractive possibility is that the hydration of the radical cation [reaction (8)] is reversible and therefore that when the pH is lowered the increasing acidity results in increasingly rapid regeneration of the cation radical, which may then undergo deprotonation [reaction (13)] rather than hydration. Analogous mechanisms have been proposed to account for the conversion of *e.g.* β-hydroxyalkyl radicals into allyl radicals[27] [reaction (15)] and hydroxyl adducts of 2-methylthiophene[24] into 2-thienyl [reaction (16)] as the pH is lowered.

$$\cdot CHMeC(OH)Et_2 \underset{H_2O}{\overset{H^+(-H_2O)}{\rightleftharpoons}} MeCH \overset{+\cdot}{=} CEt_2 \xrightarrow{-H^+} MeCH{=}CEt{-}\dot{C}HMe \quad (15)$$



(16)

If, as seems likely, the overall reaction pathway (see Scheme 1) involves the reverse of reaction (8), and subsequent occurrence of reaction (13), then it would be expected that reaction of $Me_2S(O)$ with $\cdot OH$ at low pH would lead similarly to $\cdot CH_2S(O)Me$ instead of $Me\cdot$ and $MeSO_2\cdot$. In an attempt to confirm this we carried out an investigation of the reaction between $Me_2S(O)$ and $\cdot OH$ (generated from Ti^{III} and H_2O_2 in a flow system) and found that in the pH range 1.5—0.6 the signals from $Me\cdot$ and $MeSO_2\cdot$ were removed, in accord with our hypothesis, but that no substrate-derived signals could be discerned. The e.s.r. signals from the Ti^{IV}-complexed peroxyl radicals S_1 and S_2 were, however, detected. Now the disappearance of $Me\cdot$ and $MeSO_2\cdot$ does indicate that an acid-catalysed removal of the adduct $Me_2\dot{S}(O)OH$ occurs, and we suggest that $Me_2S(O)^{+\cdot}$ is formed. Its failure to react to give $\cdot CH_2S(O)Me$ as in the photolytic system may then be attributed to both/either its expected ready reduction by Ti^{III} and/or a rapid reaction with H_2O_2 [*e.g.* as in reaction (17)].

$$Me_2S(O)^{+\cdot} + H_2O_2 \longrightarrow Me_2S(O) + H^+ + \cdot O_2H \quad (17)$$

We attempted to employ the direct photochemical decomposition of hydrogen peroxide to generate $\cdot OH$ in the absence of titanium(III) for reaction with $Me_2S(O)$ at low pH [to establish whether the reverse of reaction (6) is followed by reaction (13)]. However, no signals were detected in experi-

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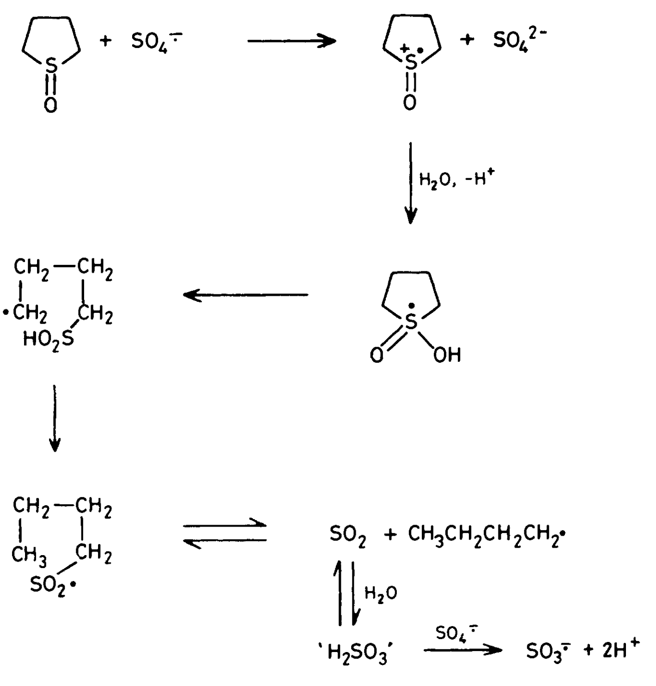
* Further, in the (slow-flow) photolysis experiments, the concentration of RSO_2H in the cavity will be higher than in the rapid-flow experiments.



Scheme 2.

ments in which both $[H_2O_2]$ and $[Me_2S(O)]$ were varied widely in both the presence and absence of acetone as potential photosensitizer: this may reflect the inefficiency of decomposition of H_2O_2 in the presence of the sulphoxide chromophore and/or reaction of $\cdot OH$ with hydrogen peroxide (to give $\cdot O_2H$).

Another apparent discrepancy which remains to be explained concerns the behaviour of cyclic sulphoxides. For example, whereas $\cdot OH$ reacts with cyclic monosulphoxides to give a mixture of alkylsulphonyl and alkyl radicals, $SO_4^{-\cdot}$ gives signals from $RSO_2\cdot$ (but not $R\cdot$) together with $SO_3^{-\cdot}$. Unlike reaction of $Me_2S(O)$, no signals from sulphinyl-conjugated radicals were detected at low pH. Such findings can be accounted for on the basis of reactions exemplified by Scheme 2, in which a first-formed radical cation is rapidly hydrated to give an intermediate identical with that generated by $\cdot OH$ addition; subsequent fragmentation (rather than loss of a proton) will give alkyl radicals and then sulphonyl radicals (*e.g. via* intramolecular hydrogen abstraction). In the photolysis system the alkyl radical concentration may be lowered relative to that in the $\cdot OH$ oxidation not only on account of oxidation by $S_2O_8^{2-}$ (see later) but also because of increased opportunity for reaction of $R\cdot$ with the sulphinic acid which builds up down the flow tube; in addition, for *cyclic* rather than acyclic species the occurrence of the intramolecular abstraction will not only destroy $R\cdot$ but increase the amount of $RSO_2\cdot$ produced: subsequent decomposition of this down the flow tube will lead to the formation of SO_2 [reaction (14), *cf.* ref. 7] and hence hydrogen sulphite, which is the likely source of $SO_3^{-\cdot}$ (see Scheme 2). In a separate experiment we confirmed that photolysis of a slowly flowing aqueous solution of hydrogen sulphite (0.1 mol dm^{-3}) and sodium peroxydisulphate (0.05 mol dm^{-3}) gave, as predicted, a strong signal from $SO_3^{-\cdot}$.

(c) *Reaction with Sulphones.*—No e.s.r. signals were detected in either flow-photolysis or rapid-flow ($Ti^{III}/S_2O_8^{2-}$) experiments conducted with $SO_4^{-\cdot}$ and dialkyl sulphones under a wide range of conditions. We believe that this simply reflects the lack of reactivity of the strongly electrophilic sulphate radical anion with substrates possessing the electron-withdrawing $S(O)_2R$ substituent (and which do not possess sulphur-centred lone pairs as a suitable site for attack).

(d) *Oxidation of Radicals by* $S_2O_8^{2-}$.—It has previously been shown [28] that e.s.r. can be employed to monitor the steady-state concentrations of radicals in flow-system studies as a function of the concentration of hydrogen peroxide (one of the components of the initiating redox couple) and that estimates can thence be obtained for the rate constants for the oxidation of radicals possessing an α-oxygen ($+M$) substituent. For reaction (18), for example, k is *ca.* 4×10^4 dm^3 mol^{-1} s^{-1}.[28]

$$\cdot CH_2OH + H_2O_2 \longrightarrow HO\cdot + HO^- + {}^+CH_2OH \quad (18)$$

Now since the reaction between Ti^{III} and H_2O_2, to give $\cdot OH$, is much faster than that between Ti^{III} and $S_2O_8^{2-}$, to give $SO_4^{-\cdot}$ (by a factor of [29] *ca.* 10),* it is in principle possible to *generate* radicals with the Ti^{III}/H_2O_2 system (*via* reaction of $\cdot OH$) in the presence of added peroxydisulphate to study the reaction of the radicals thus produced with $S_2O_8^{2-}$; radical *generation via* reaction with $SO_4^{-\cdot}$ should be avoided.

In a series of preliminary experiments we employed a three-way flow system in which the separate streams contained, respectively, Ti^{III} (0.008 mol dm^3), both H_2O_2 (0.01 mol dm^3) and $S_2O_8^{2-}$ (in the range 0—0.025 mol dm^3), and the substrate (*ca.* 0.1 mol dm^3): in each case the spectra were monitored as $[S_2O_8^{2-}]$ was steadily increased. For experiments in which the substrates MeOH, $Me_2S(O)$, and $Et_2S(O)$ were studied separately, the signals from $\cdot CH_2OH$, $Me\cdot$, and $Et\cdot$, respectively, decreased slightly but steadily as $[S_2O_8^{2-}]$ was increased. Although these trends could be accounted for in terms of the slower production of $\cdot OH$ (because of removal of Ti^{III} by $S_2O_8^{2-}$) they are also consistent with oxidation of the first-formed radicals by $S_2O_8^{2-}$. That the latter, rather than the former, is the explanation is suggested not only by our finding that the signal from $\cdot CH_2CMe_2OH$ (from Bu^tOH) remained unaltered with addition of peroxydisulphate but also by the critical results that for EtOH and Pr^iOH, for example, the signals from $\cdot CH_2CH_2OH$ and $\cdot CH_2CHMeOH$ remained unaltered in intensity whilst those from $\cdot CHMeOH$ and $\cdot CMe_2OH$ were steadily reduced (see *e.g.* Figure 3). The behaviour of $\cdot CH_2CH_2OEt$ and $\cdot CHMeOEt$ from diethyl ether mirrored that of the ethanol-derived radicals. These observations are consistent with the rapid removal, *via* oxidation by added $S_2O_8^{2-}$ [reaction (19)], of those radicals with an α-oxygen substituent (whose $+M$ effect presumably aids electron transfer *via* stabilisation of the incipient carbocation). These qualitative results indicate that the removal of unconjugated alkyl radicals ($Me\cdot$ or $Et\cdot$) is somewhat slower, and the lack of removal of $\cdot CH_2CMe_2OH$, $\cdot CH_2CH_2OH$ and $\cdot CH_2CHMeOH$ suggests that a β-oxygen substituent inhibits oxidation (evidently on account of its $-I$ effect).

$$R\cdot + S_2O_8^{2-} \longrightarrow R^+ + SO_4^{-\cdot} + SO_4^{2-} \quad (19)$$

As has been previously shown, a pseudo-steady-state is achieved in the rapid-flow system, for which a quantitative kinetic analysis is applicable.[28] In this case, the appropriate reactions to be included for generation and destruction of an oxidisable radical are (20)—(23). We believe we are justified

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* It should be noted that the rate constant for Ti^{III}/H_2O_2 is probably [30] *ca.* 2 400 dm^3 mol^{-1} s^{-1} rather than the value of [31] 590 dm^3 mol^{-1} s^{-1} previously employed [29] for the determination of $k(Ti^{III}/S_2O_8^{2-})$; the value of the latter is accordingly *ca.* 200 dm^3 mol^{-1} s^{-1}.

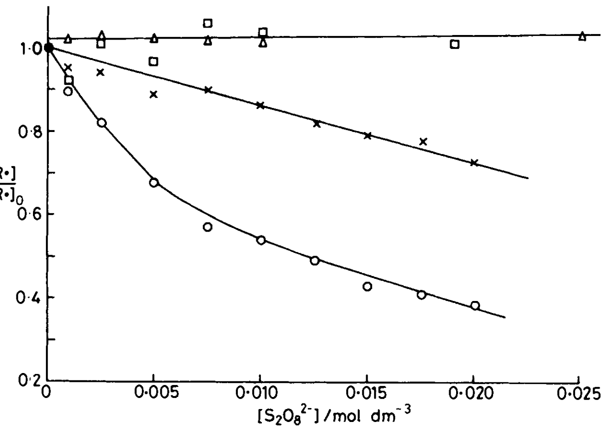

Figure 3. Variation with $[S_2O_8]^{2-}$ of $[R^{\cdot}]/[R^{\cdot}]_0$ (where $[R^{\cdot}]_0$ is the radical concentration in the absence of $S_2O_8^{2-}$) in experiments in which radicals R· were generated from the Ti^{III}/H_2O_2 couple in the presence of increasing concentrations of $S_2O_8^{2-}$: □ $\cdot CH_2CH_2OH$ (from EtOH); ○ $\cdot CHMeOH$ (from EtOH); × $\cdot CH_2OH$ (from MeOH); △ $\cdot CH_2CMe_2OH$ (from Me_3COH)

in ignoring any contribution to radical generation *via* the possible production of $SO_4^{-\cdot}$ either by reaction (4) (as noted above $k_4 \ll k_{20}$) or (22); k_{24} is known[13] to be much less than k_{21}. The destruction of alkyl radicals *via* reactions with alkanesulphinic acids (25) is also thought to be unimportant under the conditions employed.

$$Ti^{III} + H_2O_2 \xrightarrow{k_{20}} Ti^{IV} + \cdot OH + OH^- \quad (20)$$

$$\cdot OH + RH \xrightarrow{k_{21}} R^{\cdot} + H_2O \quad (21)$$

$$R^{\cdot} + S_2O_8^{2-} \xrightarrow{k_{22}} R^+ + SO_4^{-\cdot} + SO_4^{2-} \quad (22)$$

$$2R^{\cdot} \xrightarrow{2k_t} \text{non-radical products} \quad (23)$$

$$RH + SO_4^{-\cdot} \xrightarrow{k_{24}} R^{\cdot} + H^+ + SO_4^{2-} \quad (24)$$

$$R^{\cdot} + RSO_2H \longrightarrow RH + RSO_2^{\cdot} \quad (25)$$

Steady-state analysis for $[\cdot OH]$ and $[R^{\cdot}]$ in equations (20)—(23) gives (26), in which the subscript *t* refers to the

$$k_{20}[Ti^{III}]_t[H_2O_2]_t = 2k_t[R^{\cdot}]^2 + k_{22}[S_2O_8^{2-}][R^{\cdot}] \quad (26)$$

time between mixing and observation. This indicates that a plot of $k_{20}[Ti^{III}]_t[H_2O_2]_t[R^{\cdot}]^{-2}$ against $[S_2O_8^{2-}][R^{\cdot}]^{-1}$ should be a straight line, with intercept $2k_t$ and gradient k_{22}.

As illustrated in Figure 4, where data for Me·, $\cdot CH_2OH$, and ·CHMeOH are plotted in this way, the required linear relationship is found: in each case, the value of $2k_t$ (the intercept) is *ca.* 2×10^9 dm^3 mol^{-1} s^{-1}, which is as expected.[32] Table 2 lists the values derived for k_{22}, the rate constants for oxidation of the first-formed radicals by $S_2O_8^{2-}$. The results show that, as expected if electron transfer to $S_2O_8^{2-}$ is involved, the rate constant is increased by incorporation of an α(+*M*)-oxygen substituent and/or an electron-donating alkyl group at the radical centre (*cf.* ionisation potentials of 7.4 and 6.7 eV, respectively, for $\cdot CH_2OH$ and ·CHMeOH[17] and 9.84 and 8.30 eV, respectively, for Me· and Et·). Consideration of the ionisation potentials of Bu^t·, and Pr^i· (6.93 and 7.55 eV, respectively) strongly suggests that our failure to detect these radicals during *in situ* photolysis experiments with $S_2O_8^{2-}$ reflects, to a considerable extent at least, their susceptibility to rapid oxidation by $S_2O_8^{2-}$. Finally, we note that the rates of oxidation by $S_2O_8^{2-}$ of the radicals we have studied are greater than the rates of the corresponding reactions with H_2O_2 (*cf.*, *e.g.* for ·CHMeOH, a value for the rate constant for reaction with the latter of[28] 1.6×10^5 dm^3 mol^{-1} s^{-1}).

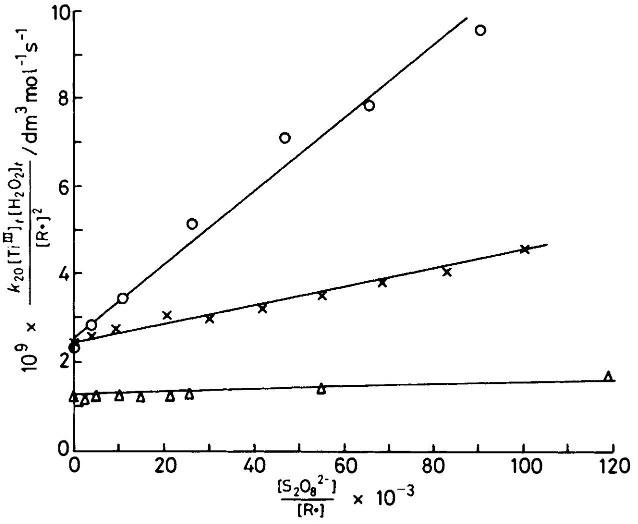

Figure 4. Variation of $k_{20}[Ti^{III}]_t[H_2O_2]_t[R^{\cdot}]^{-2}$/dm^3 mol^{-1} s^{-1} with $[S_2O_8^{2-}][R^{\cdot}]^{-1}$ when $S_2O_8^{2-}$ was added to experiments in which the Ti^{III}/H_2O_2 system was employed to generate radicals from $Me_2S(O)$(Me·, △), MeOH ($\cdot CH_2OH$, ×), and EtOH (·CHMeOH, ○)

Table 2. Rate constants for the oxidation of aliphatic radicals by peroxydisulphate, $S_2O_8^{2-}$ [a]

Radical	*k*/dm^3 mol^{-1} s^{-1}
$\cdot CH_2OH$	1.3×10^5
·CHMeOH	6.9×10^5
·CHMeOEt	7.5×10^5
$\cdot CMe_2OH$	7.1×10^5
·Me	3.3×10^4
·Et	7.4×10^4
$\cdot CH_2CH_2OH$	<*ca.* 10^4
$\cdot CH_2CH_2OEt$	
$\cdot CH_2CHMeOH$	
$\cdot CH_2CMe_2OH$	

[a] Estimated error ±20%.

Experimental

E.s.r. spectra were recorded with a Varian E-104 spectrometer equipped with 100 kHz modulation and an *X*-band klystron. Splitting constants were measured to within ±0.005 mT and *g* factors to within ±0.0001 by comparison with an aqueous solution of Fremy's salt [*a*(N) 1.3091 mT,[33] *g* 2.0055[34]]. Relative radical concentrations were determined from measurements of peak heights (where the appropriate line-widths were the same) or by spectrum simulation (using a program kindly supplied by Dr. M. F. Chiu).

The rapid-flow experiments with redox couples were conducted using a Watson-Marlow 502S flow inducer positioned on the inlet tubing of a mixing chamber which allowed the simultaneous mixing of three reactant streams shortly before passage through the cavity of the spectrometer. The compositions of the solutions to be mixed in experiments with $SO_4^{-\cdot}$ were typically as follows: stream (i) contained titanium(III) chloride (0.008—0.025 mol dm^{-3}), stream (ii) contained sodium peroxydisulphate (0.025 mol dm^{-3}), and the third stream contained the required substrate. For reactions above pH 2.5, EDTA (3—6 g dm^{-3}) was added to stream (i) together with sufficient ammonia solution (*d* 0.880) to give the required pH. For experiments at pH < 2.5, the desired amount of concentrated sulphuric acid was added to stream (i). Experiments using $\cdot$OH were carried out using a similar system except that stream (ii) contained hydrogen peroxide (0.01 mol dm^{-3}). The experimental conditions for investigating radical oxidation in this system by added $S_2O_8^{2-}$ were slightly different in that the substrate was included in stream (i), stream (ii) contained sodium peroxydisulphate (in the range 0—0.025 mol dm^{-3}), and stream (iii) contained hydrogen peroxide (0.01 mol dm^{-3}). For the kinetic studies, $[\mathrm{Ti^{III}}]_t$ was calculated from the initial concentration and exponential decay of $[\mathrm{Ti^{III}}]$ (since $[H_2O_2]_0 \gg [\mathrm{Ti^{III}}]_0$) using[30] k_{20} 2 400 dm^3 mol^{-1} s^{-1} and t 50 ms.[35] Absolute radical concentrations were obtained by comparison (using a Datalab DL4000 microcomputer) of the doubly integrated first-derivative signals with those obtained under identical conditions from $\cdot CH_2OH$ (itself compared[25] with a standard solution of $VOSO_4$).

The flow-photolysis experiments were carried out using a typical flattened aqueous solution sample cell with a built-in two-way mixer through which the solutions were forced using a Watson-Marlow MHRE flow inducer (flow rate 1.5—2.5 cm^3 min^{-1}). The cell was irradiated in the cavity of the spectrometer using the unfiltered output of an Hanovia 977B-1 1 kW mercury-xenon compact arc. The two streams typically contained $Na_2S_2O_8$ (either 0.1 mol dm^{-3} or 0.05 mol dm^{-3} with 0.3 mol dm^{-3} acetone) and the substrate (0.005—0.1 mol dm^{-3}), respectively. pH Adjustment was made using either ammonia solution (*d* 0.880) or concentrated sulphuric acid.

pH Measurements in both the flow and photolysis experiments were made using a Pye–Unicam PW9410 pH meter with the electrode inserted into the effluent stream. All solutions were degassed before use by purging with oxygen-free nitrogen.

The chemicals employed were commercial samples (and used as supplied), except for some of the sulphoxides which were obtained *in situ* by keeping the required sulphide in contact with a slight excess of $Na_2S_2O_8$ for a short period prior to flowing (a process which gives the appropriate sulphoxide in high yield[36]).

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