Electron Spin Resonance Studies. Part XLIV.[1] The Formation of Alkylsulphonyl Radicals by the Oxidation of Aliphatic Sulphoxides with the Hydroxyl Radical and by the Reaction of Alkyl Radicals with Sulphur Dioxide

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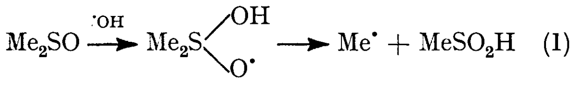
E.s.r. spectra are reported for a range of alkylsulphonyl and carbon-centred radicals detected during the oxidation of sulphoxides with the $Ti^{III}–H_2O_2$ couple in aqueous solution. Alkylsulphonyl radicals are also formed in some cases by reaction of substituted alkyl radicals with SO_2 in aqueous solution; however, hydroxy-conjugated radicals under these conditions behave as one-electron reducing agents and yield SO_2^- and carbonyl- and carboxy-conjugated radicals do not appear to react. Evidence is adduced for the ready desulphonylation of $HO_2C{\cdot}CH_2{\cdot}SO_2^{\cdot}$.

We have recently presented evidence that the reaction of dimethyl sulphoxide with the titanium(III) ion–hydrogen peroxide couple yields the methyl and methylsulphonyl radicals as in reactions (1) and (2).[1] We



$$Me_2SO \xrightarrow{\cdot OH} Me_2S(OH)(O^{\cdot}) \longrightarrow Me^{\cdot} + MeSO_2H \quad (1)$$

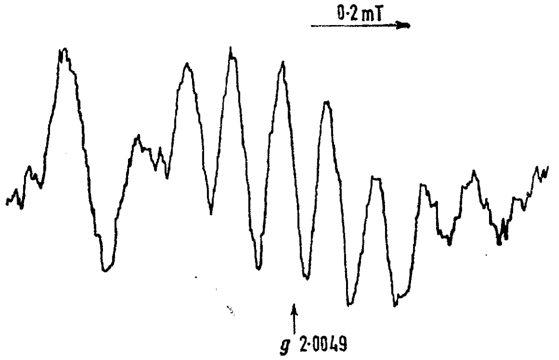
$$MeSO_2H \xrightarrow{Me^{\cdot}} MeSO_2^{\cdot} \quad (2)$$

have now extended this study to a range of sulphoxides in order to ascertain whether (substituted) alkyl and alkylsulphonyl radicals are generally available through such reactions, to examine the preference for homolysis to yield R˙ or R″˙ from an intermediate RR′S(O˙)OH, and to determine whether suitably structured alkylsulphonyl radicals desulphonylate as in reaction (3)

$$RSO_2^{\cdot} \rightleftharpoons R^{\cdot} + SO_2 \quad (3)$$

(*cf.* refs. 2 and 3). Further, we have studied the reverse of reaction (3) by generating (substituted) alkyl radicals in the presence of sulphur dioxide.

Reactions of Sulphoxides.—Sulphoxides are readily formed in high yield by reaction of the corresponding sulphides with hydrogen peroxide at ambient temperature. We utilised this method, and did not isolate the sulphoxides before employing them in reactions with the titanium(III)–peroxide couple. A high conversion of sulphide into sulphoxide was indicated in each case since sulphides and sulphoxides are of comparable reactivity towards the hydroxyl radical[4] and yet no radicals derived from the parent sulphide[5] with hydroxyl could be detected. Likewise, no sulphone-derived radicals[6] could be detected, in keeping with our expectation that further oxidation of the sulphoxide to the sulphone, which generally requires an excess of peroxide and elevated temperatures,[7] should not occur to a significant extent under our conditions.



E.s.r. spectrum of $CH_3CH_2SO_2^{\cdot}$ (*g* 2·0049) detected during the oxidation of diethyl sulphoxide with the hydroxyl radical. The extreme left-hand peak is one of the absorptions from $^{\cdot}CH_2CH_3$

The e.s.r. data obtained during reaction of sulphoxides with the titanium(III)–peroxide couple at pH 1 under flow-system conditions, and the radicals to which the spectra are assigned, are in Table 1; a typical spectrum is shown in the Figure. Reactions were carried out with both relatively low concentrations of titanium(III) (2mM) and hydrogen peroxide (6mM), and higher concentrations (10—14 and 20—36mM, respectively) (all concentrations are those after mixing the reagents).

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[1] Part XLIII, B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, preceding paper.

[2] A. Good and J. C. J. Thynne, *Trans. Faraday Soc.*, 1967, **63**, 2708, 2720.

[3] W. K. Busfield and K. J. Ivin, *Trans. Faraday Soc.*, 1961, **57**, 1044.

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

[5] (*a*) B. C. Gilbert, J. P. Larkin, and R. O. C. Norman, *J.C.S. Perkin II*, 1973, 272; (*b*) B. C. Gilbert, D. K. C. Hodgeman, and R. O. C. Norman, *ibid.*, p. 1748.

[6] B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, unpublished observations.

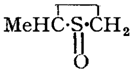
[7] See, *e.g.*, D. S. Tarbell and C. Weaver, *J. Amer. Chem. Soc.*, 1941, **63**, 2939.

The carbon-centred radicals reported under the former conditions were also generally observed under the latter; however, the sulphonyl radicals were detected only under the latter conditions and their concentrations relative to those of the carbon-centred radicals increased with increasing concentrations of titanium(III) and hydrogen peroxide. No sulphonyl radical was detected from $(HO_2C{\cdot}CH_2)_2SO$.

The following carbon-centred radicals were identified by their splitting constants and *g* factors: $Me^{\bullet}$, $Et^{\bullet}$, $^{\bullet}CH_2CH_2OH$,[8] $^{\bullet}CH_2CMe_2OH$,[9] $^{\bullet}CH_2CO_2H$,[8] $^{\bullet}CH_2CH_2CO_2H$,[10] and $^{\bullet}CMe_3$.[11] The spectrum from tetrahydrothiophen *S*-oxide with low concentrations of Ti^{III} and H_2O_2 was ascribed to $HO_2S[CH_2]_3CH_2^{\bullet}$ on the basis of its *g* factor[12] and three triplet splittings (2·17, 2·74, and 0·08 mT) in the ranges expected[13] for its α-, β-, and γ-protons, respectively. A weak spectrum with *g* 2·0026 from the six-membered analogue is similarly assigned to $HO_2S[CH_2]_4CH_2^{\bullet}$, and the spectrum from 1,4-thioxan *S*-oxide with *g* 2·0026 but no γ-proton splitting is assigned to $HO_2S[CH_2]_2OCH_2CH_2^{\bullet}$.

TABLE 1

Radicals, and their e.s.r. parameters, obtained from sulphoxides with (i) low, and (ii) high concentrations of Ti^{III} and H_2O_2

Sulphoxide	Conditions	Radicals detected	Splitting constants (mT)	*g*
Et_2SO	(i)	$Et^{\bullet}$	2·71 (3H), 2·21 (2H)	2·0026
	(ii)	$EtSO_2^{\bullet}$	0·19 (3H), 0·095 (2H)	2·0049
$MeS(O)CH_2Br$	(i)	$Me^{\bullet}$	2·29 (3H)	2·0025
	(ii)	$MeSO_2^{\bullet}$	0·094 (3H)	2·0049
$Bu^t{}_2SO$	(ii)	$Bu^tSO_2^{\bullet}$	0·255 (9H)	2·0054
$(HOCH_2CH_2)_2SO$	(i)	$HOCH_2CH_2^{\bullet}$	2·80 (2H), 2·19 (2H)	2·0026
	(ii)	$HOCH_2CH_2SO_2^{\bullet}$	0·39 (2H)	2·0050
$(HOCMe_2CH_2)_2SO$	(i)	$HOCMe_2CH_2^{\bullet}$	2·13 (2H), 0·13 (6H)	2·0026
	(ii)	$HOCMe_2CH_2SO_2^{\bullet}$		2·0051
$(HO_2CCH_2)_2SO$	(i), (ii)	$HO_2CCH_2^{\bullet}$	2·13 (2H)	2·0033
$(HO_2CCH_2CH_2)_2SO$	(i)	$HO_2CCH_2CH_2^{\bullet}$	2·66 (2H), 2·24 (2H)	2·0026
	(ii)	$HO_2CCH_2CH_2SO_2^{\bullet}$	0·26 (2H), 0·13 (2H)	2·0050
$HO[CH_2]_2S(O)Bu^t$	(i)	$\left\{\begin{array}{l}Me_3C^{\bullet}\\HOCH_2CH_2^{\bullet}\end{array}\right.$	2·26 (9H) 2·80 (2H), 2·19 (2H)	2·0027 2·0026
	(ii)	$\left\{\begin{array}{l}HOCH_2CH_2SO_2^{\bullet}\\Bu^tSO_2^{\bullet}\end{array}\right.$	0·39 (2H) 0·255 (9H)	2·0050 2·0054
$\overline{[CH_2]_4-SO}$	(i)	$HO_2S[CH_2]_3CH_2^{\bullet}$	2·74 (2H), 2·17 (2H), 0·08 (2H)	2·0026
	(ii)	$R[CH_2]_4SO_2^{\bullet}$ [a]	0·25 (2H)	2·0049
$\overline{[CH_2]_5-SO}$	(ii)	$\left\{\begin{array}{l}HO_2S[CH_2]_4CH_2^{\bullet}\\R[CH_2]_5SO_2^{\bullet}\ ^{a}\end{array}\right.$	 0·24 (2H)	2·0026 2·0049
$\overline{CH_2CH_2OCH_2CH_2SO}$	(i)	$HO_2S[CH_2]_2OCH_2CH_2^{\bullet}$	2·71 (2H), 2·19 (2H)	2·0026
	(ii)	$RCH_2CH_2OCH_2CH_2SO_2^{\bullet}$ [a]	0·38 (2H)	2·0050
 $MeHC{\cdot}\underset{\underset{O}{\Vert}}{S}{\cdot}CH_2$	(i), (ii)	$SO_2^{\bullet -}$		2·0056

[a] For the nature of R, see text.

Sulphonyl radicals were characterised by their *g* factors, in the range 2·0049—2·0054 (*cf.* $MeSO_2^{\bullet}$, *g*[1] 2·0049), and as follows. $EtSO_2^{\bullet}$ Has been detected in non-aqueous solution and has *a*(3H) 0·174, *a*(2H) 0·071 mT at −10°;[14] our values are slightly greater, no doubt as a result of solvent dependence, but retain the characteristic that *a*(β-H) > *a*(α-H).* The spectrum from $(HO_2CCH_2CH_2)_2SO$ is, by analogy, assigned to $HO_2C[CH_2]_2SO_2^{\bullet}$. The spectrum from $(HOCMe_2CH_2)_2SO$ appeared as a broad singlet (linewidth 0·13 mT); the only splittings to be expected, from the α- and γ-protons, are likely to be less than the linewidth (*cf.* ref. 14, *e.g.* $BuSO_2^{\bullet}$). The spectrum of the sulphonyl radical from $(HOCH_2CH_2)_2SO$ contained only a triplet splitting, which we attribute to the β-protons; a small α-splitting would have been concealed by the linewidth. It is notable that the β-splitting is significantly greater than that for the other sulphonyl radicals we have described; possibly the oxygen substituent acts to favour a conformation which is associated with strong hyperfine interaction. The spectra from the five- and six-membered cyclic sulphoxides showed triplet splittings compatible with the β-protons in the sulphonyl radicals displayed in Table 1; the nature of R in these radicals is discussed later.

2-Methylthiiran *S*-oxide gave, under both sets of conditions, a singlet with *g* 2·0056, the same, within the experimental error, as that reported for $SO_2^{\bullet -}$ in aqueous solution.[15]

The following features are of note in these results. First, observation of sulphonyl radicals only when

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* The α-, β-, and γ-protons in these radicals are named according to their position relative to the sulphonyl group, *e.g.* $-\overset{\gamma}{CH_2}-\overset{\beta}{CH_2}-\overset{\alpha}{CH_2}-SO_2^{\bullet}$.[14]

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

[9] W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 1963, 3119.

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

[11] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2147.

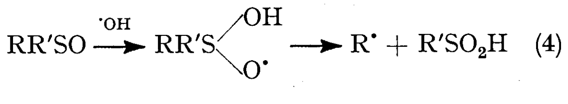
[12] R. O. C. Norman and R. J. Pritchett, *Chem. and Ind.*, 1965, 2040.

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

[14] A. G. Davies, B. P. Roberts, and B. R. Sanderson, *J.C.S. Perkin II*, 1973, 626.

[15] R. O. C. Norman and P. M. Storey, *J. Chem. Soc.* (*B*), 1971, 1009.

relatively high concentrations of $\mathrm{Ti^{III}}$ and $\mathrm{H_2O_2}$ were employed is consistent with the formation of these radicals from an initial product, *i.e.* the sulphinic acid, and the results as a whole are compatible with reactions (4) and (5). It should be noted that, whereas in the study of the reaction of dimethyl sulphoxide with this system essentially all the hydroxyl radicals were scavenged by the sulphoxide, so that abstraction from the sulphinic acid was effected by methyl, in the present study conditions could not always be adjusted for complete scavenging in this way; we presume that the abstraction in reaction (5) is by both R$^{\bullet}$ and $^{\bullet}$OH.



$$\mathrm{RR'SO} \xrightarrow{^{\bullet}\mathrm{OH}} \mathrm{RR'S}\begin{smallmatrix}\diagup\mathrm{OH}\\ \diagdown\mathrm{O}^{\bullet}\end{smallmatrix} \longrightarrow \mathrm{R}^{\bullet} + \mathrm{R'SO_2H} \tag{4}$$

$$\mathrm{R'SO_2H} \xrightarrow{\mathrm{R}^{\bullet}\text{ or }^{\bullet}\mathrm{OH}} \mathrm{R'SO_2}^{\bullet} \tag{5}$$

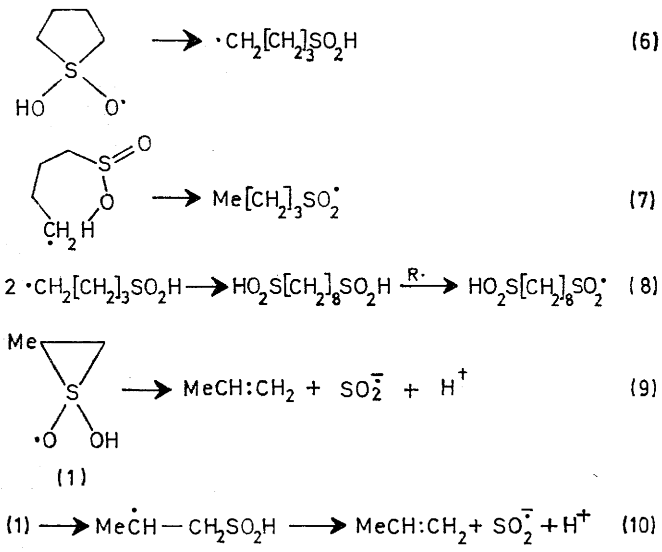
Secondly, a relatively large concentration of $\mathrm{Bu^t{}_2SO}$ was required for the detection of radicals, and we suspect that the addition of hydroxyl to this sulphoxide is sterically retarded.

Thirdly, $\mathrm{(HO_2C{\cdot}CH_2)_2SO}$ failed to yield a sulphonyl radical. Two possible explanations for this are, first, that the radical $^{\bullet}\mathrm{CH_2CO_2H}$ is relatively ineffective at abstracting hydrogen from the sulphinic acid, either owing to its delocalisation or because such abstraction occurs more readily with radicals of greater nucleophilic character such as Me$^{\bullet}$, and secondly, the sulphonyl radical $\mathrm{HO_2C{\cdot}CH_2{\cdot}SO_2}^{\bullet}$ might desulphonylate readily [reaction (3; $\mathrm{R = CH_2CO_2H}$)]. Support for at least the latter explanation was obtained from subsequent experiments (see later).

Fourthly, the unsymmetrical sulphoxide, $\mathrm{HOCH_2CH_2S(O)Bu^t}$, gave both the t-butyl and $^{\bullet}\mathrm{CH_2CH_2OH}$ radicals, in the ratio *ca.* 2·5 : 1, when low concentrations of titanium(III) and hydrogen peroxide were used, and these radicals and $\mathrm{HOCH_2CH_2SO_2}^{\bullet}$ and $\mathrm{Bu^tSO_2}^{\bullet}$ with higher concentrations. We infer that the t-butyl radical fragments slightly more readily from the intermediate adduct with the hydroxyl radical than does $^{\bullet}\mathrm{CH_2CH_2OH}$ (*cf.* ref. 16). The other unsymmetrical sulphoxide, $\mathrm{MeS(O)CH_2Br}$, yielded $\mathrm{MeSO_2}^{\bullet}$ as the only sulphonyl radical, consistent with readier fragmentation of the intermediate adduct to $^{\bullet}\mathrm{CH_2Br}$ and $\mathrm{MeSO_2H}$ than to Me$^{\bullet}$ and $\mathrm{CH_2Br{\cdot}SO_2H}$; however, the radical $^{\bullet}\mathrm{CH_2Br}$ could not be detected (there was a weak spectrum from Me$^{\bullet}$), possibly because of broadening of its e.s.r. lines owing to anisotropy in the g value and the bromine splitting (*cf.* ref. 17).

Fifthly, the carbon-centred radicals observed during the reaction of three cyclic sulphoxides presumably result from ring-opening of a hydroxy–radical adduct, as in reaction (6). The sulphonyl radicals detected from these sulphoxides might be formed by intramolecular hydrogen atom abstraction such as in reaction (7) or from the dimer of the carbon-centred radical as in reaction (8). We believe that the latter explanation is correct since it, but not the alternative, is consistent with the observed increase in the ratio of the amounts of sulphonyl and carbon-centred radicals with increase in $[\mathrm{Ti^{III}}]$ and $[\mathrm{H_2O_2}]$. The nature of R in Table 1 is assigned accordingly.

Finally, 2-methylthiiran *S*-oxide gave neither a carbon-centred nor a sulphonyl radical but solely $\mathrm{SO_2}^{-\bullet}$. We suggest that the expected adduct (1) either undergoes the extrusion reaction (9) or undergoes ring opening followed by fragmentation [reaction (10)].



Reactions of Carbon-centred Radicals with Sulphur Dioxide.—A direct route to sulphonyl radicals is by the addition of a carbon-centred radical to sulphur dioxide [the reverse of reaction (3)]. This has been shown by e.s.r. spectroscopy to occur for the methyl radical[18] and, by product studies, for aryl radicals.[19]

The hydrogen sulphite ion in aqueous solution reacts with titanium(III) ion to yield $\mathrm{SO_2}^{-\bullet}$ and with the hydroxyl radical to yield $\mathrm{SO_3}^{-\bullet}$.[15] However, at pH values $<$ *ca.* 2, the equilibrium between this ion and sulphur dioxide favours the latter (we calculate[20] that $[\mathrm{SO_2}] = 16[\mathrm{HSO_3}^-]$ at pH 0·7); thus, reaction of the $\mathrm{Ti^{III}}$–$\mathrm{H_2O_2}$ couple with an organic compound which yields a radical R$^{\bullet}$ with hydroxyl should be suited, in the presence of a strongly acidified solution of hydrogen sulphite ion, for the occurrence of the reverse of reaction (3). Now, gas-phase data show that the methyl and ethyl radicals add rapidly (k *ca.* 5×10^6 and 5×10^5 l mol^{-1} s^{-1}, respectively) and essentially irreversibly to sulphur dioxide at ambient temperature.[2] Assuming

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[16] C. Lagercrantz and S. Forshult, *Acta Chem. Scand.*, 1969, **23**, 811.

[17] S. P. Mishra, G. W. Neilson, and M. C. R. Symons, *J. Amer. Chem. Soc.*, 1973, **95**, 605.

[18] (*a*) B. D. Flockhart, K. J. Ivin, R. C. Pink, and B. D. Sharma, *Chem. Comm.*, 1971, 339; (*b*) T. Kawamura, P. J. Krusic, and J. K. Kochi, *Tetrahedron Letters*, 1972, 4075.

[19] J. M. Squire and W. A. Waters, *J. Chem. Soc.*, 1962, 2068; C. M. M. da Silva Corrêa, A. S. Lindsay, and W. A. Waters, *J. Chem. Soc.* (*C*), 1968, 1872.

[20] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Interscience, New York, 1966, 2nd edn.

that the rate constants for the additions we wished to study would be *ca.* 10^6 l mol^{-1} s^{-1} and that the sulphonyl radicals would undergo bimolecular termination at rates comparable with that for other small, uncharged radicals ($2k$ *ca.* 2×10^9 l mol^{-1} s^{-1}), we estimated that a sulphur dioxide concentration of *ca.* 10mM should be sufficient for the sulphonyl radicals to achieve a readily detectable concentration (*ca.* 10^{-6}M). A higher concentration would not necessarily be desirable since sulphur dioxide might then react in significant proportion with titanium(III) to give [15] $SO_2^{\cdot-}$ or with hydrogen peroxide or the hydroxyl radical to give [18a] $HOSO_2^{\cdot}$; further, to minimise the last reaction, the organic precursor of $R^{\cdot}$ should be present in high concentration so as to scavenge essentially all hydroxyl radicals.

Our expectations were borne out in practice. Reactions of the Ti^{III}–H_2O_2 couple at pH 0·7 in the presence of *ca.* 10mM-sulphur dioxide and a relatively high concentration of an organic compound which yields a radical $R^{\cdot}$ with hydroxyl, gave radicals $RSO_2^{\cdot}$ in a number of cases (Table 2); we discuss the exceptions in the sequel.

TABLE 2

Radicals detected during the reaction of the Ti^{III}–H_2O_2 couple with organic substrates in the presence of sulphur dioxide

Organic reagent	Radical(s) detected
Bu^tOH	$HOCMe_2CH_2SO_2^{\cdot}$
$(HOCH_2CH_2)_2SO$	$HOCH_2CH_2SO_2^{\cdot}$
$EtCO_2H$	$HO_2CCH_2CH_2SO_2^{\cdot}$ $^{\cdot}CHMeCO_2H$
Et_2CO	$EtCOCH_2CH_2SO_2^{\cdot}$ $^{\cdot}CHMeCOEt$
CH_3CO_2H	$^{\cdot}CH_2CO_2H$
Me_2CO	$^{\cdot}CH_2COMe$
MeOH	$SO_2^{\cdot-}$
EtOH	$SO_2^{\cdot-}$

Reaction with t-butyl alcohol gave the radical $HOCMe_2CH_2SO_2^{\cdot}$, and reaction with bis-2-hydroxyethyl sulphoxide under conditions which, in the absence of added sulphur dioxide, yield only $^{\cdot}CH_2CH_2OH$ (see earlier) gave $HOCH_2CH_2SO_2^{\cdot}$. When acetic acid or acetone was oxidised, the spectrum of the radical $^{\cdot}CH_2CO_2H$ or $^{\cdot}CH_2COMe$ was unquenched by the presence of sulphur dioxide and no sulphonyl radical was detected; with propionic acid, the spectrum of the radical $^{\cdot}CHMe{\cdot}CO_2H$ was unquenched by sulphur dioxide but that of $^{\cdot}CH_2CH_2CO_2H$ was replaced by the spectrum of the radical $HO_2CCH_2CH_2SO_2^{\cdot}$; likewise, with diethyl ketone the spectrum of the radical $^{\cdot}CHMe{\cdot}COEt$ was unquenched by sulphur dioxide whereas that of $^{\cdot}CH_2CH_2COEt$ was replaced by one with a(2H) 0·13, a(2H) 0·26 mT, g 2·0050, attributable to the radical $EtCOCH_2CH_2SO_2^{\cdot}$. Finally, with methanol or ethanol the spectrum of $^{\cdot}CH_2OH$ or $^{\cdot}CHMe{\cdot}OH$ was replaced, in the presence of sulphur dioxide, by a singlet of g 2·0056 which we attribute to $SO_2^{\cdot-}$.

The carbon-centred radicals we have studied which do not yield sulphonyl radicals with sulphur dioxide are of two types, namely, hydroxy-conjugated, and carbonyl- or carboxy-conjugated. In the former case, we attribute formation of the species $SO_2^{\cdot-}$ rather than a sulphonyl radical to the one-electron reducing properties of the carbon radicals, as shown, for example, by their ability to reduce nitro-compounds to nitro radical-anions.[21] In the latter case, either the addition of the carbon-centred radical to sulphur dioxide is relatively slow, and/or the equilibrium in reaction (3) lies well to the right; the former is reasonably to be expected since the (electrophilic) sulphur dioxide is likely to react faster as the nucleophilic character of the radical is increased (*e.g.* $^{\cdot}CH_2CO_2H$ should be less nucleophilic than $^{\cdot}CH_2CH_2OH$), and the latter could follow if an α-carboxy or α-carbonyl substituent were to lower the C–S bond dissociation energy in the sulphonyl radical.

Some evidence consistent with the latter explanation, and also with the view that our failure to detect the radical $HO_2C{\cdot}CH_2{\cdot}SO_2^{\cdot}$ during the reaction of $(HO_2C{\cdot}CH_2)_2SO$ with hydroxyl stems from the ready desulphonylation of this radical, was obtained as follows. A mixture of $(HO_2C{\cdot}CH_2)_2SO$ and methanol was oxidised with the Ti^{III}–H_2O_2 couple, the relative concentrations of the organic reagents being adjusted so as to give partial scavenging of hydroxyl by both the sulphoxide and methanol. As expected, the spectra of the radicals $^{\cdot}CH_2CO_2H$ and $^{\cdot}CH_2OH$ were observed, but, significantly, although the spectrum of the sulphonyl radical $HO_2C{\cdot}CH_2{\cdot}SO_2^{\cdot}$ could not be detected, that of the species $SO_2^{\cdot-}$ was observed. Thus, the results are consistent with the view that the expected sulphinic acid $HO_2C{\cdot}CH_2{\cdot}SO_2H$ yields the corresponding sulphonyl radical and that this fragments rapidly to $^{\cdot}CH_2CO_2H$ and sulphur dioxide.

EXPERIMENTAL

The spectrometer and flow system have been described in detail.[22] Splitting constants and g factors were measured by comparison with Fremy's salt [a(N) 1·3091 mT,[23] g 2·0055 [24]].

A three-stream mixing device was used in all experiments. For experiments with sulphoxides, the three streams typically contained titanium(III) chloride (6—42mM), hydrogen peroxide (18—108mM), and the sulphoxide (40—160mM), respectively. For monitoring reactions between organic radicals and sulphur dioxide, the third stream contained an organic substrate in high concentration (0·1—1·0M) together with sodium metabisulphite (6—15mM). The pH on mixing was adjusted to 0·7 or 1·0 by the addition of concentrated sulphuric acid to the titanium chloride stream.

Chemicals employed were generally commercial samples. Acetic acid, acetone, t-butyl alcohol, diethyl ketone, and sodium metabisulphite were Fisons Laboratory Reagents. Methanol and ethanol (AnalaR) were obtained from James Burrough Ltd.

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[21] M. McMillan and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1968, 590; K.-D. Asmus, A. Wigger, and A. Henglein, *Ber. Bunsengesellschaft Phys. Chem.*, 1966, **70**, 862.

[22] B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1973, 2174.

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

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

With the exception of bromomethyl methyl sulphoxide (prepared from dimethyl sulphoxide by the method of Iriuchijima and Tsuchihashi [25]), sulphoxides were prepared as their aqueous solutions by the oxidation of the corresponding sulphides with 30% hydrogen peroxide, following the method employed by Tarbell and Weaver.[7] Propylene sulphide, tetrahydrothiophen, thian, thiodiglycollic acid, 3,3′-thiodipropionic acid, and 1,4-thioxan were from R. N. Emanuel, di-t-butyl sulphide and diethyl sulphide from Koch-Light Laboratories, and thiodiglycol from B.D.H. Bis-(2-hydroxy-2-methylpropyl) sulphide was prepared from isobutylene chlorohydrin and sodium sulphide,[5a] and β-t-butylthioethanol was prepared by the method of Hurd and Wilkinson.[26]

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[25] S. Iriuchijima and G. Tsuchihashi, *Synthesis*, 1970, 588.

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