Electron Spin Resonance Studies. Part XLVIII.[1] Radicals derived from Organic Sulphites and Related Compounds

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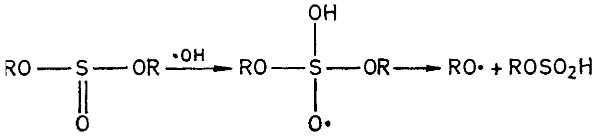
The reactions of organic sulphites and some related compounds with the hydroxyl radical have been investigated by e.s.r. spectroscopy in conjunction with a flow-system technique. There is evidence for a rapid reaction with sulphites, probably at sulphur, which yields an alkoxyl radical; this can be trapped by the nitromethane *aci*-anion, but otherwise is rapidly transformed into the isomeric 1-hydroxyalkyl radical.

We have previously studied by e.s.r. spectroscopy the reactions of several groups of sulphur-containing organic compounds with the titanium(III) ion–hydrogen peroxide system, namely, sulphides,[2,3] sulphoxides,[1,4] sulphones,[1] thiols,[5] and disulphides.[5] With sulphoxides, there is evidence that the hydroxyl radical which is formed from the redox couple reacts rapidly at sulphur (at close to the diffusion-controlled limit, at least for Me_2SO [4,6]) and that the resulting adduct, $R_2S(O\cdot)OH$, fragments to give R· and RSO_2H.[4] We were therefore prompted to study the reactions of dialkyl sulphites with the Ti^{III}–H_2O_2 couple to find whether the analogous reaction (i) competes effectively with the abstraction of hydrogen atoms from the alkyl groups and, if so, to study the behaviour of the alkoxyl species. We have also studied the reactions of three related compounds [MeS(O)OMe, MeS·S(O)Me, and MeS·S(O_2)Me] with the redox couple.



$$RO-\overset{\displaystyle O}{\overset{\|}{S}}-OR \xrightarrow{\cdot OH} RO-\underset{O\cdot}{\overset{OH}{S}}-OR \longrightarrow RO\cdot + ROSO_2H \qquad (i)$$

RESULTS AND DISCUSSION

Reactions were carried out by admixture of aqueous solutions of titanium(III) chloride, hydrogen peroxide, and the organic compound shortly before passage of the combined solution through the cavity of the e.s.r. spectrometer.[7] The pH of the combined solution was either <2 or, for experiments in which nitromethane was also included, *ca.* 9 so that the nitro *aci*-anion was present as a spin trap.[8]

Reactions at pH <2.—Dimethyl, diethyl, and dipropyl sulphite each gave two radicals of which one was identified, from the hyperfine splittings and *g*-factors,[9] as the corresponding hydroxyalkyl radical ($\cdot CH_2OH$, ·CHMeOH, and ·CHEtOH, respectively) and the other, which gave a singlet, was characterised by its *g*-factor (2.005 7) as [10,11] $SO_2^{\cdot -}$. Glycol sulphite gave both a singlet, which is assigned on the basis of its *g*-factor (2.003 1) to the species [11] $SO_3^{\cdot -}$, and a spectrum with a(2H) 0.173, a(2H) 0.035 mT, g 2.003 1, which is attributed, on the basis of the similarity of its splittings to those of $EtOSO_2\cdot$ [a(2H) 0.143, a(3H) 0.043 mT [12]], the similarity of its *g*-factor to that of $Bu^tOSO_2\cdot$ (2.003 6,[12] 2.003 4 [13]), and its likely origin (see later) to the radical $HOCH_2CH_2OSO_2\cdot$. The sulphinate MeS(O)OMe gave the radicals Me·,[4] $\cdot CH_2OH$,[9] and $MeSO_2\cdot$ [a(3H) 0.095 mT, g 2.004 9; *cf.* ref. 4] in

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[1] Part XLVII, P. M. Carton, B. C. Gilbert, H. A. H. Laue R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1975, 1245

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

[3] B. C. Gilbert, D. K. C. Hodgeman, and R. O. C. Norman, *J.C.S. Perkin II*, 1973, 1748.

[4] B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1975, 303, 308.

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

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[9] H. Zeldes and R. Livingston, *J. Chem. Phys.*, 1966, **45**, 1946.

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[13] B. D. Flockhart, K. J. Ivin, R. C. Pink, and B. D. Sharma, *Chem. Comm.*, 1971, 339.

approximately equal concentrations. Both MeS·S(O)Me and MeS·S(O$_2$)Me gave only the radical $MeSO_2\cdot$.

Reactions in the Presence of $CH_2{:}NO_2^-$.—Details of the radicals which were detected when reaction with the redox couple was carried out in the presence of the *aci*-anion of nitromethane are given in the Table. In addition, the species[14] $MeNO_2^{\cdot -}$ and[15] $HO\cdot CH_2NO_2^{\cdot -}$ were detected in each case.

Radicals trapped by the nitromethane *aci*-anion

Organic compound	R in $RCH_2NO_2^{\cdot -}$	Hyperfine splitting (mT)		
		a (N)	*a* (CH$_2$)	*a* (other H)
(MeO)$_2$SO	MeO	2.38	0.85 (2 H)	
	HOCH$_2$	2.55	1.06 (2 H)	0.04 (1 H)
	SO_3^- [a]	2.21	0.75 (2 H)	
(EtO)$_2$SO	EtO	2.38	0.86 (2 H)	
	HOCHMe	2.50	1.12 (1 H), 0.96 (1 H)	0.05 (1 H)
	EtOSO$_2$ [a]	2.18	0.64 (2 H)	
(PrO)$_2$SO	PrO	2.38	0.85 (2 H)	
	HOCHEt	2.52	1.17 (1 H), 0.93 (1 H)	0.06 (1 H)
	SO_3^- [a]	2.21	0.75 (2 H)	
$\overline{SO\cdot O\cdot CH_2\cdot CH_2\cdot O}$	$^-O_3SCH_2CH(OH)$	2.50	1.14 (1 H), 0.95 (1 H)	0.05 (1 H)
	SO_3^-	2.21	0.745 (2 H)	
	$CH_2(OH)CH_2OSO_2$	2.19	0.62 (2 H)	
MeS(O)OMe [b]	MeO	2.38	0.85 (2 H)	
	Me	2.59	0.975 (2 H)	
	MeOSO$_2$	2.18	0.64 (2 H)	

[a] Very weak signals. [b] The resonances of $CH_2(OH)CH_2NO_2^{\cdot -}$, if formed, could have been obscured by those of other radicals.

With the exception of glycol sulphite, each sulphite and methyl methanesulphinate gave a spectrum with *a*(N) 2.38 and *a*(2H) *ca.* 0.8 mT, which we attribute to radicals of the type $ROCH_2NO_2^{\cdot -}$, formed by the trapping of alkoxyl radicals. Thus, *a*(N) is smaller than for adducts of $CH_2{:}NO_2^-$ with carbon radicals[8] (*cf.* the corresponding adduct with[8] $PhCO_2\cdot$), and there was no proton hyperfine splitting other than from the nitro-bonded methylene protons, consistent with the absence of γ-protons (the linewidth was 0.03 mT; a splitting greater than this would have been detected). To confirm our assignment we prepared a radical of this type by an independent route: diethyl ether was oxidised with the redox couple in the presence of nitrite ion, and a spectrum was obtained [*a*(N) 2.45, *a*(1H) 0.18 mT] which was identical with that obtained by oxidising diethyl sulphite in the presence of the *aci*-anion of nitroethane. We infer the occurrence of reaction (ii) in the former case and the trapping of the ethoxyl radical in the latter [reaction (iii)]. Further support for the assignment is provided by the data for radicals derived from the reaction between hydroperoxides and titanium(III) ion in the presence of $CH_2{:}NO_2^{\cdot -}$.[16]

$$Et_2O \xrightarrow{\cdot OH} EtO\cdot\dot{C}HMe \xrightarrow{NO_2^-} EtO\cdot CHMe\cdot NO_2^{\cdot -} \qquad (ii)$$

$$(EtO)_2SO \xrightarrow{\cdot OH} EtO\cdot \xrightarrow{^-CHMeNO_2} EtO\cdot CHMe\cdot NO_2^{\cdot -} \qquad (iii)$$

The ascription of spectra from the acyclic sulphites and methyl methanesulphinate to adducts formed by carbon-centred radicals is based on the identity of the splittings, within the experimental error, to those previously reported;[8] a spectrum from glycol sulphite is ascribed to the adduct with $\cdot CH(OH)\cdot CH_2SO_2O^-$ on the basis of the similarity of its splittings to those of the adduct with $\cdot CH(OH)Et$ and its likely mode of formation. The adduct formed by the radical-anion $SO_3^{\cdot -}$ has been identified previously.[11] Finally, the assignment of a spectrum from glycol sulphite to the adduct formed by the radical $CH_2(OH)\cdot CH_2OSO_2\cdot$ is based on the similarity of the e.s.r. data to those for the adduct with $SO_3^{\cdot -}$ and the fact that this radical is observed directly at low pH; assignments for adducts with $EtOSO_2\cdot$ and $MeOSO_2\cdot$ are made on the same basis.

Reaction Mechanisms.—(a) *Acyclic sulphites.* Hydroxy-substituted carbon radicals are detected directly when the sulphites are oxidised at low pH and are trapped when oxidation is at high pH in the presence of $CH_2{:}NO_2^-$. We can rule out the possibility that they are derived by reaction of the hydroxyl radical with the corresponding alcohols (which could be formed, *e.g.*, by hydrolysis) since in that case we should have been able to detect the radical $\cdot CH_2CH_2OH$,[17] as well as $\cdot CHMeOH$, from diethyl sulphite (reaction of $\cdot OH$ with ethanol under similar conditions leads to signals from both radicals, with [$\cdot CH_2CH_2OH$] : [$\cdot CHMeOH$] *ca.* 1 : 10) and a mixture of radicals from propanol[17] if this is formed by hydrolysis of dipropyl sulphite. However, our results—the detection of solely the 1-hydroxyalkyl radical in each study—are consistent with the occurrence of reaction (i) followed by rearrangement of the alkoxyl radical so

$$RCH_2O\cdot \longrightarrow R\dot{C}HOH \qquad (iv)$$

formed to the related hydroxyalkyl radical [reaction (iv)]; this pathway is consistent with the trapping of the

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[14] M. McMillan and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1968, 590.

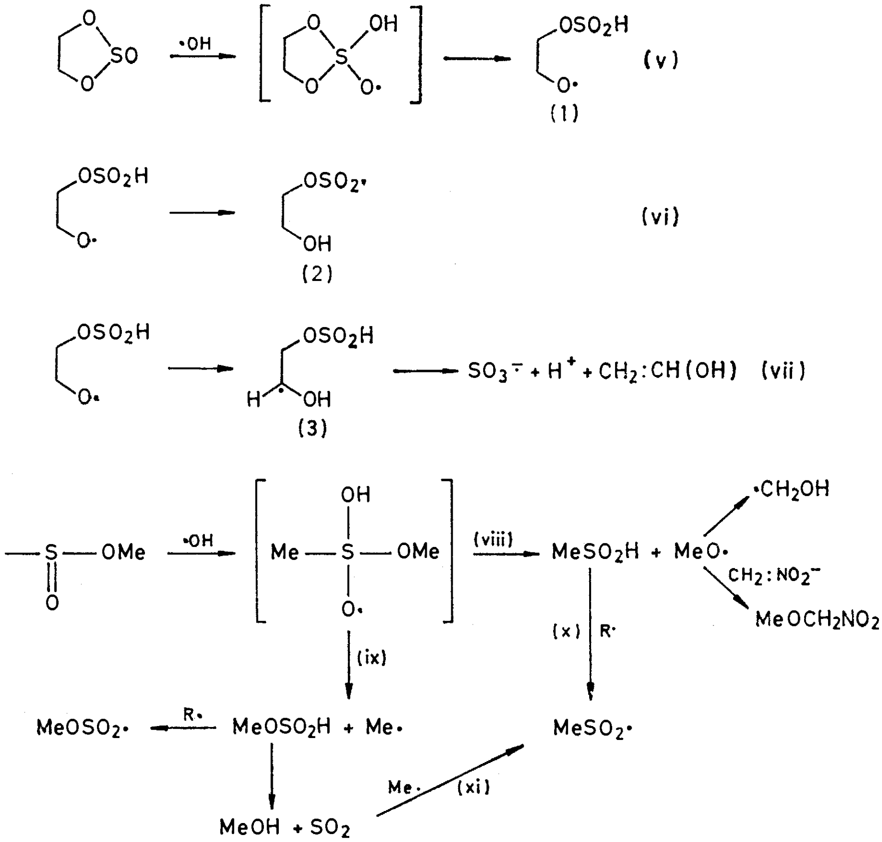
[15] D. J. Edge and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1969, 182.

[16] B. C. Gilbert, R. G. G. Holmes, H. A. H. Laue, and R. O. C. Norman, *J.C.S. Perkin II*, 1976, 1047.

[17] R. Livingston and H. Zeldes, *J. Chem. Phys.*, 1966, **44**, 1245; see also W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 1963, 3119.

alkoxyl radicals * by $CH_2{:}NO_2^-$ and there is independent evidence for the rearrangement step.[16] It is interesting that the intermediate sulphuranyl radical formed in reaction (i) fragments by S–O, rather than C–O, fission.

As expected on the basis of this reaction scheme, we found that, if the concentration of $CH_2{:}NO_2^-$ was raised in a series of experiments involving reaction of ·OH with dipropyl sulphite, the ratio of the extent of trapping of $CH_3CH_2CH_2O\cdot$ to the extent of trapping of $CH_3CH_2\dot{C}HOH$ (as judged by the intensities of the signals from the corresponding nitro anion-radicals) increased; *i.e.* increasing amounts of the alkoxyl radical were intercepted, before rearrangement, by the trap.



Scheme 1

The alkyl hydrogen sulphite which is formed in reaction (i) should decompose rapidly to the corresponding alcohol and sulphur dioxide. The alcohol is evidently not formed in sufficient concentration by the time the e.s.r. cavity is reached so as to contribute significantly to the generation of carbon radicals (see above), but the observation of the species $SO_2^{-\cdot}$ is consistent with the formation of sulphur dioxide and either its one-electron reduction by the hydroxyalkyl radical which is present,[4] or, *via* hydrogen sulphite ion, one-electron reduction by titanium(III).[11] The radical $EtOSO_2\cdot$ presumably arises, at least in part, by further (radical) oxidation of the ethyl hydrogen sulphite formed as in reaction (i; R = Et). Small amounts of $SO_3^{-\cdot}$ which give rise to the weak signals of the corresponding adduct with $CH_2{:}NO_2^-$ in the reaction of some dialkyl sulphites may arise by hydrolysis of the alkyl hydrogen sulphite to HSO_3^- (*cf.* formation of SO_2 at low pH) followed by one-electron oxidation of this ion by hydroxyl.

(b) *Glycol sulphite.* The results are accommodated by the reaction sequence (v)—(vii). The first step corresponds to that for the acyclic sulphites. Intramolecular hydrogen-atom abstraction by alkoxyl radicals is known to be a rapid process,[19] and although it usually occurs preferentially *via* a six-membered cyclic transition state,[20] it can occur *via* the seven-membered analogue if a suitably activated hydrogen is available.[21] We therefore suggest the occurrence of reaction (vi) to account for formation of the radical (2). The rearrangement of radical (1) to give (3) competes at least moderately effectively with reaction (vi), as judged by the trapping

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* We should not expect to detect the alkoxyl radicals directly by e.s.r. in solution, assuming they reached a suitable steady-state concentration, owing to line broadening from modulation of the *g*-value.[18]

[18] M. C. R. Symons, *J. Amer. Chem. Soc.*, 1969, **91**, 5924.

[19] K. U. Ingold, in 'Free Radicals,' ed. J. K. Kochi, Interscience, New York, 1973, vol. I, p. 94.

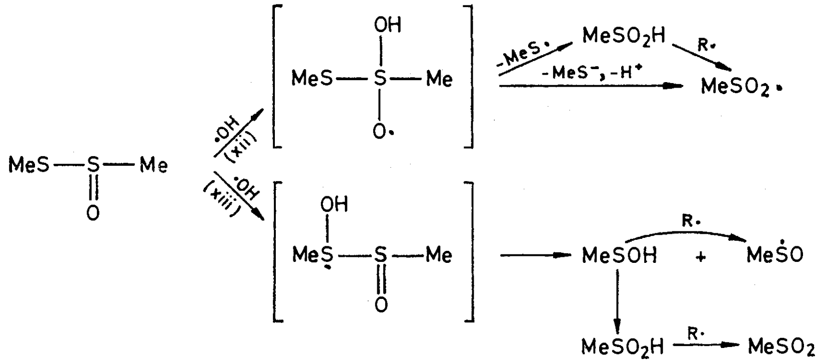
[20] K. Heusler and J. Kalvoda, *Synthesis*, 1971, 501; *Angew. Chem. Internat. Edn.*, 1964, **3**, 525.

[21] M. Lj. Mihailovic and M. Miloradovic, *Tetrahedron*, 1966, **22**, 723.

of radical (3) by $CH_2{:}NO_2^-$. However, radical (3) is structurally suited to fragmentation [*cf.*, for example,[22] $\cdot CH(OH)CH_2NMe_3^+$] as in reaction (vii), and this could account for the detection of the species $SO_3^{-\cdot}$.

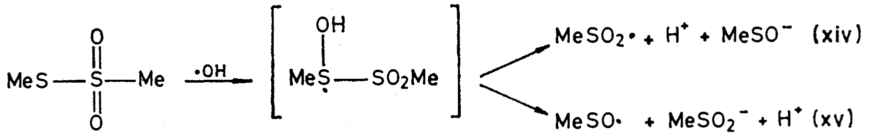
(c) *Other Substrates.*—The detection of $\cdot Me$, $\cdot CH_2OH$, and $MeSO_2\cdot$ from methyl methanesulphinate, and the trapping of $\cdot OMe$ in addition to $\cdot Me$ and $MeOSO_2\cdot$, can be accommodated by the reactions outlined in Scheme 1. Addition of hydroxyl at sulphur is followed by S–O fragmentation [reaction (viii)] and S–C fragmentation [reaction (ix)], as with sulphites and sulphoxides,[4] respectively. The former route leads to $MeO\cdot$, which, if not trapped, rearranges to $\cdot CH_2OH$, and $MeSO_2H$; the sulphinic acid is then oxidised at low pH but not high pH ($MeSO_2^-$ is much less readily oxidised by radicals than the parent acid[4,5]), as shown in reaction (x). The fission which leads to methyl also gives $MeOSO_2H$ [reaction (ix)] which is the likely precursor of $MeOSO_2\cdot$. Hydrolysis of this acid (to give methanol and SO_2) also provides a likely additional route to $MeSO_2\cdot$, *via* reaction (xi).[4]

S-Methyl methanethiosulphinate and *S*-methyl methanethiosulphonate both give rise to signals from $MeSO_2\cdot$. For the former substrate this could be formed by way of either or both the reaction pathways shown in Scheme 2; the initial reactions are typical of sulphoxides [reaction (xii)] and disulphides [reaction (xiii)] respectively, and reaction at both sites would be expected to be rapid. The fragmentation reactions of hydroxyl adducts of disulphides, the reason for believing that $MeSO\cdot$ will remain undetected, and the formation of $MeSO_2\cdot$ from the intermediate sulphenic acid, have been discussed previously.[5]



SCHEME 2

With *S*-methyl methanethiosulphonate, reaction presumably occurs predominantly at the sulphide sulphur atom to give an adduct which can fragment either directly to $MeSO_2\cdot$ [reaction (xiv)] or to $MeSO\cdot$ and $MeSO_2H$ [reaction (xv)]. MeSOH, formed as in reaction (xiv), could also be the source of $MeSO_2\cdot$, since molecular oxidation of the sulphenic acid to the sulphinic acid by H_2O_2 would be expected.[5]



We were unable to detect $MeSO_2\cdot$ in this system at pH *ca.* 7 and suggest that the direct route (xiv) is not operative here; thus detection of $MeSO_2\cdot$ only at low pH suggests that it arises from oxidation of $MeSO_2H$ [formed in reaction (xv) or from MeSOH and H_2O_2], a reaction which is not effective as a source of $MeSO_2\cdot$ when the acid is ionised.[4,5]

EXPERIMENTAL

Materials.—Dimethyl, diethyl, and glycol sulphite were available commercially. Dipropyl sulphite was prepared following the method of Suter and Gerhart,[23] and *S*-methyl methanethiosulphinate,[24] methanethiosulphonate,[25] and methyl methanesulphinate [26] were prepared according to literature procedures.

Methods.—E.s.r. spectra were measured on a Varian E-3 spectrometer with an *X*-band klystron and 100 kHz modulation. Splitting constants were determined to within ±0.01 mT, and *g*-factors to within ±0.000 1, by comparison with Fremy's salt [a(N) 1.309 1 mT,[27] g 2.005 5 [28]]. A mixing chamber was employed which allowed the simultaneous mixing of three reactant solutions *ca.* 0.04 s before passage

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

[23] C. M. Suter and H. L. Gerhart, *Org. Synth.*, Coll. Vol. II, p. 112.

[24] T. L. Moore and D. E. O'Connor, *J. Org. Chem.*, 1966, **31**, 3587.

[25] H. J. Backer, *Rec. Trav. chim.*, 1948, **67**, 894.

[26] I. B. Douglass, *J. Org. Chem.*, 1965, **30**, 633.

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

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

into the spectrometer cavity. One stream contained titanium(III) chloride (0.01M), the second contained hydrogen peroxide (0.02—0.07M), and the third contained the organic compound (0.02—0.1M). For reactions at pH 1—2, each stream was acidified with concentrated sulphuric acid (usually 2.5 ml l^{-1}). For reactions at pH > 8, the titanium(III) solution was treated with ethylenediaminetetraacetic acid (6 g l^{-1}) and ammonia (*ca.* 4 ml l^{-1}), the organic substrate was included in the hydrogen peroxide stream, and nitromethane (*ca.* 0.015M) and ammonia (*ca.* 8 ml l^{-1}) were contained in the third stream.

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