The Nature of the Radical Intermediates in the Reactions between Hydroperoxides and Sulphur Dioxide and Their Reaction with Alkene Derivatives: Electron Spin Resonance Study

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Summary The radicals $HO\dot{S}O_2$, $Me\dot{S}O_2$, and $Bu^tO\dot{S}O_2$ have been observed by e.s.r. as intermediates in the reactions between hydroperoxides and sulphur dioxide; these radicals or their precursors add to alkene derivatives to give adducts that can also be characterised by e.s.r.

THE reaction of hydroperoxides with sulphur dioxide is a convenient radical source for initiating copolymerization of sulphur dioxide with alkenes,[1] styrenes[2] *etc.* at low temperature (−80°). Recently it has been found possible to initiate the radical polymerization of vinyl monomers with this catalyst system,[3] with the important commercial consequence that poly(vinyl chloride) of increased tacticity and improved fibre properties can be obtained. The presence of a nucleophile such as methanol promotes radical as distinct from ionic intermediates,[3,4] and a strong nucleophile such as sodium methoxide can prevent sulphur dioxide from copolymerizing with the vinyl monomer.[3] The nature of the radical intermediates has, however, remained uncertain.

We now report e.s.r. spectra of radical intermediates in the reactions between RO_2H ($R = H$, Bu^t, $PhCMe_2$) and sulphur dioxide in several solvent media at 20°. The spectra were obtained by means of a flow system similar to that used by Dixon and Norman.[5] Reactant concentrations were in the range 0—0·2M, and the time between mixing and observation was about 70 ms. From separate kinetic studies (by conductance) at lower temperatures it was estimated that for $[Bu^tO_2H] = [SO_2] = 0{\cdot}1$M in methanol as solvent the half-life was about 90 ms at 20°; radical concentrations of about 3×10^{-5}M were observed under these conditions. With $[H_2O_2] = [SO_2] = 0{\cdot}1$M in water as solvent, the observed radical concentration was only about 10^{-6}M but was increased somewhat on replacing SO_2 by $NaHSO_3$.

The details of the spectra (Figure) varied with R and with solvent, but in every case the main signal [with R = H, the only signal (Figure a)] was a singlet with $g = 2{\cdot}0033 \pm 0{\cdot}0002$, assigned to $HO\dot{S}O_2$ (or SO_3^-) formed by reactions (1) or (2).

$$RO_2H + SO_2 \rightarrow R\dot{O} + HO\dot{S}O_2 \tag{1}$$

$$RO_2H + SO_2 \rightarrow H\dot{O} + RO\dot{S}O_2,\ H\dot{O} + SO_2 \rightarrow HO\dot{S}O_2 \tag{2}$$

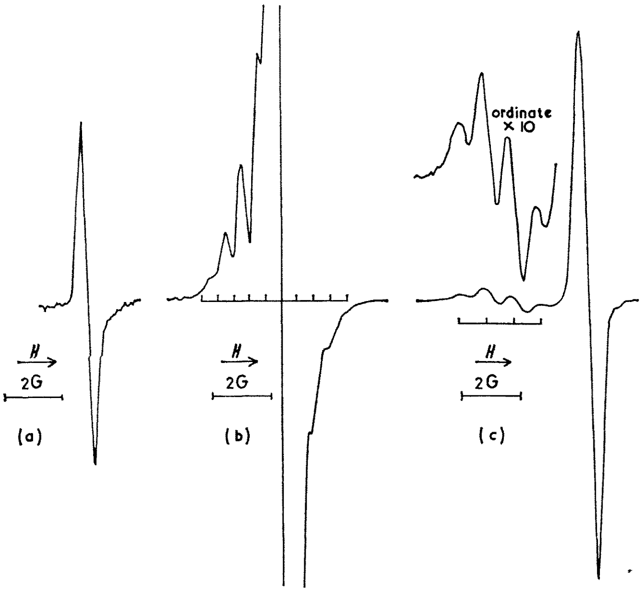

FIGURE. *First-derivative e.s.r. spectra of the transient free radicals in the reactions of* (a) H_2O_2–SO_2–H_2O, (b) Bu^tO_2H–SO_2–MeOH, (c) Bu^tO_2H–SO_2–H_2O. *Assignments* (a) $HO\dot{S}O_2$, (b) $Bu^tO\dot{S}O_2$ *and* $HO\dot{S}O_2$, (c) $Me\dot{S}O_2$ *and* $HO\dot{S}O_2$.

The radical-ion SO_3^- has previously been observed[6] in the solid state at $g = 2{\cdot}0036$ and there are good theoretical reasons for not being able to detect the spectra of $R\dot{O}$ or $H\dot{O}$ in solution.[7] In addition to the singlet the spectrum recorded during the reaction of t-butyl hydroperoxide in *methanol* also contained a multiplet. This was shown by computer simulation to fit a ten-line spectrum, centred on $g = 2{\cdot}0034$, with $a_H = 0{\cdot}28 \pm 0{\cdot}02$ G, and attributable to $Bu^tO\dot{S}O_2$ (Figure b). A corresponding seven-line multiplet was also evident for the reaction of $PhCMe_2O_2H$ in methanol. These radicals may be formed by reactions (2) or (3).

$$R\dot{O} + SO_2 \rightarrow RO\dot{S}O_2 \tag{3}$$

In *water* as solvent the spectra were different. Both organic hydroperoxides now gave a quartet centred on $g = 2{\cdot}0055 \pm 0{\cdot}0002$, attributable to $Me\dot{S}O_2$, with $a_H = 0{\cdot}9 \pm 0{\cdot}1$ G and having about half the integrated intensity of the singlet at $g = 2{\cdot}0033$. A quartet with a similar coupling constant (0·95 G) and g-value (2·0050) has been assigned by Damerau *et al.*[8] to $Me\dot{S}O_2$ in the reaction of $H\dot{O}$ with Me_2SO. SO_2^- in aqueous solution[9] also has a high g-value (2·0057). In the present system $Me\dot{S}O_2$ may be formed by reactions (4) or (5).

$$Me_3C\dot{O} \rightarrow Me_2CO + \dot{M}e,\ \dot{M}e + SO_2 \rightarrow MeS\dot{O}_2 \tag{4}$$

$$Me_3\dot{C}O + SO_2 \rightarrow Me_3CO\dot{S}O_2 \rightarrow Me_2CO + Me\dot{S}O_2 \tag{5}$$

It is not at present clear why the formation of $Me\dot{S}O_2$ rather than $RO\dot{S}O_2$ is favoured in water. Increasing the pH of the reaction medium from 2 to 5 did not result in any qualitative change in the appearance of the spectra. Acetone was detected in the products by n.m.r.

No radicals could be detected when the reaction of t-butyl hydroperoxide with sulphur dioxide was conducted in ether or acetonitrile but the addition of a few percent of water or methanol was sufficient to make the radicals appear in good yield, as expected from the work of Mazzolini.[3]

Inclusion of an alkene derivative M in one or other of the reactant solutions (0·1—1·0M in water or methanol) invariably caused a new spectrum to appear, with partial or complete elimination of the original spectrum. In thirteen cases the new spectrum was centred on $g = 2{\cdot}0033 \pm 0{\cdot}0002$ and showed hyperfine structure which could be assigned to a radical of the type XM•, where X = $HOSO_2$, $MeSO_2$, Bu^tOSO_2, or Bu^tO, depending on the system being studied. For example, styrene (in methanol) gave a spectrum which was assigned to $XCH_2\dot{C}HPh$ with the following coupling constants (G): α-H 15·32, β-H 12·12, *p*-H 5·92, *o*-H 5·00, *m*-H 1·76; a detailed analysis of the e.s.r. spectrum of a styrene radical of the type XM• has not previously been reported. In general, the β-proton coupling constants were considerably smaller than those observed by others[10] for smaller initiating species, such as HO, Me, and $HOCH_2$. For allyl alcohol and hex-1-ene (which differ from the other thirteen compounds in their ability to form 1 : 1 polysulphones) the new spectrum was centred on $g = 2{\cdot}0054$ and was assigned to radicals of the type $XM\dot{S}O_2$ by analogy with $Me\dot{S}O_2$. For acrylic, methacrylic, and itaconic acids the spectra showed evidence for the formation of "polymer" radicals XM_n•, as well as XM•.

B. D. S. thanks The Queen's University of Belfast for the award of a Visiting Research Studentship.

(*Received, December 29th,* 1970; *Com.* 2243.)

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