Electron Spin Resonance Studies. Part 60.[1] Detection of Radical-cations from Vinyl Sulphides: Evidence for a Cyclic Structure

By **Bruce C. Gilbert,* Richard O. C. Norman,** and **Peter S. Williams,** Department of Chemistry, University of York, Heslington, York YO1 5DD

Radical-cations have been detected during the oxidation of $RSCH{=}CH_2$ (R = Et, Pr^i) with $Cl_2^{\cdot-}$ or $\cdot OH$ at low pH; e.s.r. parameters indicate that these possess a cyclic sulphonium structure $\cdot\overline{CH{-}CH_2{-}\overset{+}{S}}R$. Their formation from the hydroxy-adducts may involve anchimeric assistance from the sulphur atom.

RADICAL-CATIONS have often been proposed as key reactive intermediates in aqueous systems, for example in the reactions of $SO_4^{-\cdot}$ with electron-rich alkenes,[2] in the reactions of $\cdot OH$ with arenes at low pH,[3] and in the acid-catalysed fragmentation of αβ-dioxygen-substituted radicals like $\cdot CH(OH)CH_2OH$.[4]

Direct e.s.r. evidence for such relatively short-lived species is scarce, though spectra have been detected from some methoxylated benzoate zwitterions $^{+\cdot}ArCO_2^-$ (obtained[5] by one-electron oxidation of the parent compounds with $SO_4^{-\cdot}$), from $CH_2{=}C(OMe)_2^{+\cdot}$ [formed in the fragmentation of $\cdot C(OMe)_2CH_2Cl$] and related species,[6] and from 'dimer' radical-cations $R_2SSR_2^{+\cdot}$ formed during the oxidation of sulphides (see *e.g.* ref. 7). However, e.s.r. can provide convincing circumstantial evidence for their participation. For example, in the reaction of $Cl_2^{-\cdot}$ with $CH_2{=}CHOEt$ in aqueous solution, the detection[8] of the radicals $\cdot CH_2CH(OH)OEt$ and $\cdot CH(OEt)CH_2OH$ as well as $\cdot CH(OEt)CH_2CH_2CH(OH)OEt$ and $\cdot CH(CH_3)OCH{=}CH_2$ can be understood in terms of the hydration of, addition (to alkene) by, and proton loss from a first-formed but undetected radical-cation $CH_2{=}CHOEt^{+\cdot}$; in the corresponding reaction of $CH_2{=}CHOEt$ with $\cdot OH$, the same intermediate evidently results from acid-catalysed loss of hydroxide from first-formed hydroxy-adducts. Similar reactions have been described for furan and thiophen and some derivatives.[1]

We here report the results of an investigation of the reactions of some vinyl sulphides with both $Cl_2^{-\cdot}$ and $\cdot OH$ and present direct evidence for the participation of radical-cations of novel structure.

RESULTS AND DISCUSSION

Reactions were carried out in the cavity of an e.s.r. spectrometer with a three-way flow mixing system with a dead-time of *ca.* 80 ms. The hydroxyl radical and the chlorine radical-anion were generated from the Ti^{III}–H_2O_2 and Ti^{III}–H_2O_2–Cl^-–H^+ reactions [reactions (1) and (1)—(4), respectively], as described previously.[1,8]

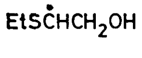
When $EtSCH{=}CH_2$ (0.006 mol dm^{-3}) was oxidised with $\cdot OH$ in the pH range 2—9, only one radical was detected (see Figure): it had a(1H) 1.69, a(2H) 0.97, a(2H) 0.20 mT, g 2.0047 and is assigned the hydroxy-adduct structure (1) (*cf.* radicals of this type obtained[9] from β-hydroxy-substituted sulphides). It was also detected at pH 2.0 in the reaction of $EtSCH{=}CH_2$ with $Cl_2^{-\cdot}$; it is presumably then formed from the corresponding radical-cation by hydration. When the pH was lowered below 2, in experiments with either $\cdot OH$ or $Cl_2^{-\cdot}$, the signal from (1) was reduced in intensity and spectra from two further radicals became detectable; these were more clearly seen at pH 0, when (1) was no longer observed (see Figure). The first consisted of two doublets (1.68 and 2.75 mT) and a triplet (0.19 mT), with g 2.0047. The second comprised three doublet splittings of 3.975, 3.275, and 2.05 mT, with g 2.0026; the lines of this spectrum (and especially the inner four lines) appeared broad (the lineshape and the peak-to-peak linewidth of *ca.* 0.2 mT for the outside lines suggested the presence of further unresolved splittings). For a given concentration of the sulphide the relative proportions of the two radicals were independent of pH, but the use of higher substrate concentrations resulted in enhancement of the signal from the first relative to that of the second.

$$Ti^{III} + H_2O_2 \longrightarrow Ti^{IV} + \cdot OH + \cdot OH^- \qquad (1)$$

$$\cdot OH + Cl^- \rightleftharpoons HOCl^{\cdot} \qquad (2)$$

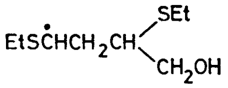
$$HOCl^{\cdot} \xrightarrow{H^+} H_2O + Cl\cdot \qquad (3)$$

$$Cl\cdot + Cl^- \rightleftharpoons Cl_2^{\cdot} \qquad (4)$$



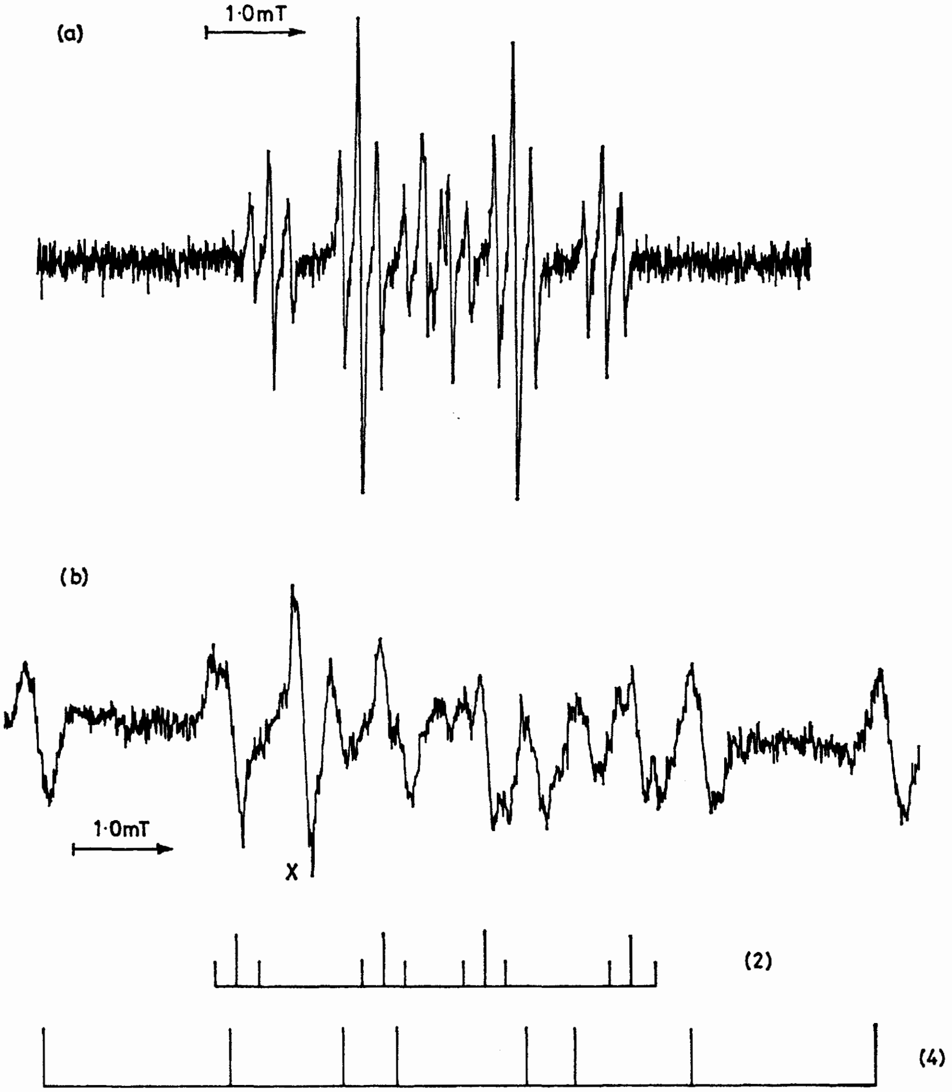
$EtS\dot{C}HCH_2OH$

(1)



(2)

The first of these is assigned the dimeric structure (2) on the following basis. First, the g-value (2.0047), the (α-proton) splitting of 1.68 mT, and the small triplet of 0.19 mT are compatible with the partial structure $-CH_2{-}S{-}\dot{C}H{-}$.[7a,9] Secondly, these splittings and the doublet splitting of 2.75 mT are closely similar to those observed[9] for the related species $\cdot CH(SMe)CH_2CH(NH_3^+)CO_2^-$, in which a doublet of 2.97 mT was assigned to the *sum* of the splittings from the two β-protons; these are non-equivalent owing to the presence of an adjacent chiral centre, and restricted rotation results in conformational exchange at a frequency comparable to the difference between their hyperfine splittings, so that the inner two lines of the expected four are broadened beyond detection. {Although the β-protons in an alternative dimer-type radical which could be obtained from EtS-$CH{=}CH_2$, $\cdot CH(SEt)CH_2CH_2CH(OH)SEt$, are also expected to be non-equivalent [by analogy with the ethyl vinyl ether-derived species[8] $\cdot CH(OEt)CH_2CH_2CH(OH)$-OEt] the difference would be expected to be too small to account for the considerable broadening implied by our failure to detect the inner lines.} Thirdly, the enhancement of the signal from the species at higher substrate concentrations suggests that more than one molecule of sulphide is involved in its formation.



(a) E.s.r. spectrum of radical (1) obtained from the reaction of •OH with $EtSCH{=}CH_2$ at pH *ca.* 2.0. (b) E.s.r. spectra of (2) and (4) obtained from the reaction of ·OH with $EtSCH{=}CH_2$ at pH *ca.* 0 (the peak marked × is from a Ti^{IV}–$\cdot O_2H$ complex)

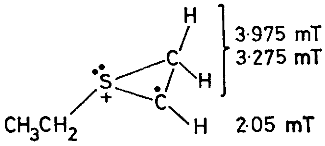
The *g*-factor (2.0026) and doublet splitting of 2.05 mT for the second species suggest that the unpaired electron is associated effectively only with carbon and that it interacts with a single α-proton in a species which is effectively planar at the radical centre. Further, the two doublets of 3.975 and 3.275 mT (which presumably arise from interactions with β-protons) are much larger than expected for a species in which free rotation about the C_α–C_β bond occurs (*cf.* the β-splitting for $\cdot CH_2Me$ of[10] 2.69 mT) and imply conformational fixing, with dihedral angles subtended by the β-protons and the half-filled orbital of *ca.* 30°.

The appearance of the signal from this radical as that from the adduct (1) disappears suggests, by analogy with the behaviour of the radical $\cdot CH(OEt)CH_2OH$ from ethyl

$$\underset{(1)}{\mathrm{EtS\dot{C}HCH_2OH}} \xrightarrow{H^+,\,-H_2O} \underset{(3)}{\mathrm{EtSCH{=}CH_2^{+\cdot}}} \qquad (5)$$

vinyl ether at low pH, that the mechanism of its formation involves acid-catalysed elimination of OH^- from (1) [reaction (5)].

The radical-cation with the formal open-chain structure (3) (with both spin and charge delocalised onto sulphur, *e.g.* $EtS\overset{+}{C}H{-}\dot{C}H_2 \leftrightarrow EtS\dot{C}H{-}\overset{+}{C}H_2 \leftrightarrow Et\overset{+}{S}{=}CH{-}\dot{C}H_2$) is clearly not compatible with the observed e.s.r. parameters [such conjugation would be expected both to raise the *g*-value significantly from the free-spin value and also to reduce the splitting from the two (α) protons to a value somewhat less than 2.3 mT]. Other structures which might have been anticipated on the basis of the reaction of $[EtOCH{=}CH_2]^{+\bullet}$, for example $\bullet CHMeSCH{=}CH_2$ (which would be obtained by deprotonation) and $\bullet CH_2CH(OH)SEt$ [which would be obtained, together with $\bullet CH(SEt)CH_2OH$, *via* hydration, *cf.* $\bullet CH_2CH(OH)OEt$ from ethyl vinyl ether] can similarly be ruled out. On the other hand, the cyclic radical-cation (4) possesses the appropriate structural features and, for the following reasons, we propose that this is the unusual radical detected.

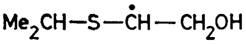


(4)

First, the β-protons in such a species would not only subtend relatively small dihedral angles (*ca.* 30°) with the orbital of the unpaired electron but would also (on the assumption that it possesses a non-planar geometry around sulphur) be non-equivalent. Secondly, the radical $\bullet CH_2S(O)Me$ possesses[11] e.s.r. parameters [a(2H) 2.0 mT, g 2.0025] which suggest that in this species there is little, if any, delocalisation of the unpaired electron onto sulphur [in contrast to the considerable delocalization in $\bullet CH_2SCH_3$, for which a(2H) is 1.65 mT and g 2.0049]; by analogy, we would anticipate that conjugation between the unpaired electron and the lone-pair on sulphur may well be disfavoured for such a sulphonium-substituted species (4).* This is exactly what is indicated by the *g*-value and the magnitude of the α- and β-splittings.

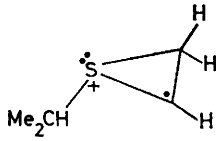
In an attempt to obtain further evidence for this assignment we also oxidised $Pr^iSCH{=}CH_2$ and $EtSCH{=}CHMe$ under similar conditions. The behaviour of the former closely resembled that of $EtSCH{=}CH_2$; thus during its oxidation with either $Cl_2^{-\bullet}$ or •OH at pH *ca.* 2.0, a signal assigned to the hydroxy-adduct (5) [with a(α-H) 1.66, a(β-H) 0.97, a(γ-H) 0.16 mT and g 2.0046] was detected, whereas at pH *ca.* 0.5 this signal was largely replaced by a spectrum with doublet splittings of 3.98, 3.15, and 2.10 mT (g 2.0028), attributed to (6). The broad lines of the spectrum from (6) appear to contain ill-resolved long-range splittings (presumably from the protons in the *S*-alkyl group).

In contrast, reaction of $EtSCH{=}CHMe$ under a variety of conditions led to the detection only of a complex spectrum, dominated by splittings of *ca.* 1.3 mT,



$Me_2CH{-}S{-}\dot{C}H{-}CH_2OH$

(5)

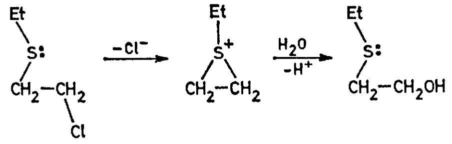


(6)

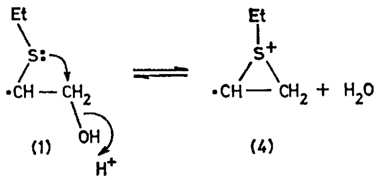
which is tentatively assigned to the allyl radical $EtSCH{=}CH{-}\dot{C}H_2$; its ready formation suggests that rapid deprotonation of an intermediate radical-cation may now be involved.

The role of the sulphur substituent in stabilizing the cyclic sulphonium structures (4) and (6) appears to be in marked contrast with that shown by oxygen in related oxygen-substituted radical-cations; thus the 1,1-dimethoxyethene radical-cation[6] is best represented as $(MeO)_2\overset{+}{C}{-}\dot{C}H_2$ rather than as a cyclic oxonium structure (though a strict comparison is impossible in the absence of e.s.r. data for the relatively elusive radical-cations with single oxygen substituents, *e.g.* $EtOCH{=}CH_2^{+\bullet}$).

It is also notable, first, that sulphur exerts a strong neighbouring-group effect in, for example, the hydrolysis of β-chloro-sulphides [*cf. e.g.* reaction (6)[13]]; it is possible that the formation of (4) from the hydroxy-adduct (1) involves similar anchimeric assistance [reaction (7)]. This is presumably a reversible reaction, as indicated, since the radical-cation (4), when formed with $Cl_2^{-\bullet}$ by direct electron abstraction, gives the adduct (1) at pH > 1.



(6)



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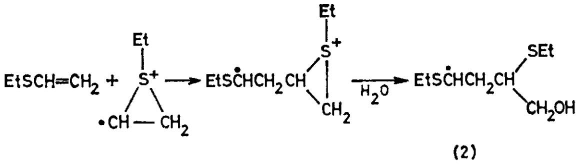

(8)

Secondly, in contrast to the behaviour of non-conjugated sulphides (R_2S) under similar circumstances, sulphur-centred dimer radical-cations ($R_2SSR_2^{+\bullet}$) are not detected. The detection instead of an increased con-

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* It would also follow that (4) would not be expected to resemble the oxiranyl radical[12] which, as a result of the presence of the mesomerically electron-donating oxygen substituent within a small ring, is markedly ' bent ' at the radical centre and has a positive α-proton splitting (2.33 mT) and a low β-proton splitting (0.61 mT).

centration of the dimeric radical (2) in the oxidation of ethyl vinyl sulphide as the substrate concentration was increased is consistent with the reaction of a carbon-centred radical (rather than a sulphur-centred species) with another molecule of substrate [reaction (8)]. In the oxidation of $Pr^iSCH=CH_2$, the analogous radical is not detectable, presumably because of the increased steric demands of both reactants.

EXPERIMENTAL

Details of the spectrometer, spectrum analysis, and measurement, and of the flow system have been described previously.[1] Concentrations of reagents in the three-way flow system were as follows: for oxidations with $\cdot OH$, stream (i) contained 0.007 mol dm^{-3} titanium(III) [added as 12.5% (w/v) titanium(III) chloride solution (Fisons technical grade) or 15% (w/v) titanium(III) sulphate solution (Fisons technical grade)], stream (ii) contained *ca.* 0.035 mol dm^{-3} hydrogen peroxide [added as 100-volume hydrogen peroxide (B.D.H. Ltd.)], and stream (iii) contained the substrate at the required concentration (typically *ca.* 0.015 mol dm^{-3}). Concentrated sulphuric acid was usually added to stream (i) only to bring the pH (on mixing) to the required value. For experiments at pH > 2.5, edta (3 g dm^{-3}) was added to stream (i) and the pH was adjusted as required with either concentrated sulphuric acid or ammonia (*d* 0.880). For experiments with $Cl_2^{-\cdot}$, sodium chloride was added to either stream (i) or to both streams (i) and (ii) to yield a concentration (after mixing) of at least 1 mol dm^{-3}.

Ethyl vinyl sulphide [14] was prepared from 2-hydroxyethyl sulphide (itself prepared by the reaction of ethanethiol with 2-chloroethanol in the presence of sodium ethoxide [15]) by the method of Price and Gillis.[16] Isopropyl vinyl sulphide [17] and prop-1-enyl vinyl sulphide [16] were prepared by analogous routes. These compounds were redistilled before use. All other materials were commercially available and were used without further purification.

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