Electron Spin Resonance Spectra of Ether Radical Cations generated by Radiolysis

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Exposure of dilute solutions of ethers in trichlorofluoromethane (freon) to ^{60}Co γ-rays at 77 K gave the corresponding ether cations or derivatives thereof, as judged by their e.s.r. spectra. Dimethyl and diethyl ethers gave the primary cations, the unpaired electron being largely confined to oxygen but with considerable delocalisation onto β-protons. For n-propyl and larger alkyl substituents, hydrogen shifts occur to give alkyl radicals. Several cyclic monoethers gave primary cations again exhibiting very large β-proton hyperfine coupling constants. For example, the oxetane cation had four equivalent β-protons with coupling constants of 64 G. However, ethylene oxide (oxirane) was exceptional, with four equivalent β-protons with couplings of only 16 G. It is suggested that either the orbital on oxygen is switched from the normal π (b_1) orbital to the in-plane σ (a_1) orbital or ring opening has occurred. For tetrahydropyran the product had two protons with 34.5 G splitting, two with 15 G splitting, two with 11 G splitting and two with *ca.* 2.5 G splitting. We suggest that the β-proton coupling is low because of the conformation of the cation.

Acetals exhibited remarkably large hyperfine coupling to the two methylene protons (*ca.* 145 G as a result of σ–π delocalisation within this unit. For *s*-trioxane cations only two of the three oxygen atoms participate strongly in the SOMO with two strongly coupled protons. However, a second radical species was detected in this system which showed an unusually large *g*-value variation (g_x = 2.0286, g_y = 2.0067, g_z = 2.0023) as well as very large proton coupling. It is suggested that this species is essentially an alkoxide radical formed by ring opening.

For 1,2-diethers weak $O\dot{-}O$ σ* interaction is thought to occur. Thus, 1,4-dioxane, for example, exhibits only small proton splittings, which is expected in a σ* system.

The cation formed from the vinyl ether $EtOCH{=}CH_2$, which is of interest since such cations are thought to be of importance as intermediates in the free-radical oxidations of vinyl ethers, has e.s.r. parameters which suggest that the limiting structure $Et\overset{+}{O}{=}CH{-}\dot{C}H_2$ dominates, the spin-density on the methylene group being *ca.* 89%. Cations formed from $(RO)_2CH{-}CH{=}CH_2$ rearranged to give the stable $(R\overset{+}{O})_2C{-}\dot{C}HMe$ radicals. Also for $MeOC{\equiv}CH$, the cation has a structure close to the limiting $Me\overset{+}{O}{=}C{=}\dot{C}H$ form.

We have also studied the effect of ionizing radiation on solutions of ethers in sulphuric acid. Electron addition gave alkyl radicals but in several cases there was evidence for the formation of cations $R_2O^{+\cdot}$ ($R_2OH^+ + HSO_4^{\cdot} \longrightarrow R_2O^{+\cdot} + H_2SO_4$) on annealing above 77 K. If this is correct, the extent of electron delocalisation on to β-protons for these ions in sulphuric acid is reduced relative to the cations in freon.

All attempts to prepare alcohol cation radicals, $R\dot{O}H^+$, by these procedures failed. For freon solutions, this is thought to be because of extensive association due to hydrogen bonding in even the most dilute solutions. This leads to intermolecular hydrogen transfer giving the radicals $R_2\dot{C}OH$ which were detected by e.s.r. spectroscopy. An alternative explanation is that the radicals $R\dot{O}H^+$ can transfer protons to the solvent.

To many chemists, ionizing radiation represents a sledgehammer which will break molecules into a wide variety of fragments. This is not the case, and in properly controlled systems the products formed are frequently simpler and more readily predictable than those formed by high-energy u.v. light. In the field of organic chemistry, it is possible to study the reactions of substrates with electrons or with ' holes,' giving either the parent radical anions and radical cations, or simple products thereof.[1,2] For dilute solutions of a substrate X in solvents such as ethers or alcohols, electron addition to X dominates, because thermalised electrons ejected in the initial stages do not react readily with solvent molecules and hence are able to migrate to X. However, the resulting solvent cations undergo rapid reactions which prevent their migration by charge transfer [see, for example, reactions (1)—(3)]. In contrast, for solvents such as alkyl halides,[3] tetrachloromethane[4] and, in particular, trichlorofluoromethane (freon),[5-9] ejected electrons are captured by the solvent with high efficiency, but the cations are mobile *via* electron transfer and can migrate to solute molecules which will react provided their ionization potentials are less than that of the solvent (*ca.* 11.9 eV for freon). These reactions are exemplified in equations (4)—(6).

$$ROH \xrightarrow{\gamma} R\dot{O}H^+ + e^- \qquad (1)$$

$$e^- + X \longrightarrow X^{-\cdot} \qquad (2)$$

$$R\dot{O}H^+ + ROH \longrightarrow R\dot{O} + ROH_2^+ \qquad (3)$$

$$CFCl_3 \xrightarrow{\gamma} CFCl_3^+ + e^- \qquad (4)$$

$$e^- + CFCl_3 \longrightarrow {}^{\cdot}CFCl_3^- \longrightarrow {}^{\cdot}CFCl_2 + Cl^- \qquad (5)$$

$$CFCl_3^+ + X \longrightarrow CFCl_3 + X^{+\cdot} \qquad (6)$$

Organic radicals that have been prepared in this way include a range of hydrocarbon cations,[4,7,8,10] cations of aldehydes and ketones,[11] various silicon-, germanium-, and tin-centred cations,[12-15] aromatic[9] and aza-aromatic[5] cations, and some sulphur- and phosphorus-centred cations.[16,17] The first reports of ether radical cations were by Shida and his co-workers,[18] who prepared tetrahydrofuran (THF) and methyl-substituted THF cations together with $Me_2O^{+\cdot}$ cations, and by Wang and Williams,[19] who studied the $Me_2O^{+\cdot}$ cation. These studies revealed that hyperfine coupling to β-protons can be very large for $R_2O^{+\cdot}$ cations, that for $Me_2O^{+\cdot}$ being *ca.* 43 G for six equivalent protons. Several years previously,[20] we had attempted to prepare such cations using solutions in sulphuric acid, since this had proven to be a satisfactory procedure for the preparation of other cation radicals.[21,22] We were unable to identify any cations with confidence, and hence we also decided to use the freon technique.[23] We were particularly interested to see if the very large β-proton hyperfine coupling constants observed for $MeO^\cdot$ and $RCH_2O^\cdot$ radicals in the solid state [24-26] was also found for $R_2O^{+\cdot}$ radicals. This is a particularly pertinent question in view of the remarkable difference found for the ^1H coupling assigned to $MeO\cdot$ radicals in the gas phase (23.2 G) [27] and in solid methanol at 4 K (52 G).[24] Extensive σ–π delocalisation is expected for these oxygen-centred radicals because it involves electron donation from the C–H σ-orbital, which should increase on going from $R_3C^\cdot$ to $R_3N^{+\cdot}$ or $R_2N^\cdot$ and $R_2O^{+\cdot}$ or $RO^\cdot$ radicals. The average coupling constants for β-protons increase steadily for this series, and the gas-phase value of 23.2 G is completely anomalous, for reasons that are not at present understood.

We were also interested in the possibility of forming σ* radicals,[2] $R_2O\overset{\cdot}{-}OR_2{}^+$, from ether cations. It is well established that reaction (7) occurs rapidly and almost exclusively for the

$$R_2S^{+\cdot} + R_2S \longrightarrow (R_2S\overset{\cdot}{-}SR_2)^+ \qquad (7)$$

corresponding sulphur systems,[28-30] and for other 'heavy atom' systems such as $R_3P^{+\cdot} \longrightarrow (R_3P\overset{\cdot}{-}PR_3)^+$ [31] or $RI^{+\cdot} \longrightarrow (RI\overset{\cdot}{-}IR)^+$ [32] but examples of such structures involving oxygen are rare.[33]

It also seemed of interest to study some unsaturated systems such as vinyl ethers. In particular, vinyl ether cations such as $R\overset{+}{O}{=}CH{-}\dot{C}H_2$ have recently been invoked as key intermediates in several free-radical processes, but they were not directly detectable by e.s.r. spectroscopy,[34] so it was of interest to learn more about their e.s.r. spectra and structure.[35] Some of our attempts to prepare ether cations from solutions of ethers in sulphuric acid are described and, finally, we report our attempts to prepare alcohol radical cations using similar procedures, and discuss reasons for our apparent failure. Alcohol radical cations have not yet been studied by e.s.r. spectroscopy. However, the new photoionization–matrix isolation technique developed by Knight and his co-workers [36] promises to be the best way forward.

Experimental

Various sources of $CFCl_3$ [Aldrich Chemical Co., Gillingham, Dorset,; B.D.H. Chemicals Ltd., Poole, Dorset; and Fluka A.G. Chemische Fabrik, Bucks] were all found to give quite strong e.s.r. signals due to cations of trace impurities after irraditaion at 77 K. The best purification procedure that we have yet used is to pass $CFCl_3$ through a finely powdered γ-alumina column (B.D.H. Chemicals Ltd.) at least twice, but even so, residual impurity signals were still obtained. In *all* the systems described herein, these features were insignificant compared with those from substrate radicals.

Ethers and alcohols were the best available grades and were purified, if necessary, by standard procedures, their purities being checked by n.m.r. spectroscopy. Dilute solutions (*ca.* 0.001 mole fraction) in freon were cooled to 77 K to give small polycrystalline beads. Dilute solutions in H_2SO_4 or D_2SO_4 (*ca.* 98%) were prepared by slow addition to the acid at 0 °C with rapid stirring, and also frozen in liquid nitrogen to give small beads after removal of oxygen. These were exposed to ^{60}Co γ-rays at 77 K in a Vickrad source to doses of up to 0.5 Mrad, the results being independent of dose in this range.

E.s.r. spectra were measured with a Varian E-109 spectrometer at 77 K calibrated with a Hewlett-Packard 5246L frequency counter and a Bruker B-H12E field probe, which were standardized with a sample of diphenylpicrylhydrazyl (DPPH). Samples were annealed by decanting the liquid nitrogen from the insert Dewar flask and continuously monitoring the e.s.r. spectra. They were re-frozen to 77 K for careful study whenever significant changes were observed. In our experience, this is the best procedure for detecting transient radical products. To obtain e.s.r. spectra at different temperatures we used a Varian variable-temperature assessory.

Results and Discussion

Acyclic Monoethers.—Good e.s.r. spectra for $Me_2O^{+\cdot}$ cations have been given by Shida and his co-workers,[18] and by Wang and Williams.[19] They comprise a binomial septet with $A(^1H) = 43$ G, each feature being asymmetric because of small *g* and *A* anisotropy. This anisotropy is largely lost at 120 K.[18] Our results are in complete agreement. As with $Me_3C^\cdot$ radicals, it seems that there is effectively free rotation of the methyl groups at 77 K.

Diethyl ether gave a similar result (Figure 1). All four β-protons are equivalent, giving a five-line spectrum, but the hyperfine coupling has increased from 43 to 68.7 G. Thus in this case rotation must be strongly restricted. If the usual $\cos^2\theta$ law [1] holds for the β-proton coupling of these cations, as expected, then 43 G for $Me_2O^{+\cdot}$ is an average value (θ = 45°) whilst the large value for $Et_2O^{+\cdot}$ cations must be for θ = 30°.

$$A_{\beta H} = B + A^\circ \cos^2\theta \qquad [1]$$

If B, which is expected to be relatively small, is set equal to zero, we predict from equation [1] a coupling of *ca.* 64.5 G for θ = 30°, which is appreciably less than the observed coupling (*ca.* 68.7 G). This means that the effective coupling for four protons is greater than that for the six β-protons of $Me_2O^{+\cdot}$ cations. This presumably reflects the delocalisation for the two extra protons (see below). The 30° conformation, which provides maximum C–H delocalisation, seems to be strongly preferred, since we were unable to produce an averaged result on annealing. The extra splitting seen in Figure 1 is an admixture of g_x, g_y, and g_z features, and possibly extra small splittings from the methyl protons.

In marked contrast, results for di-n-propyl ether and others with longer alkyl chains gave no clear evidence for species with large proton hyperfine coupling constants. The spectrum for the di-n-propyl derivative comprised a quintet of broad anisotropic lines which we tentatively assign to the $H_2\dot{C}[CH_2]_2OH^+(Pr)$ radical, formed as in (I) (Figure 2). Our results for concentrated solutions of $Me_2O^{+\cdot}$ and $Et_2O^{+\cdot}$ together with those for THF cation systems [18] show that intermolecular hydrogen abstraction reactions take place readily. Thus, for example, on annealing, the spectrum for Et_2O^+ cations showed extra features which we assign to the outer lines for $CH_3\dot{C}HOEt$ radicals.

Results for di-isopropyl radicals are less clear. We had expected to detect the parent cations with a large triplet splitting from two equivalent β-protons. In fact, the broad, poorly defined spectrum has two broad outer lines which, if part of a triplet, give a splitting of 45 G (Figure 3). This could indicate 'free' rotation giving an average coupling or a coincidental orientation of *ca.* 45 ° for both protons. However, there are strong central features which cannot be accommodated on this model. We can pick out a 21 G triplet from these features but the spectrum is too poorly defined to warrant detailed speculation. We conclude either that there are two or more

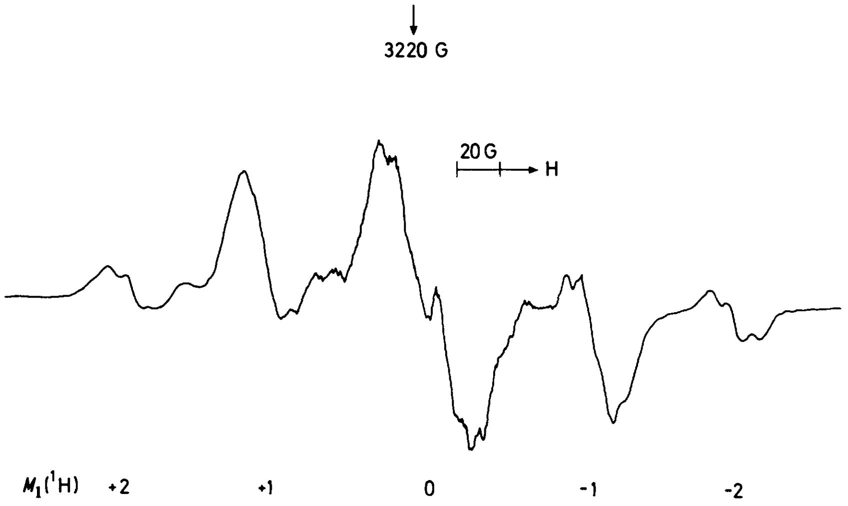


Figure 1. First derivative X-band e.s.r. spectrum for a dilute solution (*ca.* 0.1% mole fraction) of diethyl ether in $CFCl_3$, after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to $Et_2\dot{O}^+$ cations

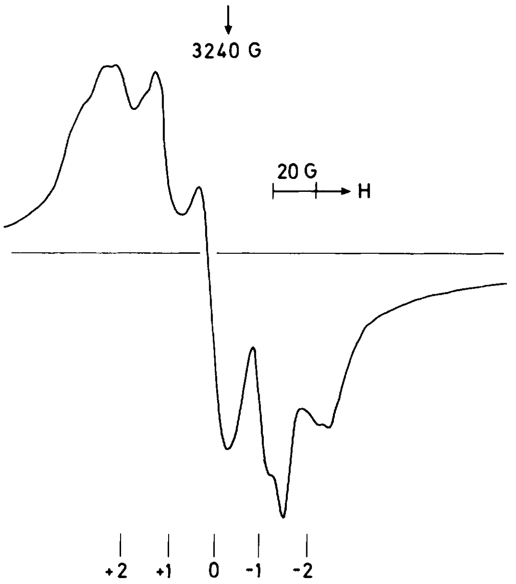


Figure 2. First derivative X-band e.s.r. spectrum for a dilute solution (*ca.* 0.1% mole fraction) of di-n-propyl ether in $CFCl_3$, after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to $H_2\dot{C}[CH_2]_2\overset{+}{O}(H)(Pr)$ cations

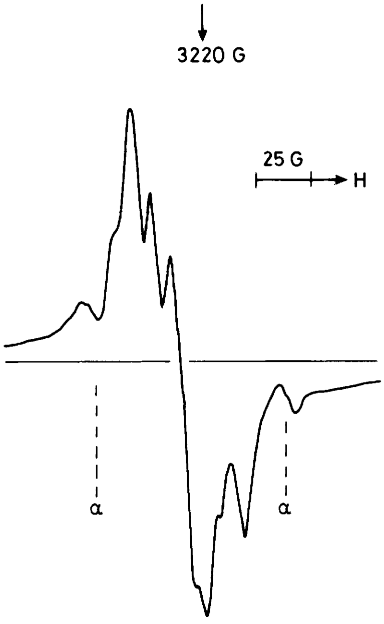
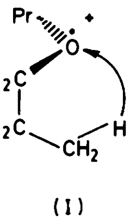


Figure 3. First derivative X-band e.s.r. spectrum for a dilute solution (*ca.* 0.1% mole fraction) of di-isopropyl ether in $CFCl_3$, after exposure to ^{60}Co γ-rays at 77 K, showing outer features (α) tentatively assigned to $(Pr^i)_2\dot{O}^+$ cations



(I)

preferred conformations which place the two β-protons in various interacting sites, or that one such conformation favours large γ-proton couplings.

Monocyclic Ethers.—Our results for THF were identical with those of Shida and his-co-workers.[18] They showed that the two pairs of protons giving 89 and 40 G coupling at 77 K became equivalent on the e.s.r. time-scale at *ca.* 150 K, the estimated activation barrier to conformational inversion being 1.65 kcal mol^{-1}. In contrast, the *cis*- and *trans*-2,5-dimethyl derivatives were conformationally stable in the available temperature range. The 2-monomethyl derivative underwent some conformational change in the same temperature range with partial averaging of the β-proton couplings (Table 1).

We have extended this study to other cyclic ethers. Results for the four-membered ring ether were similar to that for THF with A ($^1H_\beta$) = 65 G, at *ca.* 100 K (Figure 4). Also the two γ-protons gave a remarkably large coupling of *ca.* 11 G at this temperature. At 77 K the spectrum was extremely complex, indicating inequivalence of these protons. The large γ-proton

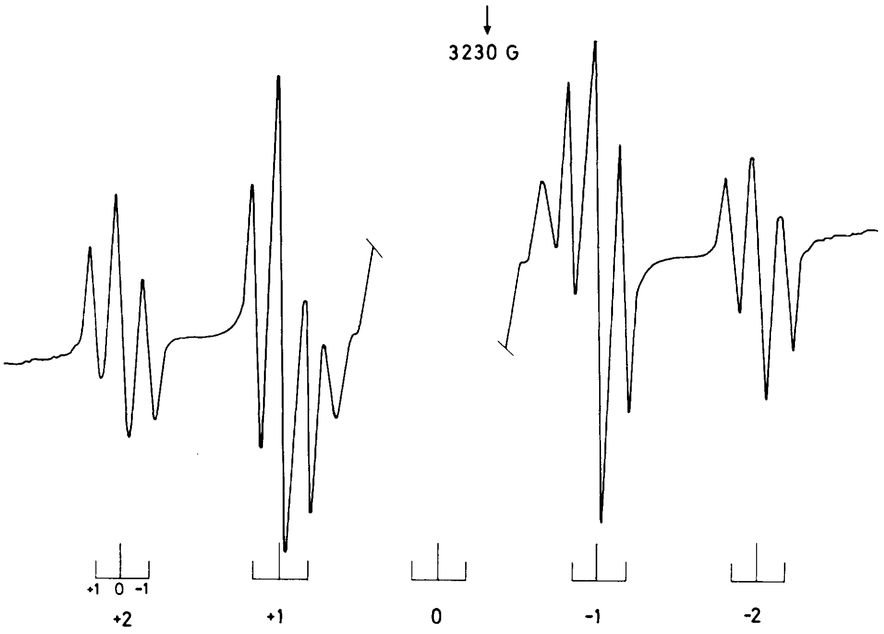


Figure 4. First derivative *X*-band e.s.r. spectrum for a dilute solution (*ca.* 0.1% mole fraction) of oxetane in $CFCl_3$, after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to oxetane cations

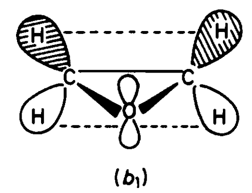
coupling suggests that there is a second-order effect occurring from the relatively high spin-densities on the two adjacent CH_2 groups. This effect is discussed below for the acetal cations.

The e.s.r. spectra for the oxetane systems always included strong central features due to some other radical. We have not been able to identify this species.

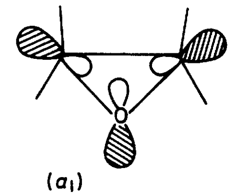
In marked contrast, the three-membered ring ether, oxirane, had four equivalent protons, but with a greatly reduced coupling of only 16 G (see Figure 2 of ref. 35). This was unexpected since for the normal π structure (II) there is good σ–π overlap and extensive delocalisation would be expected. We can suggest three explanations. One is that some ready rearrangement has occurred, the most probable being C–C bond fission to give the 'allyl'-type radical $(H_2\dot{C}\cdots O\cdots\dot{C}H_2)^+$. The data are well accommodated by this structure except that the normally marked anisotropic features associated with α-protons are not apparent. If structure (II) is correct, we need to discover some reason why delocalisation onto the CH_2 groups is inhibited. This might arise because strong 'π' bonding between the two CH_2 groups deepens the in-phase orbital required for delocalisation, making it less able to participate in the SOMO [see (II)]. This seems unlikely to us in view of the relatively weak π-type interaction between adjacent methylene groups, and the fact that our unpublished results for the sulphur analogue give a proton coupling almost equal to those for the four- and five-membered ring systems.

We therefore favour structure (III) where the SOMO is non-bonding σ on oxygen (a_1). This orbital has no strong interaction with the four protons and only a small hyperfine coupling is expected. There has been some controversy regarding the correct ordering of the orbital energy levels for oxirane. Thus, for example, Basch *et al.*[37] concluded that the oxygen *nb* (π; b_1) orbital is the SOMO for the cation, whilst the calculations of Pople *et al.*[38] favoured the oxygen *nb* (σ; a_1) orbital, which is the orbital that we favour. Mollere and Houk[39] also favour a_1 as the SOMO for this cation. In the light of this controversy and the evident proximity of the two orbitals, we strongly favour the a_1 orbital as the SOMO for the relaxed cation.

(II)



(III)



Results for tetrahydropyran (THP; oxacyclohexane) were also not readily interpreted. The best spectra were obtained using CCl_2F–CF_2Cl as solvent at *ca.* 110 K. Even so, the spectrum is unexpectedly complex (Figure 5), and gives no evidence of four very strongly coupled protons as found for THF. However, a reasonable fit is obtained using the data given in Table 1. The splittings assigned to the β-protons (34.5 G and 15 G) are smaller than usual, but can be interpreted in terms of the conformation indicated in (IV), with θ in the region of 60°, rather than the structure for THF (V) with θ close to zero. If equation (1) is used for both protons, the coupling constants fit satisfactorily for $\theta_1 = 67°$ and $A(^1H)_{av} = 48$ G. A similar calculation for THF^+ gives $\theta = 11°$ and $A(^1H)_{av} = 46.5$ G. These 'average' values agree with that for Et_2O^+ (46 G) so there is good agreement for these cations having four coupled β-protons. The reduced value of 43 G for Me_2O^+ must then reflect the extra delocalisation due to the two extra C–H bonds. This, in turn, suggests that delocalisation *via* C–H bonds is more important than that *via* C–C bonds. This is a possible explanation for the extreme orientational preference exhibited by Et_2O^+ cations for temperatures up to *ca.* 160 K. However, the unusually large coupling to two extra protons (11 G) presumably reflects quite strong σ–π overlap with the β C–C bond indicated in (IV).

Studies of molecular models suggest that conformation (IV) is possible for the THP cation. An alternative to this is that hydrogen transfer from the unique CH_2 group has occurred, giving radical (VI). However, the lines are unacceptably narrow for a radical that should exhibit a large anisotropic α-proton coupling, and we cannot find a reasonable fit for this radical,

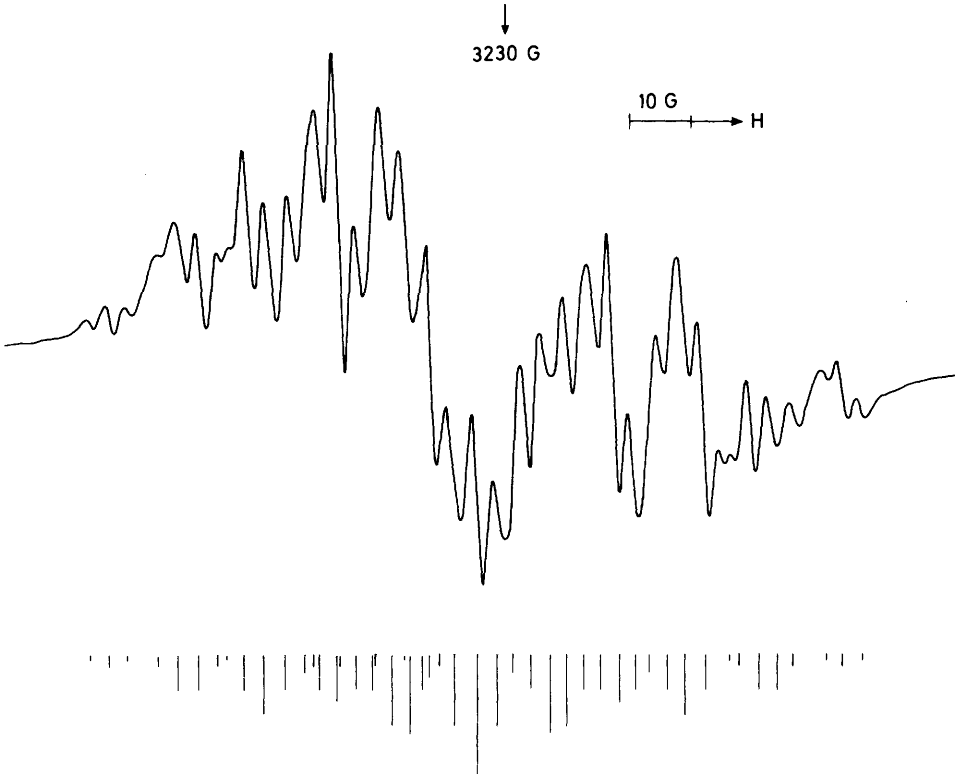
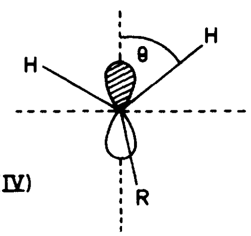
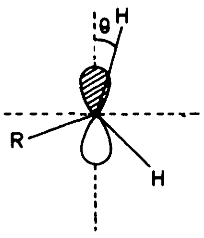


Figure 5. First derivative *X*-band e.s.r. spectrum for a dilute solution (*ca.* 0.1% mole fraction) of tetrahydropyran in CCl_2F-CF_2Cl, after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to tetrahydropyran cations. (The stick diagram is based on the data in Table 1.)



(IV)



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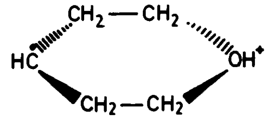

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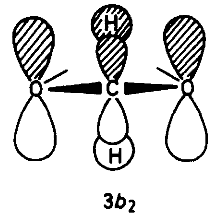


(VII)

the proton coupling constants of which are largely predictable. We therefore favour the previous formulation.

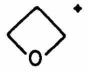
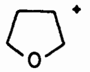
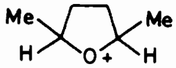
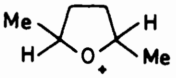
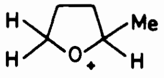
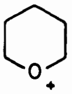
In several cases, particularly for the oxirane and oxetane cations, extra small splittings were sometimes observed which were probably due to very weak hyperfine coupling to chlorine from one neighbouring solvent molecule.

1,1-*Diethers* (*Acetals*).—In parallel studies to ours,[40] both Williams' and Shida's groups have studied the cations of various acetals.[41,42] All the results show remarkably large proton hyperfine coupling to the methylene protons in the $-O-CH_2-O-$ group. This has been explained in terms of the π–σ–π delocalised SOMO (VII), which is comparable with that proposed by Whiffen in his original interpretation of the spectrum for cyclohexadienyl radicals.[43] The extent of delocalisation is far larger for the acetal cations because of the high electron affinity of positive oxygen. This conjugation reduces the electron demand by the unit and hence coupling to other β-protons on the outer groups is greatly reduced (Table 2).

Results for 1,3-dioxacyclopentane (1,3-dioxolane) are more clear-cut, the spectrum comprising a major triplet (153 G) showing second-order splitting on the central features, with a subsidiary quintet splitting of 11 G from the remaining protons. A typical spectrum is shown in Figure 1 of ref. 40. Equivalence within the two sets of protons suggests that the cation frame is essentially planar. Results for 1,3-dioxacyclohexane are similar[40,41] except that the large CH_2 proton coupling of *ca.* 140 G is somewhat reduced, and the peripheral β-protons are split into pairs (26.3 and 12.4 G) indicating, as expected, a fixed, non-planar ring conformation. This should result in an inequivalence of the two strongly coupled CH_2 protons. This was reported by us (Table and Figure 1 of ref. 40) but not by Snow *et al.*[41] Snow *et al.*[41] also report similar data for the cation of dimethoxymethane (Table 2).

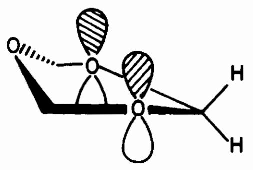
The cation of *s*-trioxane is interesting in that the SOMO seems to be largely confined to a unique $-O-CH_2-O-$ unit. That this should be so is in accord with π-overlap consider-

Table 1. E.s.r. parameters for monoether radical cations

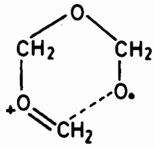
Cation (CFCl$_3$ solvent)	Proton hyperfine coupling (G)[a] β-H	γ-H
$\mathrm{Me_2O}^{+\cdot}$	43 (6 H), 43[b] 43.6, 42.8, 42.5[c]	
$\mathrm{Et_2O}^{+\cdot}$	68.7 (4 H)	
$\mathrm{(Me_2CH)_2O}^{+\cdot}$	45[d]	
	16 (4 H)	
	64 (4 H)	11 (2 H)
	89 (2 H), 40 (2 H) 89 (2 H), 40 (2 H)[b] 59 (2 H), 22 (2 H)[e]	
	97 (2 H)[b]	
	95 (1 H), 35 (1 H)[b]	
	{83 (1 H), 42 (2 H) 78 (1 H), 49 (2 H) (146 K)[b]	
	34.5 (2 H), 14 (2 H)	11 (2 H), 3 (2 H)

[a] 1 G = 10^{-4} T. [b] Ref. 18. [c] Ref. 19. [d] Tentative. [e] D$_2$SO$_4$ solvent.

(VIII)



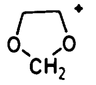
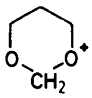
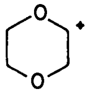
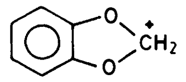
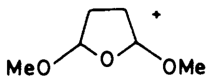
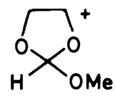
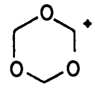
(IX)



ations provided the ring retains its expected buckled conformation at one end, whilst flattening to provide better overlap at the other, as indicated in (VIII). The outer features comprise asymmetric quartets indicating coupling to two inequivalent protons (11 G and 23 G). This suggests a skew conformation and requires that the remaining two β-protons give zero coupling. This is a puzzling result, but we can discover no reasonable alternative explanation. Such a distortion should migrate around the ring to give a septet for six equivalent protons, given sufficient thermal energy, but we have not been able to observe this behaviour. Again, in our view, the strongly coupled methylene protons are unlikely to be equivalent, but this is difficult to judge because of the presence of a second, most interesting set of lines and a central line of unknown origin (Figure 6).

This second spectrum is remarkable amongst all those reported here in exhibiting a very marked anisotropy, clearly due to a shift in $g_{\parallel}$ from the free-spin value (Table 2). Although the yield of this species was relatively high in all our studies, it was not mentioned by Snow *et al.* We are reasonably sure that it is an alternative electron-loss product from *s*-trioxane, and suggest that it is, in essence, an alkoxyl radical (RO·). These always have strongly shifted $g_{\parallel}$ features,[24,25] and exhibit large hyperfine coupling to β-protons. If this is correct, however, we need to explain why our $g_{\mathrm{max.}}$ value of 2.0286 is less than ' normal ' for such radicals (2.054—2.093) whilst $\Sigma A(\beta\mathrm{H})$ of 175 is greater than usual (141—156 G).[26] We can explain the former fact in terms of the postulated structure given in (IX). We suggest that the newly born, vibrationally hot cation undergoes C–O bond scission as an alternative to the bending distortion shown in (VIII). Such alternative, but concurrent, mechanistic pathways have frequently been observed on electron addition,[1,2] although they seem to be relatively rare in studies on radical cations. We have not detected any thermal conversion of one species into the other. The driving force for this breakdown lies in the relative stability of the $\mathrm{C{-}\overset{+}{O}{=}CH_2}$ moiety. This is, in essence, an alkylated formaldehyde unit of the type postulated for vinyl cations,[34,35] discussed later. The interaction suggested by the dotted line in (IX) is thought to be of the ' π-complex ' type involving little delocalisation but with sufficient bonding to lift the formal degeneracy of the

Table 2. Di- and tri-ether cations

Cation (in $CFCl_3$)	^1H Hyperfine coupling (G)	
	$^-OCH_2O^-$ β-protons	Other β-protons
$MeOCH_2OMe^+$	136.1 (2 H) [a]	31.3 (2 H), 6.0 (4 H) [a]
$MeOCH_2CH_2OMe^+$	*ca.* 10 (10 H)	
	153 (2 H) 153 (2 H) [a]	11 (4 H) 11.2 (4 H)
	140 (2 H_{av}) [b] 140.6 (2 H) [a]	26 (2 H), 12.5 (2 H) 26.3 (2 H), 12.4 (2 H) [a]
	11 (4 H), 8 (4 H)	
	22.4 (2 H)	5.0 (2 H, aromatic)
	135 (2 H) [a]	32 (2 H) [a]
	*ca.* 150 (1 H)	*c*
	162 (2 H_{av}) [b] 160.2 (2 H)	23 (1 H), 11 (1 H)

[a] Ref. 41. [b] 2 H not exactly equivalent. [c] Subsidiary structure poorly defined.

$2p_\pi$ orbitals on the $-CH_2\dot{O}$ oxygen thereby reducing $g_{max.}$ to the observed value. The value of $g_{max.}$ is largely a function of the environment for such species,[44,45] the normal source of splitting being hydrogen bonding. We require that the π-interaction suggested herein be more effective than hydrogen-bonding in lifting this degeneracy. The increase in delocalisation onto the two β-protons can then be understood in terms of the positive charge effect. That this mode of breakdown is unique to *s*-trioxane amongst the present systems is puzzling. For example, the same process is available to 1,3-dioxacyclohexane, but no trace of such a species was obtained.

The related derivative, 2,5-dimethoxytetrahydrofuran, was studied by Snow *et al.*[41] The results make a most interesting contrast with that for *s*-trioxane in that there are *two* strongly coupled protons. This can only occur if there is full delocalisation within the unit $^-O^-C^-O^-C^-O^-$ giving a five-centred π/σ system. This interesting contrast presumably reflects the inability of the cyclic derivative to attain the optimum structure for π-delocalisation that can be readily achieved by the dimethoxy derivative.

It is also interesting that for the dimethoxymethane cation, methyl group rotation is strongly restricted, giving two relatively strongly coupled protons (*ca.* 32 G) and four weakly coupled protons. This makes an interesting contrast with the results for $Me_2\dot{O}^+$, which exhibits unrestricted rotation at 77 K.

Another interesting aspect of these results is that, for the alkyl derivatives $^-O^-CH(R)^-O^-$, there is a strong tendency to dissociate to give $R^\cdot$ radicals (8),[42] but this was not mentioned as a significant event for the 2,5-dimethoxytetrahydrofuran

$$[{}^-OCH(R)O^-]^{+\cdot} \longrightarrow R^\cdot + [{}^-OCHO^-]^+ \qquad (8)$$

cation. The systems studied by Shida and his co-workers[42] (2-methyl-1,3-dioxacyclopentane, 2-methyl-1,3-dioxacyclohexane, 3-methyl-2,4-dioxapentane, 2,4,6-trimethyl-1,3,5-trioxacyclohexane, and their ethyl analogues) gave no evidence for the parent cations at 77 K, so reaction (8) is normally complete at that temperature. Evidence for the parent cation of 2-methyl-1,3-dioxacyclopentane was obtained after radiolysis at 4 K, however. The driving force for dissociation (8) comes from the relative stability of the carbocations $R\overset{+}{O}{=}CH(OR)$. This is a similar factor to that which contributes to the stability of the radical cations studied by Schulte-Frohlinde and his co-workers.[46,47]

We selected the acetal 1-ethoxytetrahydrofuran to probe this situation further, and to see if the five-membered ring was responsible for the lack of reactivity of the dimethoxy

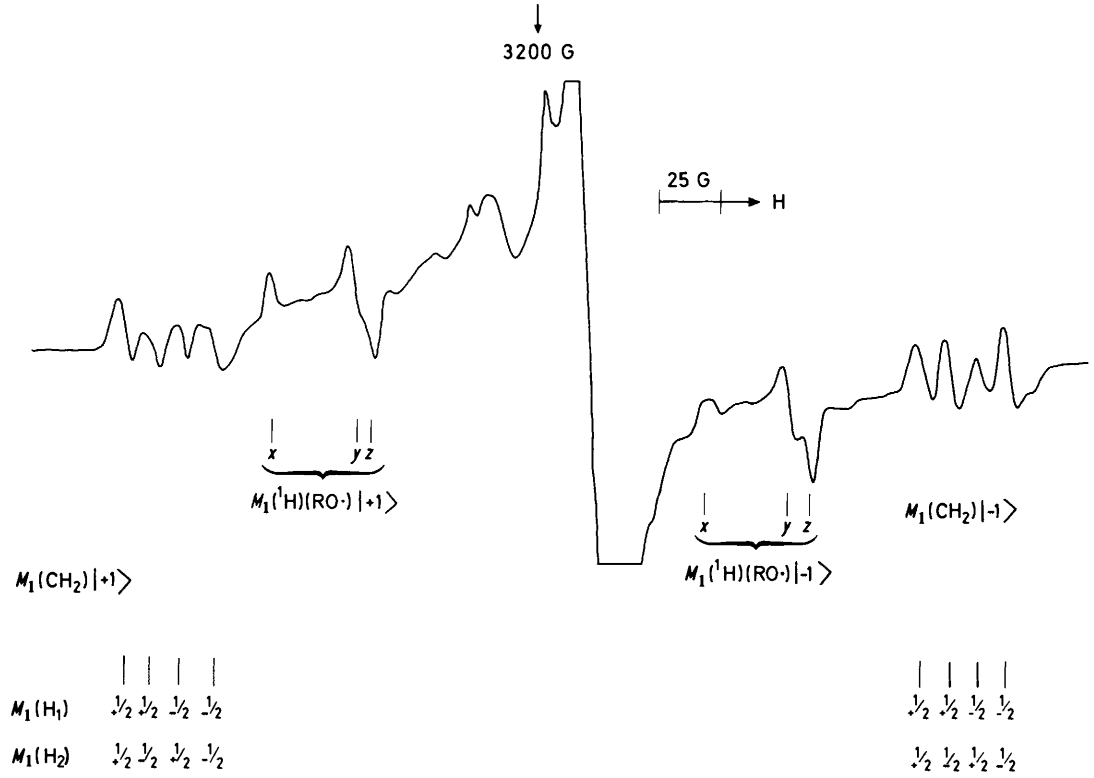
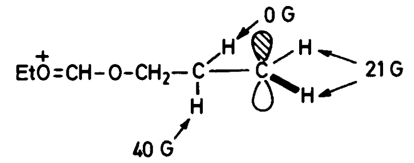
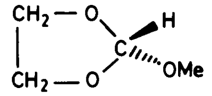


Figure 6. First derivative *X*-band e.s.r. spectrum for a dilute solution (*ca.* 0.1% mole fraction) of *s*-trioxane in $CFCl_3$, after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to *s*-trioxane cations and RO˙ radicals

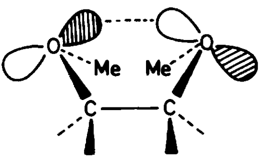
(X)



(XI)



(XII)



derivative. The results show no sign of a species with a very large proton hyperfine coupling. A set of five equally spaced lines with intensity ratio 1 : 2 : 2 : 2 : 1 was obtained which can be satisfactorily accommodated by the coupling constants shown in (X). Thus the THF ring system has not inhibited the expected rearrangement in this case.

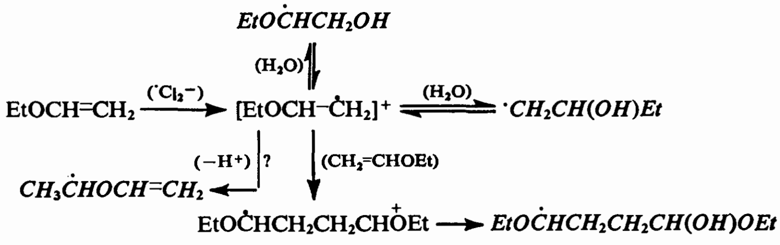
In contrast, the trioxy derivative $MeOCH_2OCH_2OMe$ gave only $H_2\dot{C}OCH_2R$ radicals [1 : 2 : 1, A (^1H) = 19 G] presumably formed *via* a cyclic transition state. The methoxy derivative (XI) gave a complex doublet spectrum with a total splitting of 150 G suggesting that the parent cation was stable. In this case there can be no extra delocalisation, but the acetal cation would need to lose MeO˙ radicals to give the normal unimolecular breakdown (8) which clearly does not occur in this case.

1,2-Diethers.—We have only studied 1,4-dioxane and dimethoxyethane in this class. Our interest lay in the possibility that, because of steric encouragement, these cations might give some evidence for intramolecular $O\dot{-}O$ σ* bonding[33] (XII). The results, whilst not definitive, seem to us to support this suggestion. As stressed above, our results, and especially those of Shida and his co-workers,[18] establish that the normal reaction between R_2O^+ cations and R_2O molecules is hydrogen atom transfer. However, for these diethers σ* formation is apparently favoured over any intramolecular hydrogen transfer.

Our expectation for the β-proton hyperfine coupling constants in such $(R_2O\dot{-}OR_2)^+$ σ* cations is that they should be reduced by a factor of *ca.* 3 relative to those for the normal R_2O^+ cations. This effect, exhibited by the systems $R_3P^{+\cdot} \longrightarrow (R_3P\dot{-}PR_3)^+$ and $R_2S^{+\cdot} \longrightarrow (R_2S\dot{-}SR_2)^+$,[16,17] arises, in our view, because of the raising of the σ* level relative to the SOMO of the parent cations.[17]

For dioxane the proton coupling, apparently for eight nearly equivalent protons (Figure 7) is only *ca.* 9.5 G. Resolution was enhanced at *ca.* 120 K and the best fit was then for a set of four protons with 11 G coupling and a set of four with 8 G coupling (Table 2). It is noteworthy that all structure was lost when the perdeuteriated diether was studied.

For dimethoxyethane cations, the spectra were poorly resolved, but the basic coupling was *ca.* 9 G and the total spread *ca.* 80 G so the σ* formulation seems to us to be most reasonable.



Scheme.

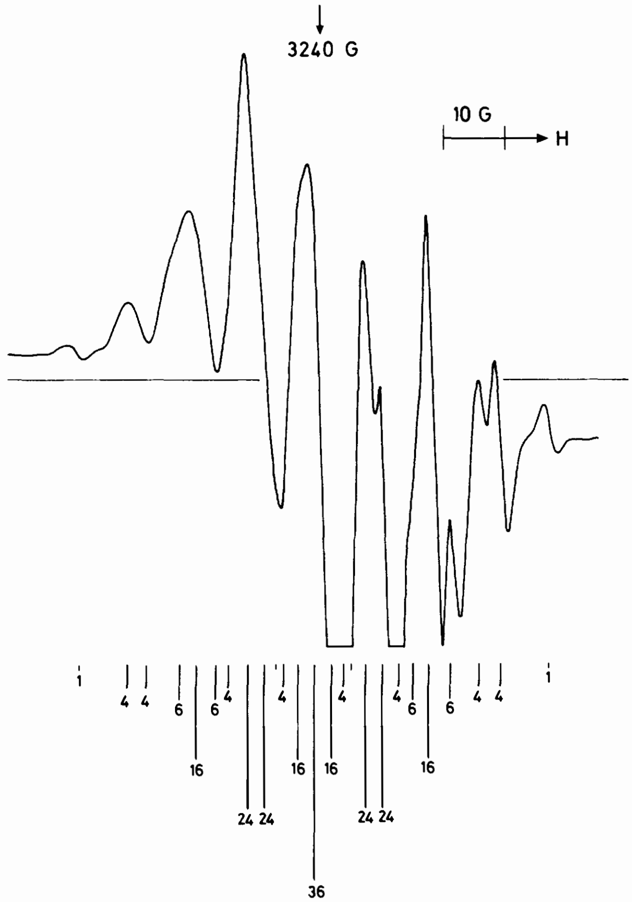


Figure 7. First derivative *X*-band e.s.r. spectrum for a dilute solution (*ca.* 0.1% mole fraction) of 1,4-dioxane in $CFCl_3$, after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to dioxane cations

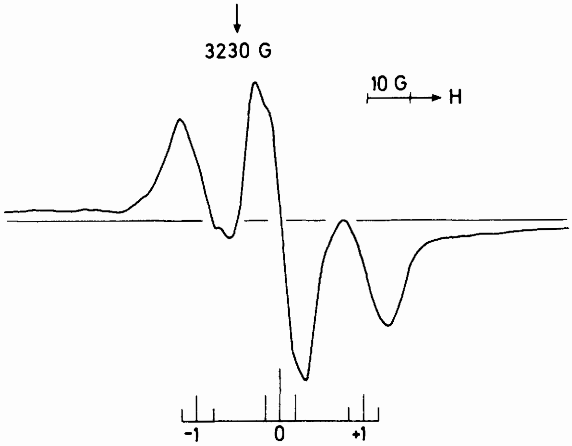
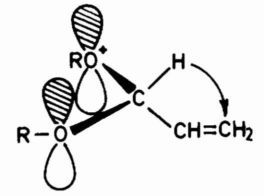


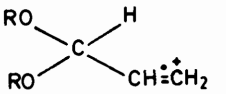
Figure 8. First derivative *X*-band e.s.r. spectrum for a dilute solution (*ca.* 0.1% mole fraction) of ethyl vinyl ether in $CFCl_3$, after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to vinyl ether cations

(XIII) $R\overset{+}{O}{=}CH{-}\dot{C}H_2$

(XIV)



(XV)



Vinyl Ethers.—Our interest in vinyl ether cations stemmed from the perceptive studies of Gilbert *et al.*,[34] who linked a range of radical products into a single scheme by postulating the loss of an electron when vinyl ethers were treated with one-electron oxidants as the first stage of reaction. They were unable to detect these cations directly, but the species italicised in the Scheme were detected and characterised by e.s.r. spectroscopy. We selected $EtOCH{=}CH_2$ for study, and interpret the spectrum obtained from irradiated freon solutions in terms of the parent cation (XIII). The parameters derived from the resulting spectrum (Figure 8) are given in Table 3. They show that this limiting structure is, in fact, a good representation, the estimated spin-density on the $-\dot{C}H_2$ group being *ca.* 89% based on a value of 22 G for unit spin-density. This is supported by the very small splitting from the CH_2 protons of the ethyl group. Thus the species resembles the neutral $O{=}CH{-}\dot{C}H_2$ radical rather than the ether cations studied herein. The positive charge is largely confined to the region of the oxygen atom, and the unpaired electron to the terminal methylene group.

We have also studied the cations derived from the allyl acetals $(RO)_2CHCH{=}CH_2$. These were of potential interest in that the two sites for electron loss, indicated in (XIV) and (XV), are potentially linked *via* the acetal carbon. In the event, however, the acetal hydrogen atom appears to have moved to the terminal methylene to give the cations $(RO)_2\overset{+}{C}{-}\dot{C}HMe$. Our e.s.r. data (Table 3; *cf.* Figure 1 of ref. 35) agree well with those for similar radicals studied in fluid solution and unambiguously identified by e.s.r. spectroscopy.[46,47] The mobility of this hydrogen atom accords with its very large hyperfine

Table 3. Vinyl ether and related cations

Cation (in $CFCl_3$)	^1H Hyperfine coupling (G) α-H	β-H	^1H in ^-OR
$H_2\dot{C}{-}CH\overset{+}{O}Et$	19.4 (2 H)		3.5 (2 H)
$Me\dot{C}H{-}C(OMe)_2^+$	19 (1 H)	24 (3 H)	1.5 (3 H)
$Me\dot{C}H{-}C(OEt)_2^+$	19 (1 H)	24 (3 H)	
$H_2\dot{C}{-}C(OMe)_2^+$ [a]	20.55 (2 H)		3.1 (3 H), 0.66 (3 H)
$H_2\dot{C}{-}C(OEt)_2^+$ [a]	20.6 (2 H)		3.36 (2 H), 0.6 (2 H)
$Me\dot{C}H{-}C(OMe)_2^+$ [a]	18.8 (1 H)	24.5 (3 H)	2.8 (3 H), 0.7 (3 H)
$H\dot{C}{=}COMe$	22 (1 H)		11 (3 H)

[a] Ref. 46.

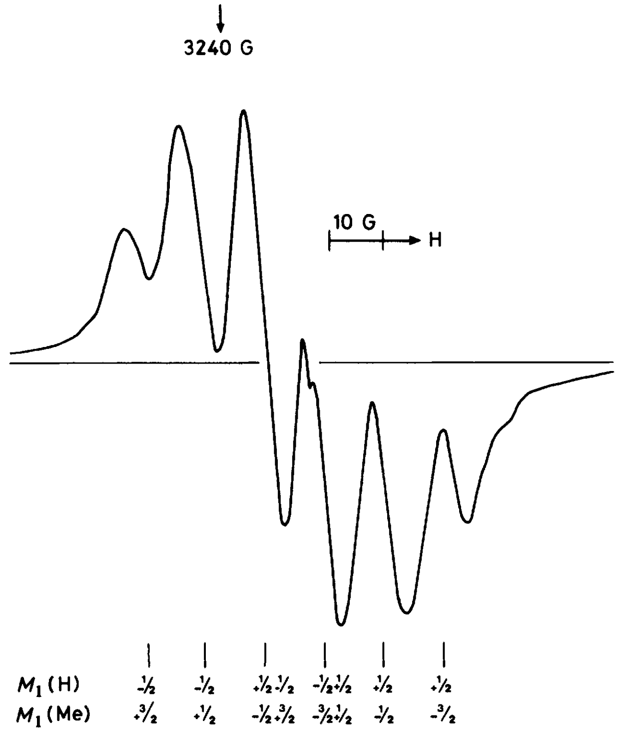


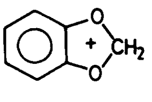
Figure 9. First derivative *X*-band e.s.r. spectrum for a dilute solution (*ca.* 0.1% mole fraction) of $H{-}C{\equiv}COMe$ in $CFCl_3$, after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to $H\dot{C}{=}\overset{+}{C}OMe$ cations

coupling in acetal cation systems, and with Shida's observation of the loss of alkyl radicals from such systems.[42]

The structure of these cations is similar to that for the simple vinyl ether cations, being close to those for the neutral ester radicals $ROCO{-}\dot{C}H_2$, for which delocalisation of the unpaired electron is also small.[48]

We also prepared the cation $Me\overset{+}{O}{=}C{=}\dot{C}H$ for comparative purposes (Figure 9). As expected, the limiting structure depicted is favoured, but the relatively large methyl proton coupling of 11 G shows that π-delocalisation onto oxygen is much greater than for the vinyl ether cations. Based on the average value of 43 G (from $Me_2O^{+\cdot}$) this gives a spin density on oxygen of *ca.* 0.25. If this is to be largely balanced by 0.75 on the terminal methine group, we need a *Q* value [49,50] of *ca.* 29 to accommodate the e.s.r. parameters. This is unusually high, so the oxygen spin density may have been overestimated.

It was also of interest to study the cation of 1,2-benzodioxole (XVI). This gave a well defined triplet assigned to the



(XVI)

unique $-CH_2-$ unit with a large splitting of 22.4 G. Evidently, the Whiffen effect still applies for the reduced spin density on the two oxygen atoms. If we compare this splitting with those for the acetal radical cations we estimate a spin density on the $-O{-}CH_2{-}O-$ unit of *ca.* 14%.

Ethers in Sulphuric Acid.—We know of no previous studies of the radiolysis of ethers in strong acids. We have shown that solutions of alcohols (ROH_2^+ ions) in sulphuric acid glasses give alkyl radicals by dissociative electron capture (9).[51] We also detected $R_2\dot{C}OH_2^+$ radicals formed by hydrogen atom abstraction (10). There was no clear evidence for primary

$$ROH_2^+ + e^- \longrightarrow R^\cdot + H_2O \qquad (9)$$

$$R_2CHOH_2^+ + HSO_4^\cdot \longrightarrow R_2\dot{C}OH_2^+ + H_2SO_4 \qquad (10)$$

cation formation by electron loss. Nevertheless, this medium is often a good source of primary cations. For example, R_3PH^+ ions gave $R_3P^{+\cdot}$ cations,[52] RS–SR gave $(RS\dot{-}SR)^+$ π-cations.[53,54]

As expected, the major organic radical product at 77 K was the alkyl radical. For example, Me_2O gave $^\cdot CH_3$ radicals (11), diethyl ether gave ethyl radicals, and THF gave $^\cdot CH_2CH_2CH_2$-$CH_2OH_2^+$ radicals, as estimated from the resulting e.s.r. spectra.

$$(CH_3)_2OH^+ + e^- \longrightarrow {}^\cdot CH_3 + CH_3OH \qquad (11)$$

On annealing, evidence for hydrogen abstraction to give $R_2\dot{C}O(H)R^+$ cations was obtained, but in addition, outer hyperfine features not associated with either of these classes of radicals were observed (see, for example, Figure 10).

For Me_2O solutions in D_2SO_4, outer lines were detected which, if associated with Me_2O^+ cations, give $A(^1H) = 39$ G and $g_{av} = 2.0085$. The marked *g* shift and large hyperfine coupling are in good accord with expectation for the cation. The definite reduction in hyperfine coupling (from 43 to 39 G) is worrying, and must be ascribed to a solvation effect. It is noteworthy that a comparable reduction was observed for $(R_2SSR_2)^+$ radicals.[54] However, the nature of this solvation is not clear.

Relatively well defined outer features were obtained from solutions of THF in D_2SO_4 (Figure 10). However, if these are assigned to $(THF)^+$ cations the total hyperfine coupling (*ca.* 162 G) is far less than that for these cations in freon (258 G).

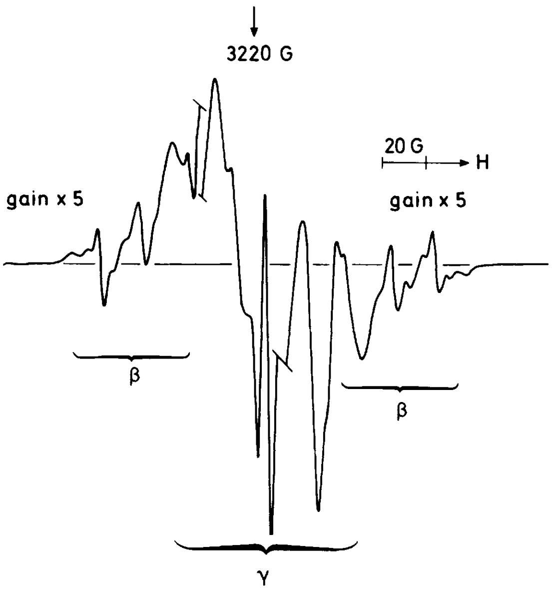


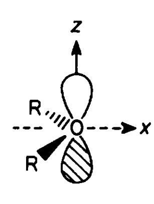
Figure 10. First derivative *X*-band e.s.r. spectrum for a solution (*ca.* 1% mole fraction) of tetrahydrofuran in D_2SO_4, after exposure to ^{60}Co γ-rays at 77 K, and annealing to 133 K to give partial loss of $HSO_4^{\cdot}$ radicals, showing outer features (β) possibly due to THF cations. [The central lines (γ) are due to $^{\cdot}SO_3^-$, $HSO_4^{\cdot}$, and $(H_2\dot{C}R)$ radicals; note the spin-flip features on the outer lines.]

Thus the assignment is far from clear. We cannot think of any alternative assignment, but if the $(THF)^+$ assignment is correct, it suggests that there is some factor forcing the β-protons into sites of poorer σ–π overlap. The lines for this species are remarkably narrow, and exhibit well resolved proton spin-flip satellite lines which were strongly power-dependent.[55] The broad outer lines shown in Figure 10 give a further coupling of *ca.* 11 G for two extra protons. If these are assigned to two of the four γ-protons, this coupling is far greater than that for THF^+ cations in freon. If we assume that the conformation is similar to that for THF^+, we can fit equation [1] with $\theta = 7°$ and $B = 60$ G. The alternative, that the conformation is constrained to resembling that of THP^+, gives $\theta = 68°$, but B then equals *ca.* 156 G which is unacceptably large. These results are therefore not in good accord with expectation for THF cations, but we have no other explanation at present.

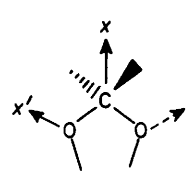
We conclude that, although the major reaction is dissociative electron capture, nevertheless hydrogen atom loss according to reaction (12) probably also occurs in the radiolysis of these solutions.

$$R_2OH^+ + HSO_4^{\cdot} \longrightarrow R_2O^{+\cdot} + H_2SO_4 \qquad (12)$$

Significance of the g-*Tensor Components.*—In several cases, resolution was sufficient to show three distinct *g*-features, as pointed out by Snow *et al.*[41] As expected, the *g* shifts are much smaller than those for corresponding $RO^{\cdot}$ radicals, which generally have $g_{max.}$ values in the range 2.054—2.093.[44] For R_2O^+ cations, $g_{min.}$, which is close to the free-spin *g* value (2.0023), must lie along *z* in (XVII). Fields along *x* or *y* couple the SOMO with filled σ-orbitals, but a field along *y* also connects the SOMO with the ' lone-pair ' (*x*) orbital which will give a maximum shift. Thus we equate $g_{max.}$ (*ca.* 2.01) with g_y and $g_{int.}$ (*ca.* 2.007) with g_x. For the acetal cations spin on *both* oxygen atoms will contribute. Again, $g_{min.}$ will be g_z, normal to the radical ' plane ', but $g_{max.}$ will now be a mixture of the monoether g_x and g_y values [*cf.* (XVIII)]. This is, in our view, the reason for the clear reduction in $g_{max.}$ (*ca.* 2.008) observed for these cations.



(XVII)



(XVIII)

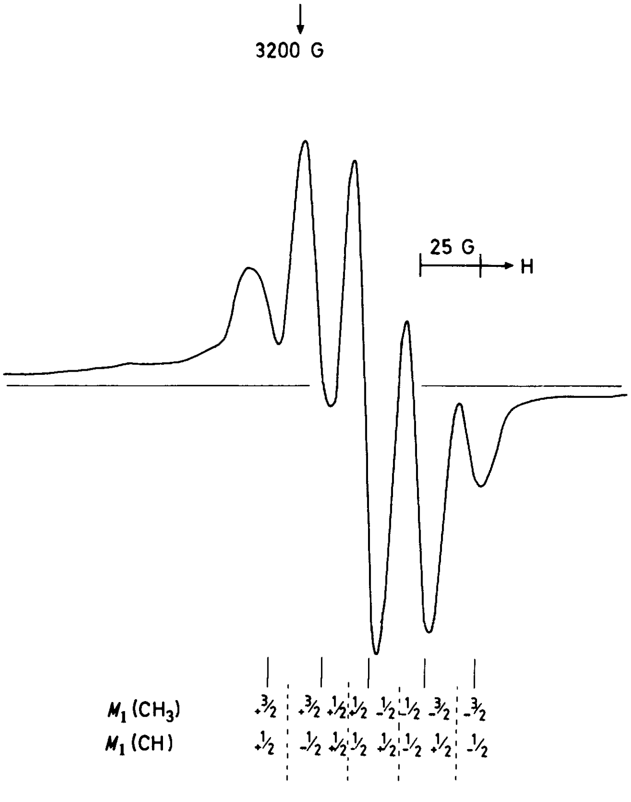


Figure 11. First derivative *X*-band e.s.r. spectrum for a dilute solution (*ca.* 0.1% mole fraction) of $EtOCH_2CH_2OH$ in $CFCl_3$, after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to $CH_3\dot{C}HOCH_2CH_2OH_2^+$ radicals

Experiments with Alcohols.—We know of no successful e.s.r. studies of the parent cations of alcohols, $(R\dot{O}H)^+$. These are expected to have *g* tensors and β-proton hyperfine coupling constants close to those for their related ether cations, and the α-proton coupling is expected to be close to those for $^{\cdot}OH$ radicals [56] and $H_2O^{+\cdot}$ cations [57] [*ca.* (—) 26 G]. However, they are expected to be strong acids with a tendency to form $RO^{\cdot}$ radicals. These should be detectable in sulphuric acid because of the strong hydrogen bonding which lifts the orbital degeneracy, but they probably would not be detected in freon solutions.

Most of our attempts to prepare $R\dot{O}H^+$ cations in freon solutions have failed. They generally gave well defined spectra assignable to α-hydroxyalkyl radicals, $R_2\dot{C}OH$.[58] We think that the major pathway to these radicals involves reaction within alcohol clusters. There is a very strong tendency for alcohol molecules to form small cyclic, hydrogen-bonded aggregates in inert media, which is greatly enhanced on cooling.[59] We confirmed by i.r. spectroscopy that such aggregation was indeed occurring in our systems. Radiation processes involving such aggregates are expected to give $R_2\dot{C}OH$ radicals, just as is the case for pure alcohols. In most cases dilution to the limit of detection followed by very rapid freezing still gave $R_2\dot{C}OH$ radicals as the major product.

As a system with reduced intermolecular hydrogen-bonding we studied 2-ethoxyethanol, which, in dilute solution, is expected to form cyclic hydrogen-bonded molecules. The resulting spectrum (Figure 11) comprises a quintet ($A \approx 20$ G) which we assign to $CH_3\dot{C}HOCH_2CH_2OH_2^+$ radicals. Clearly this approach to the preparation of alcohol cations has little to commend it.

Results for n-propyl alcohol in very dilute solutions were dominated by features assigned to $H_2\dot{C}CH_2CH_2OH$ radicals. Cyclohexanol gave a septet [$A_1 = 25$ G (2 H); $A_2 = 12$ G (2 H)] probably due to the cyclic radical formed by loss of the unique β-proton, and t-butyl alcohol gave $H_2\dot{C}CMe_2OH$ radicals together with some $^{\cdot}CH_3$ radicals. The formation of CH_3 radicals suggests the previous formation of $Me_3C\dot{O}$ radicals, which are a known source of methyl, or possibly direct loss of methyl from $Me_3C\dot{O}H^+$ cations (13).

$$Me_3C\dot{O}H^+ \longrightarrow {}^{\cdot}CH_3 + Me_2C{=}OH^+ \qquad (13)$$

We also made a careful study of radical radiolysis products from solutions of alcohols in sulphuric acid, despite our previous failure to detect parent radical cations.[51] In all cases, electron capture gave the expected alkyl radicals in good yield, but we were unable to detect any extra features giving unambiguous evidence for the formation of $R\dot{O}H^+$ cations.

It is interesting to note that some recent calculations suggest that $H_3C\dot{O}H^+$ cations are less stable than the isomeric $H_2\dot{C}OH_2^+$ cations,[60] and there is mass spectroscopic evidence to support this,[61] in addition to chemical expectation. However, the calculated barrier for the 1,2-hydrogen shift of *ca.* 100 kJ mol^{-1} appears to preclude interconversion in our low-temperature studies.

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Received 1st *July* 1983; *Paper* 3/1131