Electron Spin Resonance Studies. Part XXXIII.[1] Evidence for Heterolytic and Homolytic Transformations of Radicals from 1,2-Diols and Related Compounds

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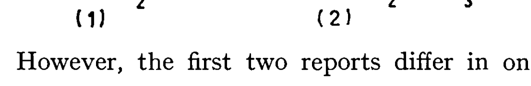
The reactions of the hydroxyl radical with a number of compounds containing the unit $-CHX-CHY-$, where X = OH or OMe and Y = OH, OAc, Halogen, or a protonated amino-group, have been studied by e.s.r. spectroscopy. The transient species involved have been identified on the basis of their hyperfine splittings and g-factors; in the case of the radical $\cdot CH(OH)\cdot CH_2NH_3^+$ and its derivatives, clear trends in the proton and nitrogen splittings are observed as the NH hydrogen atoms are successively replaced by methyl groups, and these have been rationalised in terms of an interaction involving both hydroxy- and amino-substituents.

The data not only support the view that radicals containing the fragment $-\dot{C}(OH)-C(OH)<$ undergo acid-catalysed elimination of water but also reveal further details of this reaction and information about related heterolytic processes; for example, there is evidence that the radical cation $Me\overset{+}{O}=CH-\dot{C}H_2$ is formed transiently from the radical $\cdot CH(OMe)\cdot CH_2X$ (X = Cl or OAc). Amines do not appear to fragment heterolytically from radicals of the type $\cdot CH(OH)\cdot CH_2NR_3^+$, but the formation of the species $Me_3N^{\cdot +}$ from the choline cation suggests that the C–N bond in the species $\cdot CH(OH)\cdot CH_2NMe_3^+$ readily undergoes homolysis.

EVIDENCE has previously been adduced, from e.s.r. spectroscopic observations, that when ethylene glycol is oxidised with the hydroxyl radical [from the titanium(III) ion-hydrogen peroxide system[2] or photolysis of hydrogen peroxide[3]], the first-formed radical (1) undergoes dehydration to give the radical (2) in an acid-catalysed reaction (i).[2,3] A number of related transformations has been documented,[2] and support for the occurrence of reaction (i) has subsequently been obtained from an investigation in which the radical (1) was generated by γ-irradiation of an aqueous solution of the glycol;[4] moreover, this study also provided evidence that the radical (2) reacts with more of the glycol to yield acetaldehyde and regenerate the radical (1), a chain process thereby being propagated.[4]



$$H-O-\dot{C}H-CH_2-OH^{\cdot}H^+ \longrightarrow O=CH-\dot{C}H_2 + H_3O^+ \quad (i)$$

(1) (2)

However, the first two reports differ in one detail,

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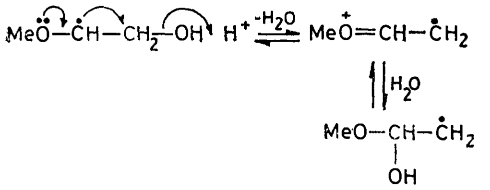
[1] Part XXXII, A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, preceding paper.

[2] A. L. Buley, R. O. C. Norman, and R. J. Pritchett, *J. Chem. Soc. (B)*, 1966, 849.

[3] R. Livingston and H. Zeldes, *J. Amer. Chem. Soc.*, 1966, **88**, 4333.

[4] C. E. Burchill and K. M. Perron, *Canad. J. Chem.*, 1971, **49**, 2382.

namely, the hyperfine splittings quoted for the radical (1); the values recorded from the titanium(III)–peroxide system were [2] $a_H(2)$ 2·06, $a_H(1)$ 1·54 mT, and those from the photolytic system were [5] $a_H(1)$ 1·754, $a_H(2)$ 0·994, $a_H(1)$ 0·1044, $a_H(1)$ 0·0316 mT. This paper describes an investigation of this discrepancy. We have found that the oxidation of ethylene glycol by the titanium(III)–peroxide system is more complex than originally envisaged; in particular, we have ascertained that the spectrum previously assigned to the radical (1) is that of a radical derived from two molecules of the glycol, although the spectrum of radical (1) can be discerned under appropriate conditions and the radical does indeed undergo the dehydration shown in reaction (i). We have also elucidated further the scope of reactions of the type (i), both with hydroxide ion as the leaving group and with other leaving groups, and have examined their relationship to the transformation (ii) which was previously studied during the reaction of methyl vinyl ether with the hydroxyl radical.[6] For these purposes, we have employed the titanium(III)–peroxide system for the generation of radicals.

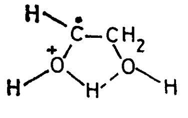


(ii)

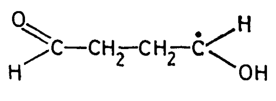
E.s.r. Spectra from Diols and Related Compounds, and Their Assignments.—(a) *Ethylene glycol.* At first inspection, it appeared possible that, of the two spectra previously ascribed to the radical (1), that obtained with use of the photolytic system was the one wrongly attributed; thus, the triplet splitting of 0·994 mT seemed too small to be associated with the methylene protons in radical (1). However, it has now become apparent that, for radicals of the type $\cdot CHY\cdot CH_2X$, $a(CH_2)$ is far smaller when X is an electronegative substituent such as OH and Y is OH or OMe than for other members of the class (*e.g.*, X or Y is alkyl), and a possible explanation for this has been advanced [1] (see also later). Thus, there is no reason to question this assignment, especially as the smallest two of the three single-proton splittings are compatible with the presence of two hydroxy-protons. We therefore examined further the radicals detected with the use of the titanium(III)–peroxide system.[7,8]

When ethylene glycol was oxidised at pH 2 under the conditions used before, the spectra of the two radicals reported previously were observed.[2] However, some very weak lines from a further radical were just detectable, and when the pH was raised above 2 these became more intense; above pH 2·5 they constituted the only spectrum observed, and they increased in intensity up to pH 4. The parameters of the new radical [$a_H(1)$ 1·80, $a_H(2)$ 0·94, $a_H(1)$ 0·10 mT; g 2·0031] are very similar to those of the radical (1) from the photolytic system,[5] except that the smallest splitting for that radical (0·0316 mT) was not observed, probably because of the greater line-widths which are commonly associated with the aqueous titanium(III)–peroxide as compared with the photolytic system. We therefore assign our new spectrum to the radical (1).

We next re-examined the spectrum earlier attributed to radical (1), eventually finding conditions (increase in the concentration of the glycol and the peroxide each by a factor of three, pH 1·6) under which its intensity was so considerably enhanced, and that of the radical (2) so reduced, that a further small hyperfine splitting could just be resolved as a 1 : 3 : 3 : 1 quartet, a 0·055 mT. Now the g-factor of this species, 2·0031, is within the range of those for radicals in which the tervalent carbon atom is conjugated to one hydroxy- or alkoxy-substituent,[9,10] and this, together with the values for the largest two of the three splitting constants, is compatible with the partial structure $\cdot CH(OH)\cdot CH_2$–. The problem in complete elucidation then lay in accounting for the small quartet splitting; thus, there seemed no likelihood of the formation from the reagents concerned of a radical containing a methyl group, and in any case the species $\cdot CH(OH)\cdot CH_2Me$ has different e.s.r. parameters.[5] We therefore first considered the possibility that this splitting reflected interaction with three protons which, though inequivalently sited, become equivalent by means of a transformation which occurs at a rate above the fast-exchange limit. Structure (3) might have the requisite properties. First, a much higher value for $a(\beta\text{-}CH_2)$ than in the case of the radical (1) is reasonable since, although in each radical both carbon atoms are bonded to hydroxy-groups, the stereochemistry of (3) is unsuitable for the interaction which is thought to be responsible for the low value for $a(\beta\text{-}CH_2)$ in (1).[1] Secondly, rapid enough rotation of the C–O bonds and intramolecular migration of the hydrogen-bonded proton from one oxygen to the other could serve to produce the equivalence we have referred to. However, when ethylene glycol was immersed and then oxidised in deuterium oxide, the spectrum concerned was unaltered; since the hydroxy-protons in a radical such as (3) would undergo rapid solvent exchange and be replaced by deuterium, the possibility that the spectrum is of this species can be ruled out.



(3)



(4)

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[5] R. Livingston and H. Zeldes, *J. Chem. Phys.*, 1966, **44**, 1245.

[6] D. J. Edge, B. C. Gilbert, R. O. C. Norman, and P. R. West, *J. Chem. Soc.* (*B*), 1971, 189.

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

[8] R. O. C. Norman and P. R. West, *J. Chem. Soc.* (*B*), 1969, 389.

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

[10] A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Soc.* (*A*), 1971, 124.

We next considered the possibility that the small quartet splitting arises from differently sited protons which, fortuitously, have the same splitting constant to within the limits of the measurement. Such a species is (4), the two γ- and one δ-(aldehydic) protons giving the observed quartet, and we believe that this is indeed the radical concerned on the basis of the following evidence.

First, we generated the related radical $\cdot CH(OH)\cdot CH_2CH_2CH_2OH$ by the oxidation of butane-1,4-diol; as expected, it was the predominant species detected, its characterisation on the basis of its hyperfine splittings and g-factor (Table 1) being unambiguous. It is notable that not only are its α- and β-proton splittings almost exactly the same as those in the radical considered to be (4), but so also is its γ-proton splitting. Secondly, although no splitting from the δ-protons could be resolved in the radical $\cdot CH(OH)\cdot CH_2CH_2CH_2OH$, a splitting from a δ-proton of magnitude (0·035 mT) similar to that in the radical (4) has been found for the radical (5), the γ-proton splitting for which is also similar to that for (4).[11,12] Thirdly, and of greatest importance, we generated radicals of the type (6) by addition of carbonyl-conjugated radicals to vinyl ethers (the details are discussed later), finding that not only was $a(\gamma\text{-}CH_2)$ in each case the same or closely similar to the value attributable to the corresponding protons in the radical (4) but also, for the two examples in which $R^1 = H$, the splitting constant for this (aldehydic) proton was the same or nearly the same as that attributable to the aldehydic proton in (4) (Table 3).

TABLE 1

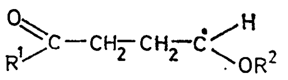
Hyperfine splitting constants (mT) and g-factors for radicals derived from diols and related compounds

Parent compound	Radical	$a(\alpha\text{-H})$	$a(\beta\text{-H})$	$a(\gamma\text{-H})$	a(other)	g
$CH_2OH\cdot CH_2OH$	$\cdot CH(OH)\cdot CH_2OH$	1·80	0·94		0·10 (OH)	2·0031
	$\cdot CH_2\cdot CHO$	1·90				2·0045
	$\cdot CH(OH)\cdot CH_2CH_2CHO$	1·53	2·03	0·055	0·055 (CHO)	2·0031
$CH_2OH\cdot CH_2CH_2CH_2OH$	$\cdot CH(OH)\cdot CH_2CH_2CH_2OH$	1·525	2·025	0·065		2·0031
$CH_3CH(OH)\cdot CH_2OH$	$\cdot CH_2\cdot CH(OH)\cdot CH_2OH$	2·23	2·46			2·0025
	$\cdot CHMe\cdot CHO$	1·81	2·15		0·20 (CHO)	2·0043
	$\cdot CH_2COMe$	1·97 [a]			0·10 (Me)	2·0041
	$\cdot CH(OH)\cdot CH(OH)Me$	1·715	1·235	0·06	0·06 (OH)	2·0031
	$\cdot CMe(OH)\cdot CH_2OH$		2·10 (3H) 0·915 (2H)			2·0031
$CH_3CH(OH)\cdot CH(OH)CH_3$	$\cdot CHMe\cdot COMe$	1·86	2·23		0·21 (Me)	2·0039
	$\cdot CMe(OH)\cdot CH(OH)Me$		0·85 (1H) 2·06 (3H)			2·0031
$CH_2Cl\cdot CH_2OH$	$\cdot CH(OH)\cdot CH_2OH$	1·80	0·94		0·10 (OH)	2·0031
	$\cdot CH_2\cdot CHO$	1·90				2·0045
	$\cdot CH(OH)\cdot CH_2CH_2CHO$	1·53	2·03	0·055	0·055 (CHO)	2·0031
	$\cdot CHCl\cdot CH_2OH$	2·06	1·50		0·29 (Cl)	2·0057
	$\cdot CH_2\cdot CH(OH)_2$	2·26	1·87			2·0025
$CH_2Cl\cdot CH_2OMe$	$\cdot CH(OMe)\cdot CH_2OH$	1·725	0·875	0·175		2·0031
	$\cdot CH_2\cdot CH(OH)OMe$	2·26	1·90			2·0025
	$\cdot CH_2\cdot OCH_2CH_2Cl$	1·71		0·18		2·0032
$CH_2OMe\cdot CH_2OAc$	$\cdot CH(OMe)\cdot CH_2OAc$	1·76	0·80	0·20		2·0030
	$\cdot CH_2\cdot OCH_2CH_2OAc$	1·70		0·20		2·0032

[a] Triplet with broadened central line.[2]

$CH_2{=}CH{-}CH_2{-}\dot{C}H_2$

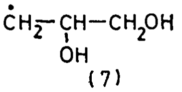
(5)



(6)

In summary, the relative concentrations of radicals (1), (2), and (4) observed under the conditions used were: pH 1, (2) : (4) = >5 : 1; pH 2, (2) : (4) = 1 : 3, with a trace of radical (1); pH 2·5—4, only radical (1) detectable; pH 1·6 and increase in peroxide and glycol concentration by a factor of 3, (2) : (4) = <1 : 10.

(b) *Other* 1,2-*diols*. Oxidation of propane-1,2-diol at pH 1 gave three radicals. Two were identified by their spectra as the species (7) and (8),[2] and the spectrum of the third was consistent with its ascription to the radical (9); thus, the g-factor (2·0043) indicates that it is a carbonyl-conjugated radical,[9] a large quartet splitting (2·15 mT) is compatible with a β-methyl group, and the large (1·81 mT) and small (0·20 mT) doublet splittings are reasonable for the α- and the aldehydic [2] proton, respectively. The concentrations of the radicals (7), (8), and (9) were in the ratio 1 : 12 : 3.



$\dot{C}H_2{-}CH(OH){-}CH_2OH$

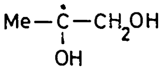
(7)

$\dot{C}H_2{-}CO{-}Me$

(8)

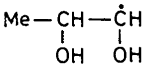
$Me{-}\dot{C}H{-}CHO$

(9)



$Me{-}\dot{C}(OH){-}CH_2OH$

(10)



$Me{-}CH(OH){-}\dot{C}H(OH)$

(11)

As the pH was raised, the spectrum of the radical (8) decreased in intensity and, by pH 4·6, disappeared, while those of two new radicals appeared. Of these, one had a large quartet splitting (2·10 mT) compatible with the presence of a β-methyl group, a g-factor (2·0031) in the range of those of hydroxy-conjugated radicals,[9] and a triplet splitting (0·915 mT) reasonable [1] for a CH_2OH group attached to the tervalent carbon atom; it is

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[11] J. K. Kochi, P. J. Krusic, and D. R. Eaton, *J. Amer. Chem. Soc.*, 1969, **91**, 1877.

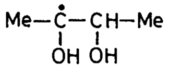
[12] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2147.

assigned the structure (10). The other radical had the same g-factor, indicating hydroxy-conjugation, a very small quintet (0·06 mT) compatible with the presence of a γ-methyl group and a hydroxy-group which have fortuitously equal splittings, and two doublet splittings (1·715 and 1·235 mT); it is assigned the structure (11), the larger doublet splitting being ascribed to the α-proton on the basis that a similar value would be expected to that for the radical (1), and the smaller to the β-proton. The relative concentrations of the radicals (7), (9), (10), and (11) at pH 4·6 were 2 : 1 : 6 : 10.

Oxidation of butane-2,3-diol at pH 6·2 gave the radical[2] (12) and a species assigned the structure (13) on the basis of its g-factor (2·0031) (consistent with hydroxy-conjugation) and quartet splitting (2·06 mT) (consistent with a β-methyl group); the doublet splitting (0·85 mT) is attributed to the single β-proton. At pH 1 only the former radical was observed.

$Me{-}CO{-}\dot{C}H{-}Me$

(12)



$Me{-}\dot{C}(OH){-}CH(OH){-}Me$

(13)

(c) 2-*Chloroethanol*. Oxidation at pH 2 gave a mixture of three radicals identified by their spectra as (2), (4), and $\cdot CHCl\cdot CH_2OH$, the spectrum of the last being identical with one we obtained by addition of the hydroxyl radical to vinyl chloride (*cf*. a previous report of this radical which gave significantly different splitting constants [13]); the relative concentrations of the radicals (2) and (4) were approximately the same as when the species were generated from ethylene glycol at this pH, but the spectrum of the radical $\cdot CHCl\cdot CH_2OH$ was very weak and its concentration could not have been more than 10% of that of (2). In the pH range 3·6—4·2, the radicals (2) and (4) were not detected; the spectrum of the radical $\cdot CHCl\cdot CH_2OH$ was accompanied by a weak spectrum of the radical (1) and a stronger one which consisted of a triplet (a_H 2·26 mT) of doublets (a_H 1·87 mT), g 2·0025. The g-factor of this species is that of a hydrocarbon-like radical [9] and shows that there is no hydroxy-group at the tervalent carbon; this and the splitting constants are best accommodated by the structure (14) [*cf*. the radical $\cdot CH_2\cdot CH(OH)(OMe)$, for which $g = 2{\cdot}0025$, $a(\alpha\text{-H}) = 2{\cdot}24$, $a(\beta\text{-H}) = 1{\cdot}89$ mT [6]]. The radical $\cdot CH(OH)\cdot CH_2Cl$ was not detectable.

$\dot{C}H_2{-}CH(OH)_2$

(14)

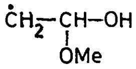
(d) 2-*Bromoethanol*. Oxidation at pH 2 gave the radicals (2) and (4) in the same proportions as from 2-chloroethanol, but there was no trace of a spectrum which could be ascribed to the radical $\cdot CHBr\cdot CH_2OH$.

(e) 2-*Iodoethanol*. No organic radicals could be detected spectroscopically when 2-iodoethanol was oxidised at pH 2 or pH 4; under the former conditions the two singlets derived from titanium(IV)–peroxide complexes [14] were observed.

(f) 2-*Chloroethyl methyl ether*. Oxidation at pH 5·6 gave three radicals. Two were identified by their splitting constants and g-factors as the species (15) and (16), and the third had a g-factor (2·0032) compatible with an oxygen-conjugated species [9] and two triplet splittings (1·71 and 0·18 mT) in the ranges expected for the α- and γ-protons, respectively, in the species (17), to which the spectrum is assigned. The relative concentrations of the species (15), (16), and (17) were 4 : 1 : 1·6. At pH 1, the three radicals were still present, but in relative concentrations 1 : 1 : 1·5.

$MeO{-}\dot{C}H{-}CH_2OH$

(15)



$\dot{C}H_2{-}CH(OMe){-}OH$

(16)

$\dot{C}H_2{-}O{-}CH_2CH_2Cl$

(17)

(g) 2-*Methoxyethyl acetate*. Oxidation at pH 5·2 gave two radicals the g-factors of which (2·0030 and 2·0032) indicated oxygen-conjugation.[9] The former radical had a doublet splitting (1·76 mT) and a quartet splitting (0·20 mT) in the regions expected for the α- and methoxy-protons, respectively, in the radical (18), for which a splitting of 0·80 mT for the methylene-protons is reasonable. The other radical had two triplet splittings (1·70 and 0·20 mT) in the regions expected, respectively, for the α- and γ-protons in the species (19) and is assigned as such. The two radicals were present in relative concentrations 1·3 : 1.

When the pH was reduced to 1, the spectrum of the species (18) was reduced in intensity and that of the radical (16) appeared; the relative concentrations of the radicals were (16) : (18) : (19) = 0·2 : 0·9 : 1. [As we shall see later, the radical (15) would also be expected under these conditions; however, a small concentration would have escaped detection since its spectrum would be hidden beneath that of the species (18), which has closely similar e.s.r. parameters.]

$MeO{-}\dot{C}H{-}CH_2OAc$

(18)

$\dot{C}H_2{-}O{-}CH_2CH_2OAc$

(19)

(h) *Ethanolamine and related compounds*. Oxidation of ethanolamine at pH 1 gave the spectrum recorded before [15] and ascribed to the radical (20a) except that a small doublet splitting (0·12 mT), attributable to the hydroxyl proton, was now resolved. The mono- and di-N-methylated derivatives behaved similarly; assignment of the spectra (Table 2) to the radicals (20b) and (20c), respectively, is based on comparison with the data for (20a), although a notable difference is that the small quartet (0·10 mT) and triplet (0·14 mT) splittings indicate observable interaction with the N–H, as well as the O–H, protons in (20b) and (20c), respectively, whereas none

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[13] W. E. Griffiths, G. F. Longster, J. Myatt, and P. F. Todd, *J. Chem. Soc.* (*B*), 1967, 530.

[14] H. Fischer, *Ber. Bunsengesellschaft Phys. Chem.*, 1967, **71**, 685.

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

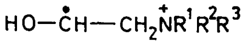
was detected in (20a). The quaternary ion $HOCH_2$-$CH_2NMe_3^+$ gave two radicals. One is assigned the structure (20d) on the basis of its *g*-factor (2·0031) and splitting constants and comparison with the data for the species (20a, b, c); the small doublet splitting of 0·16 mT is attributed to the hydroxy-proton, and in accord with this the splitting was removed when oxidation was conducted in deuterium oxide. The spectrum of the second radical (*g* 2·0038) could be analysed in terms of a nitrogen splitting (2·03 mT) and interaction with nine equivalent protons (2·86 mT), although the two wing lines (the intensity of which would be less than 1% that of the central lines) could not be discerned with certainty, nor could the appropriate intensity distribution be fully confirmed. This spectrum could be assigned to the radical cation $Me_3N^{\cdot+}$, but the possibility that it was that of the species $Me_2NH^{\cdot+}$ could not be excluded. Thus, the spectrum of the latter species, which has been well characterised[16] [a_N 2·053, a(α-H) 2·828, a(Me) 2·856 mT, and the appropriate second-order splittings], could appear closely similar to ours if less well resolved; moreover, this species has recently been obtained by electron bombardment of aqueous trimethylamine at pH 1 when the species $Me_3N^{\cdot+}$ might have been expected. To distinguish between these possibilities, oxidation was carried out in deuterium oxide; the spectrum remained unchanged [although that of the accompanying radical (20d) lost its smaller doublet splitting; see earlier], so that, since the species $Me_2NH^{\cdot+}$ would be expected to undergo rapid exchange, we infer that the spectrum is that of $Me_3N^{\cdot+}$. Two further pieces of evidence can be quoted in support of this assignment. First, the spectrum was satisfactorily simulated by the splittings given above and a line-width of 0·05 mT. Secondly, oxidation of the quaternary ion $HOCH_2{\cdot}CH_2NEt_3^+$ gave the related species $Et_3N^{\cdot+}$. In this case, this was the only radical detected and its identification from the spectrum (Figure) is unambiguous; the simulation shown in the Figure is based on $a_N(1)$ 2·02, $a_H(6)$ 2·21 mT, the latter splitting being attributed to the six methylene protons. It is notable that this splitting is smaller than for the methyl-protons in the species $Me_3N^{\cdot+}$ (2·86 mT), indicating a preference in the former case for conformations in which $<\cos^2\theta>$ is less than $\frac{1}{2}$ (*cf.* radical cations from aminoethylenes[17] and other nitrogen-containing radicals[18]).

TABLE 2

Hyperfine splitting constants (mT) and *g*-factors for radicals derived from ethanolamine and related compounds

Parent compound	Radical	a(α-H)	a(β-H)	a(N)	a(other)	g
$CH_2OH{\cdot}CH_2NH_3^+$	$\cdot CH(OH){\cdot}CH_2NH_3^+$	1·79	1·17	1·04	0·12 (1H)	2·0031
$CH_2OH{\cdot}CH_2NH_2Me^+$	$\cdot CH(OH){\cdot}CH_2NH_2Me^+$	1·855	1·10	1·10	0·10 (3H)	2·0032
$CH_2OH{\cdot}CH_2NHMe_2^+$	$\cdot CH(OH){\cdot}CH_2NHMe_2^+$	1·90	0·99	1·19	0·14 (2H)	2·0033
$CH_2OH{\cdot}CH_2NMe_3^+$	$\cdot CH(OH){\cdot}CH_2NMe_3^+$	1·94	0·85	1·36	0·16 (1H)	2·0031
	$Me_3N{\cdot}^+$		2·86	2·03		2·0038
$CH_2OH{\cdot}CH_2NEt_3^+$	$Et_3N{\cdot}^+$		2·21	2·02		2·0035

FIGURE Central portion of the spectrum of the radical cation $Et_3N{\cdot}^+$ (a) observed, (b) simulated. [The extra large peak in (a) is from a titanium(IV)–peroxide complex.]


$HO-\dot{C}H-CH_2\overset{+}{N}R^1R^2R^3$

(20)

	R^1	R^2	R^3
a;	H	H	H
b;	H	H	Me
c;	H	Me	Me
d;	Me	Me	Me

The hyperfine splittings of the radicals (20a—d) display well-defined trends; as the extent of methylation is increased, a(N) and a(α-H) increase whereas a(β-H) decreases. Now, it has previously been pointed out that radicals of the type $\cdot CHY{\cdot}CH_2X$ in which Y is a hydroxy- or alkoxy-group and X is an electronegative substituent such as OH, OAc, or NH_3^+ have unusually low β-proton splittings. It has been argued that this is the result of a stabilising interaction represented for the radical (21) by the contribution of the canonical structures (22) and (23). This interaction is maximal for the conformation (24) in which the C–N bond eclipses the half-filled carbon *p*-orbital, so that this conformation tends to be heavily populated and the average value of θ (the dihedral angle for the β-C–H bonds and the half-filled orbital) approaches 60°. Since a(β-H) rises with $\cos^2\theta$, this in itself leads to lower β-proton splittings than for the radicals $\cdot CHY{\cdot}Me$ for which $<\cos^2\theta> = \frac{1}{2}$, but additionally it is likely that a(β-H) is lowered further because the interaction referred to results in deformation of the geometry at the β-carbon atom from tetrahedral towards coplanar as far as the bonds to the hydrogen and α-carbon atoms are concerned, so that the β-protons are even less well sited for the hyperconjugative inter-

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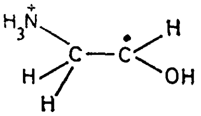
[16] P. Neta and R. W. Fessenden, *J. Phys. Chem.*, 1971, **75**, 738.

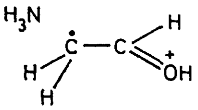
[17] B. C. Gilbert, R. H. Schlossel, and W. M. Gulick, jun., *J. Amer. Chem. Soc.*, 1970, **92**, 2974.

[18] D. H. Geske, *Prog. Phys. Org. Chem.*, 1967, **4**, 179.

action on which a(β-H) (largely) depends. Finally, there is evidence that radicals of this type are more nearly coplanar (less 'bent') at the tervalent carbon atom than those in which the β-substituent is absent.[1] In the light of these ideas, the trends noted in the hyperfine splitting constants for the radicals (20a—d) can be rationalised as follows. As methyl groups are successively introduced, the interaction we have referred to becomes more powerful; that is, the contributions of structures such as (22) and (23) are increased by replacing NH by NMe. Consequently, conformations of the type (24) become increasingly heavily populated so that a(β-H) falls; at the same time, the degree of bending at the α-carbon atom decreases, so that[10] a(α-H) rises, and it is notable that its value for the radical (20d) (1·94 mT) is somewhat closer to that for the (planar) ethyl radical (2·24 mT) than to that for the (bent) species ·CHMe·OH (1·50 mT). Finally, the increase in a_N is consistent with the view that, as with a β-proton, the main interaction with a β-quaternary nitrogen is of the hyperconjugative type.



(21)



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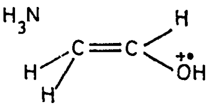
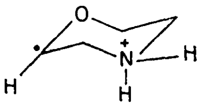
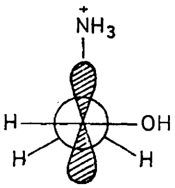


(23)

We examined this interpretation further by studying the oxidation of morpholine. Only one radical was detected, and its assignment as (25) is consistent with



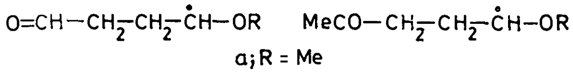
(25)



(24)

its g-factor (2·0031) as well as with expectation, since the quaternary nitrogen atom should strongly retard the formation of its isomer. The spectrum showed a large doublet splitting (4·40 mT) which we interpret as equal to the sum of the splittings for the axial and equatorial β-protons, with interconversion of the two chair conformations occurring at a rate comparable with the difference between these splittings such that the central line of the expected triplet is broadened beyond detection (*cf.* the analogous radical from 1,4-dioxan[19]); a smaller doublet splitting (1·85 mT), attributable to the α-proton; a splitting from nitrogen (0·40 mT); and a small triplet (0·11 mT) which could be caused either by the NH protons or the protons of the methylene group adjacent to oxygen. The salient point of difference between this radical and those of the type (20) is that the former is prevented from adopting a conformation in which the β-C–N bond eclipses the half-filled p-orbital and has a far smaller nitrogen splitting.

E.s.r. Spectra of Radicals trapped by Vinyl Ethers.—When ethylene glycol was oxidised in the presence of methyl vinyl ether at pH 1, only very weak resonances from the radical (2) could be detected; the main spectrum (g 2·0032) consisted of a doublet splitting (1·42 mT), a triplet (1·96 mT), and two quartets (0·145 and 0·055 mT). The g-factor is in the range expected for an oxygen-conjugated radical, and the doublet and the larger quartet splitting are in the ranges expected for the α- and methoxy-protons, respectively, in the radical (26a), to which the spectrum is assigned; the triplet splitting is attributed to the β-methylene protons and the smaller quartet to the γ-methylene and the aldehydic δ-protons which are fortuitously equivalent.



$O{=}CH{-}CH_2{-}CH_2{-}\dot{C}H{-}OR$ (26)

$MeCO{-}CH_2{-}CH_2{-}\dot{C}H{-}OR$ (27)

a; R = Me
b; R = Et

When ethyl vinyl ether was used in place of methyl vinyl ether, only one radical was detected; it is assigned the structure (26b) and the splittings are attributed as in Table 3, each on the basis of arguments analogous to those for the radical (26a). When the experiment was repeated at pH 2, the spectrum of the radical (4) accompanied that of the adduct (26b); the relative concentrations of the species were 1 : 2·5. When the experiment was repeated at pH 4, the spectrum of the radical (1) was observed and there was no sign of an adduct formed by its addition to the vinyl ether.

When propane-1,2-diol was oxidised in the presence of methyl or ethyl vinyl ether at pH 1, the main spectra were of the radicals (7)—(9) and the adducts formed by the ether with the hydroxyl radical,[6] but there were weak resonances which are attributed, following the arguments for the radical (26a), to the species (27a, b). These radicals were also detected in low concentration when acetone was oxidised in place of the diol, being accompanied in this case by radical (8) and the appropriate adduct of the ether and the hydroxyl radical.

Mechanisms of Reaction.—(a) 1,2-*Diols*. The results are consistent with the view[2] that the initially formed radical undergoes acid-catalysed elimination of water, as represented for the case of ethylene glycol by reaction (i). In addition, two further aspects of the reaction have been revealed.

First the radicals from the three diols we have studied differ significantly in the ease with which they undergo the elimination. Thus, the radical (9) from propane-1,2-diol is present in detectable concentrations at pH 4·6 whereas its isomer (8) is only observed when the pH is reduced further; the radical (2) from ethylene glycol is only observed at pH $\leqslant$ *ca.* 2; and the radical (12) from butane-2,3-diol is observed even at pH 6·2. It is probable that the species (9) and (12) are formed more readily from their precursors than are (2) and (8) (*i.e.*

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[19] W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 1964, 4850.

are less dependent for their formation on acid catalysis) because of the stabilising influence conferred upon the transition states leading to them by the methyl group which is conjugated with the (developing) tervalent carbon atom.

Secondly, the formation of the radical (4) has to be accounted for. The most likely pathway is reaction of the radical $\cdot CH_2\cdot CHO$ with the enolic tautomer (29) of acetaldehyde; the feasibility of this reaction is indicated by the readiness with which the radical $\cdot CH_2\cdot CHO$ reacts with the structurally similar vinyl ethers (this point is considered further later), and the enol (29) could well be the initial product of the reaction [4] between the radical $\cdot CH_2\cdot CHO$ and ethylene glycol, its tautomerism yielding acetaldehyde (see above).

TABLE 3

Hyperfine splitting constants (mT) for radicals, $\cdot CH(OR^2)\cdot CH_2CH_2COR^1$, derived from vinyl ethers ($g = 2{\cdot}0032$ in each case)

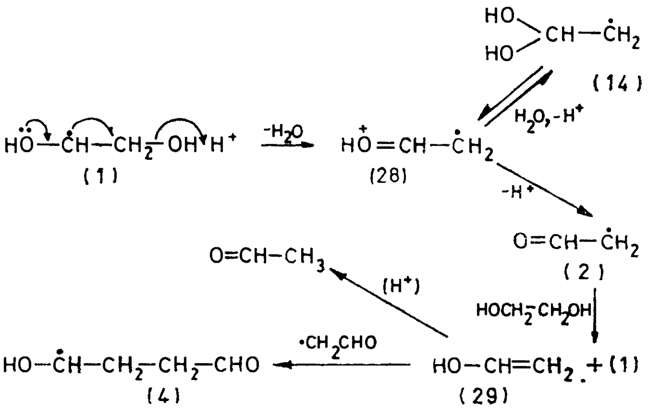
Radical	$a(\alpha\text{-H})$	$a(\beta\text{-H})$	$a(\gamma\text{-H})$	$a(R^1)$	$a(R^2)$
$\cdot CH(OMe)\cdot CH_2CH_2CHO$	1·42	1·96	0·055	0·055 (1H)	0·145 (3H)
$\cdot CH(OEt)\cdot CH_2CH_2CHO$	1·44	1·94	0·050	0·050 (1H)	0·14 (2H)
$\cdot CH(OMe)\cdot CH_2CH_2COMe$	1·40	1·91 [a]	0·060		0·15 (3H)
$\cdot CH(OEt)\cdot CH_2CH_2COMe$	1·40	1·91 [a]	0·055		0·14 (2H)

[a] ±0·05 mT.

The increase in the relative concentrations of the radicals (2) and (4) which occurs when the pH is reduced from 2 (ratio 1 : 3) to 1 (>5 : 1), under otherwise identical conditions, is in accord with this interpretation; thus, at the lower pH the enol (29) will be removed more rapidly by acid-catalysed tautomerism, reducing the probability of its trapping the radical (2) to give (4). It is also in accord with the interpretation that, at an intermediate pH (1·6) but with higher concentrations of reagents, the ratio of the observed concentrations of (2) and (4) should be relatively low (<1 : 10), since the higher concentration of the glycol will promote the likelihood of the reaction giving the enol (29) and thence the radical (4).

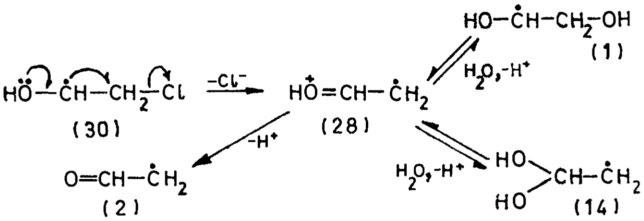
Our suggested mechanism is summarised in Scheme 1. The intervention of the species (28) is not certain [that is, the conversion (1) ⟶ (2) may be a one-step process]; the species is included in the Scheme because the reactions of 2-chloroethyl methyl ether indicate the mediation of the analogous species (32) (see later). Likewise, although it is not certain that the radical (14) is present, the possibility is suggested by the behaviour of 2-chloroethanol described below.

Finally, it is noteworthy that, despite the fact that we should not expect the concentration of the enol (29) to reach a significant fraction of that (0·1M) of the ethyl vinyl ether used in the trapping experiments, the observed concentration of the radical (4) at pH 2 was comparable with that of the adduct (26b) with the vinyl ether. A possible, although seemingly unlikely, explanation is that the formation of the radical (4) involves, at least in part, a cage reaction; that is, the reaction of the radical (2) with ethylene glycol to give the radical (1) and the enol (29) is followed, before diffusion from the solvent cage, by the acid-catalysed conversion of the radical (1) into (2) and union of the latter with the enol. One alternative possibility is that the radical $\cdot CH_2\cdot CHO$ is particularly selective and reacts much faster with the enol than with the vinyl ether. This could in turn reflect the importance of polar factors in determining the stability of the transition states, $\cdot CH_2\cdot CHO$ being an electrophilic radical and the enol being a stronger donor than the vinyl ether. In this context, it is notable that vinyl ethers are themselves strongly selective amongst radicals of differing polar characteristics; thus, under the conditions we have used, ethyl vinyl ether reacts readily with the electrophilic radical $\cdot CH_2\cdot CHO$ (the spectrum of which is fully quenched in the presence of the ether), less readily with $\cdot CH_2\cdot COMe$ (a residual signal from which accompanies that of the corresponding adduct with the ether), and not to a detectable extent with the species $\cdot CH_2\cdot CH(OH)\text{-}CH_2OH$ or the nucleophilic radical $\cdot CH(OH)\cdot CH_2OH$. It fails also to react readily with the radical $\cdot CHMe\cdot CHO$, but this could be for steric reasons.



SCHEME 1

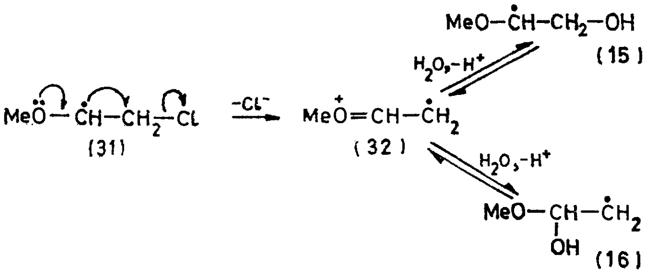
(b) 2-*Chloroethanol*. Two radicals would be expected, initially, from the oxidation of 2-chloroethanol. One, $\cdot CHCl\cdot CH_2OH$, is observed directly even at pH 2; the acid-catalysed loss of hydroxide ion is evidently not as ready as from the radical (1), no doubt because of the weaker $+M$ effect of a chloro- as compared with a hydroxy-substituent. The other, (30), is not observed even at lower acidities (pH 3·6—4·2). However, we should expect the radical (30) to be formed readily, more so indeed than its isomer $\cdot CHCl\cdot CH_2OH$ (*cf.* the strong activating effect of a hydroxy-substituent towards abstraction from adjacent C–H by the electrophilic hydroxyl radical), and the observations are satisfactorily accounted for by the hypothesis that it is both formed readily and reacts readily, by loss of chloride ion, as in Scheme 2. The remaining steps suggested in this Scheme are justified as follows. First, mediation of the radical cation (28) can account for the observation, at pH 3·6—4·2, of the radicals (1) and (14) by reaction with water; these reactions are analogous to those suggested to account for the formation of the species $\cdot$CH(OMe)-CH$_2$OH and $\cdot$CH$_2\cdot$CH(OH)(OMe) from methyl vinyl ether and the hydroxyl radical, by way of the radical cation (32) (see further later). Secondly, the formation of the radical (2) [and thence the radical (4), as in Scheme 1] requires only the reasonable supposition that not only can the species (1) give (2) by acid-catalysed elimination but so also can the 1,1-diol-containing radical (14), *via* reversal of the reaction leading to its formation. In summary, the salient differences between the behaviour of the radicals (1) and (30) are, first, that chloride-ion loss from the latter occurs more readily than hydroxide-ion loss from the former and, secondly, that radical (14) is not detected during oxidation of the glycol but is during that of the chloro-compound because, at the acidity required for generation of its precursor (28) at a significant rate in the former system, species (14) is reconverted too rapidly into (28), and thence into (2), for it to reach detectable concentration.



Scheme 2

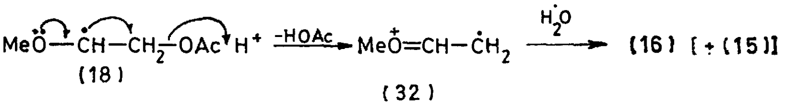
2-Bromoethanol behaves in the same way as 2-chloroethanol in giving the radicals (2) and (4), presumably by way of the species $\cdot$CH(OH)$\cdot$CH$_2$Br. However, 2-iodoethanol appears to behave differently. Despite the facts that the abstraction, by hydroxyl, of a hydrogen atom from the hydroxymethyl group in this compound should be easier than from that in (protonated) ethanolamine and that iodide is a better leaving group than chloride or bromide ion, neither the radical $\cdot$CH(OH)-CH$_2$I nor the products from heterolytic elimination of iodide ion could be observed. We tentatively suggest that the radical $\cdot$CH(OH)$\cdot$CH$_2$I is indeed formed but rapidly loses an iodine *atom*, a reaction which (because of the relatively weak C–I bond strength) should occur more readily than the corresponding processes for the bromo- or chloro-containing radicals. We should not necessarily expect to detect the resulting iodine atom in solution by e.s.r. spectroscopy.[20]

(c) 2-*Chloroethyl methyl ether*. As expected, the radical (17) was observed at pH 1 as well as in the less acidic medium. Its isomer (31), which we should expect to be formed approximately as readily, was not detected, but the presence of the radicals (15) and (16) is consistent with the mediation of the radical (31) and its ready loss of chloride ion to give the radical cation (32), from which (15) and (16) can both be derived by reaction with water (Scheme 3). The intervention of the radical cation (32) has previously been suggested to account for the acid-catalysed isomerisation of the radicals (15) and (16) when the former is derived from methyl vinyl ether and the hydroxyl radical;[6] moreover, our finding that there is a relatively higher concentration of the latter radical in the more acidic of the media we have used is consistent with the previous evidence that not only is the isomerisation acid-catalysed but also the radical (16) is the more stable.



Scheme 3

(d) 2-*Methoxyethyl acetate*. Only two radicals, (18) and (19), were observed of the four which could in principle be formed by abstraction from C–H, but this is reasonably in accord with the view that the ether-oxygen should activate the two adjacent C–H bonds to abstraction. As expected, the radical (19) was observed in the strongly acidic medium (pH 1). The decrease in relative concentrations of the species (18) and (19) on reduction of the pH from 5·2 to 1, together with the appearance of the species (16), provides evidence for the acid-catalysed loss of acetate ion from (18) and reaction of the resulting radical cation (32) with water, but the elimination occurs less readily than that from the radical (1) at the same pH. [Radical (15) would also be expected, but could escape detection; see earlier.]



(iii)

(e) *Ethanolamine and related compounds*. The abstraction of hydrogen at pH 1 apparently exclusively from the hydroxy-substituted carbon atom in ethanolamine, its *N*-methyl and *NN*-dimethyl derivatives, and the choline cation is in accord with the electrophilic character of the hydroxyl radical. However, there is no

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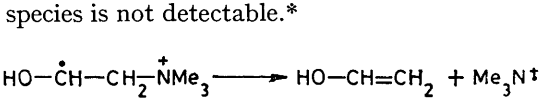
[20] P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, 1967, p. 96.

evidence for fragmentation of the resulting radicals (20) into the radical $\cdot CH_2\cdot CHO$ and an amine, and this is perhaps surprising in the light of the ready fragmentation of the chloro- and hydroxy-substituted analogues. In contrast, with the radical (20d) from the choline cation it would appear that an alternative type of fragmentation occurs, as in reaction (iv); if so, we should infer that the triethyl analogue of choline also gives a radical of the type (20) but in this case fragmentation to give the radical cation $Et_3N^{\cdot +}$ occurs so much more readily that the former species is not detectable.*



$$\mathrm{HO{-}\dot{C}H{-}CH_2{-}\overset{+}{N}Me_3 \longrightarrow HO{-}CH{=}CH_2 + Me_3N^{\cdot +}} \qquad (iv)$$

Finally, evidence has recently been presented that the homolytic fragmentation of a radical has a stereoelectronic requirement involving maximal overlap between the half-filled orbital in the reactant and the bond to be broken.[21] It is perhaps relevant that the radicals which we have found to undergo fragmentation, either heterolytically or homolytically, exist preferentially in a conformation of this type.

EXPERIMENTAL

Varian V4502 and E-3 spectrometers, each with 100 kHz modulation, were employed. Hyperfine splittings were measured to within ±0·01 mT (except where stated) both directly and by comparison with an aqueous solution of Fremy's salt (a_N 1·30 mT) [22] which was also used for g-factor determinations (g 2·0055).[22] Spectrum simulation, with a programme kindly supplied by Dr M. F. Chiu, was used to confirm the splitting constants and to determine relative concentrations of radicals. pH measurements were made to within ±0·1 unit with an Electronic Instruments model 23A pH meter and a phthalate buffer as standard. All materials were commercial samples or were obtained by standard methods.

Two types of mixing chamber were employed, with flow rates of 100 ml/min for each reactant stream. The majority of the reactions were carried out with a two-entry mixing cell based on the Varian design; one stream contained 0·02M-titanium(III) chloride and the diol (0·5M) and the second contained 0·033M-hydrogen peroxide. For experiments at pH <2, the required amount of concentrated sulphuric acid was added to the first stream; for experiments at higher pH, disodium ethylenediaminetetra-acetate (6 g/l) was added to the titanium(III) solution and the pH was adjusted with ammonia (*d* 0·880). When halogenohydrins were oxidised, they were added to the peroxide stream (0·5M). For the experiments with enol ethers, a three-entry single-stage mixing chamber [23] was used; one stream contained 0·02M-titanium(II) chloride and the substrate (0·5M), the second contained 0·033M-hydrogen peroxide, and the third contained a 0·1M solution of the enol ether. The pH was adjusted to 1·0 by adding concentrated sulphuric acid to the titanium(III)-containing solution.

For the experiments involving deuterium oxide (99·7% D, Ryvan Chemical Co., Ltd.) a special small-scale apparatus was designed with integral glass mixing chamber and sample cell. For the experiment with 2-hydroxyethyltrimethylammonium chloride one stream contained 0·2M-titanium(III) chloride in D_2O (100 ml) and the other contained 0·33M-hydrogen peroxide in D_2O (100 ml); each was saturated with quaternary salt. The effluents of the experiment were collected and a mixture of D_2O and water was distilled out *in vacuo* and employed for the experiment with ethylene glycol. Concentrations were exactly the same as for the experiment with the quaternary salt except that glycol was present as a 5M-solution in each side.

The award of an I.C.I. Fellowship to one of us (J. P. L.) is gratefully acknowledged.

[1/2103 *Received*, 10*th November*, 1971]

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* The possibility that the radical cations arise by heterolysis of the first-formed radicals followed by one-electron oxidation was discounted by our finding that neither trimethyl- nor triethyl-ammonium chloride gave a detectable spectrum under conditions in which the choline cation and its triethyl analogue were oxidised.

[21] A. L. J. Beckwith and G. Phillipou, *Chem. Comm.*, 1971, 658.

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

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