572. Electron Spin Resonance Studies of Oxidation. Part I. Alcohols.

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When acidic solutions of titanous ion and hydrogen peroxide react immediately before passing through the cavity of an electron spin resonance spectrometer, a singlet is observed in the spectrum which is attributed to the hydroxyl radical. The addition of alcohols to the reactants results in the replacement of this signal by the spectra of organic radicals formed by abstraction of a hydrogen atom from a C–H bond or (in one case) by addition to C=C. Analysis of the spectra gives evidence about the structures of the radicals and hence about the course of the reaction.

Coupling constants for protons in different environments are reported and discussed.

FREE radicals produced by the abstraction of a hydrogen atom from alcohols have been extensively studied by electron spin resonance spectroscopy.[1,2] The technique which has been used consists of freezing a mixture of hydrogen peroxide and the alcohol, transferring the resulting glass to the cavity of an electron spin resonance spectrometer, and then observing the signals produced on ultraviolet irradiation. Hydroxyl radicals are produced initially and these diffuse and react with the alcohols.

From the point of view of studying the hyperfine structure of the spectra this solid-state method suffers from the disadvantage that the individual lines are considerably broadened by anisotropic coupling and complete resolution is not always obtained. Irradiation of solutions does not provide a practicable method for studying the radicals because they are generated comparatively slowly and are usually too short-lived to reach a steady concentration large enough for observation. We therefore investigated the possibility of generating radicals by a fast reaction, using a flow system in which the radicals could be observed less than 0·02 second after the reactants had been mixed.

We first studied in this way the reduction of hydrogen peroxide by transition-metal ions, which is reported to give hydroxyl radicals.[3] When ferrous ion reacted with hydrogen peroxide only a spectrum of six peaks, ~100 gauss apart, due to manganous ion impurity, was observed, and this signal could have masked one due to the hydroxyl radical. When, however, titanous ion, which did not give a detectable signal itself, reacted with hydrogen peroxide in acidic solution a sharp line of width 1 gauss was observed.*

The radicals likely to be present in this system are hydroxyl and perhydroxyl, produced by the reactions:

$$Ti^{3+} + H_2O_2 \longrightarrow Ti^{4+} + \cdot OH + OH^-$$

$$\cdot OH + H_2O_2 \longrightarrow H_2O + \cdot O_2H$$
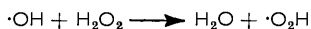
The spectrum of the perhydroxyl radical had been observed previously when hydrogen peroxide was oxidised by ceric ion, and consisted of a very broad singlet of width 27 gauss.[5] We repeated and confirmed this observation, and also examined the peroxyl radicals obtained by the oxidation by ceric ion of t-butyl and cumyl hydroperoxide, each of which gave a singlet.[4]

Spectra which have been ascribed to hydroxyl and perhydroxyl radicals have been

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* The stability and resolution of the spectrometer have been greatly improved since our preliminary result was reported.[4]

[1] Fujimoto and Ingram, *Trans. Faraday Soc.*, 1958, **54**, 1304.
[2] Symons and Townsend, *J.*, 1959, 263; Gibson, Symons, and Townsend, *J.*, 1959, 269; Symons, *J.*, 1959, 277.
[3] Uri, *Chem. Rev.*, 1952, **50**, 375.
[4] Dixon and Norman, *Nature*, 1962, **196**, 891.
[5] Saito and Bielski, *J. Amer. Chem. Soc.*, 1961, **83**, 4467.

observed in the solid state; both are doublets.[6] It is reasonable, however, that both spectra should be singlets in aqueous solution at room temperature because of the rapid exchange of the proton with the solvent. Coupling with a hydroxyl-proton in solution has been reported, but only in a very strongly acid medium.[7]

We therefore attribute the signal from titanous ion and hydrogen peroxide to the hydroxyl radical. In support of this assignment, titanous ion and t-butyl hydroperoxide gave a quartet $(1:3:3:1$; coupling constant 22 gauss) characteristic of the methyl radical.[8,9] This is consistent with the formation of the t-butoxyl radical which is known to break down to methyl: [10]

$$Ti^{3+} + Me_3C \cdot O_2H \longrightarrow Ti^{4+} + Me_3C \cdot O \cdot + OH^-$$

$$Me_3C \cdot O \cdot \longrightarrow \cdot CH_3 + Me_2CO$$
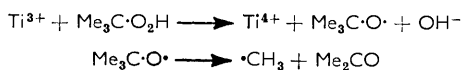
The amplitude of the signal from the reaction of hydrogen peroxide and titanous ion was examined as a function of the flow rate and the concentrations of the reactants. At constant concentrations the amplitude increased with increase in the flow rate, and the variations of log (amplitude) with log (concentration) at the maximum flow rate (about 5 ml. per second) are shown in Fig. 1. At low concentrations the slopes of both plots are unity, indicating that the radical concentration is proportional to $[Ti^{3+}]$ and to $[H_2O_2]$.

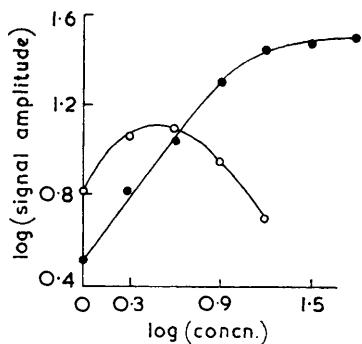Fig. 1. Variation of signal with reactant concentrations.

● H_2O_2; ○ Ti^{3+}.

Two further observations were made. First, when sulphuric or perchloric acid was used to acidify the reactants the signal was much larger than when hydrochloric acid was used, possibly because of complex-formation by chloride ion. Secondly, when ferrous ion was added to the titanous solution the amplitude of the signal decreased, but the singlet was still observable despite the presence of the spectrum due to manganous ion. Evidently the one-electron reduction of hydrogen peroxide by titanous ion proceeds more readily than that by ferrous ion, as previously suggested.[11]

Aliphatic Radicals.—When aliphatic alcohols were added to the reactants the signal ascribed to ·OH was replaced by spectra due to organic radicals. In the simpler cases these were readily analysed.

(a) *Monohydric alcohols.* Methanol gave a triplet, each of whose lines is apparently an incompletely resolved doublet (Fig. 2). This corresponds to the expected radical ·$CH_2 \cdot OH$ in which there is coupling with the two protons on carbon and possibly very weak coupling with the proton on oxygen.

t-Butyl alcohol gave a triplet of septets (Fig. 3) which is ascribed to ·$CH_2 \cdot C(CH_3)_2 \cdot OH$ formed by abstraction of a β-hydrogen atom. It should be noted that, although the

[6] Kroh, Green, and Spinks, *J. Amer. Chem. Soc.*, 1961, **83**, 2201.
[7] Bolton, Carrington, and dos Santos-Veiga, *Mol. Phys.*, 1962, **5**, 465.
[8] Gordy and McCormick, *J. Amer. Chem. Soc.*, 1956, **78**, 3243.
[9] Smaller and Matheson, *J. Chem. Phys.*, 1958, **28**, 1169.
[10] Walling, " Free Radicals in Solution," John Wiley and Sons, Inc., New York, 1957, p. 443.
[11] Cahill and Taube, *J. Amer. Chem. Soc.*, 1952, **74**, 2312.

FIG. 2. Spectrum from methanol.
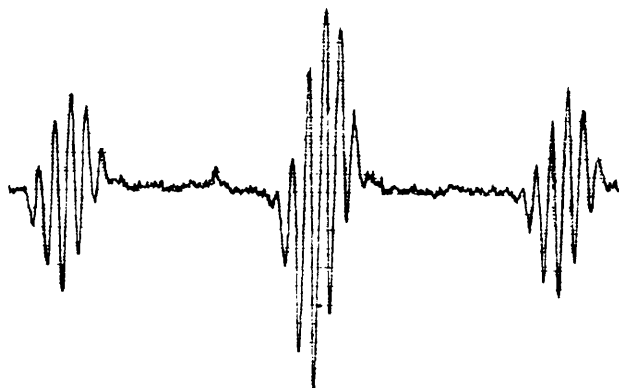

FIG. 4. Spectrum from ethanol.

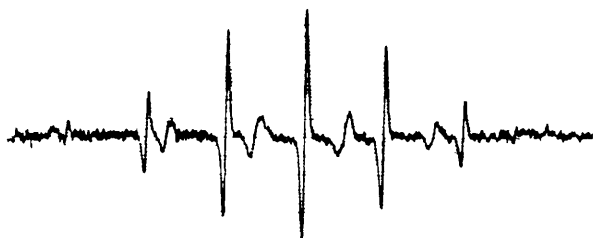FIG. 3. Spectrum from t-butyl alcohol.

FIG. 5. Spectrum from propan-2-ol.

FIG. 6. Spectrum from propane-1,3-diol.
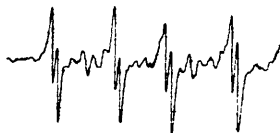
FIG. 7. Spectrum from propargyl alcohol.

FIG. 8. Spectrum from allyl alcohol.

stronger coupling is due to the protons on C_1, the six C_3-protons also give rise to significant splitting.*

Ethanol gave two quartets (Fig. 4), corresponding to $CH_3 \cdot CH(OH) \cdot$ in which the

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* The designations α, β, etc., refer to the position of the group concerned relative to that of the hydroxyl group, and C_1, C_2, etc., refer to the position relative to the carbon which bears the unpaired electron.

stronger coupling occurs with the three C_2-protons, and which is formed by abstraction of α-hydrogen.

Isopropanol (Fig. 5) gave a septet, expected for $(CH_3)_2C(OH)\cdot$ formed by abstraction of α-hydrogen, on which was superimposed a weak quartet. The latter is ascribed to $\cdot CH_2\cdot CH(OH)\cdot CH_3$, formed by abstraction of β-hydrogen, which is to be expected by analogy with the result for t-butyl alcohol. Two of the three hydrogen atoms which couple with the unpaired electron are in a different environment from the third, but it is shown later that the coupling constants of C_1- and C_2-protons are very similar when there is no hydroxyl group on C_1.

Aliphatic alcohols of more complex structure, such as propan-1-ol, butan-1-ol, and butan-2-ol, gave spectra of great complexity which corresponded to the presence of at least two radicals in each case. Isobutyl alcohol also gave a complex spectrum, but it contained four lines of equal intensity, rather more intense than the remainder, consistent with the presence of $(CH_3)_2CH\cdot CH(OH)\cdot$ in which (unequal) coupling occurs with the C_1- and C_2-protons.

(b) *Dihydric and polyhydric alcohols.* Propane-1,3-diol gave two triplets (Fig. 6), compatible with a radical $\cdot CH(OH)\cdot CH_2\cdot CH_2OH$. Pinacol gave a triplet, and pentaerythritol a doublet, corresponding to $\cdot CH_2\cdot CMe(OH)\cdot CMe_2\cdot OH$ and $\cdot CH(OH)\cdot C(CH_2\cdot OH)_3$, respectively.

The two αβ-diols, glycol and propane-1,2-diol, behaved differently: each gave a triplet, similar to that from methanol, superimposed on rather ill-defined lines. It is possible that the initially formed radicals undergo further reaction, including C–C bond cleavage, and that the observed radical in each case is $\cdot CH_2\cdot OH$, for formaldehyde is one of the products of the oxidation of glycol by Fenton's reagent.[12]

(c) *Unsaturated alcohols.* The two unsaturated alcohols examined behaved differently from each other. Propargyl alcohol gave four doublets (Fig. 7) (coupling constants: 18·5, 10·2, and 1·2 gauss), consistent with the resonance-stabilised radical $CH{\equiv}C\cdot CH(OH)\cdot$ ⟵⟶ $\cdot CH{=}C{=}CH\cdot OH$ in which the principal coupling occurs with the two protons on carbon and the smallest coupling arises from the proton on oxygen.

Allyl alcohol gave a spectrum consisting of a sextet on which was superimposed a weaker quartet (Fig. 8). Neither spectrum corresponds to the radical $\cdot CH(OH)\cdot CH{=}CH_2$ which would be formed by abstraction of hydrogen, but they are compatible with the products (I) and (II), respectively, of the addition of $\cdot OH$ to the double bond. The former contains

$$CH_2{-}\overset{\displaystyle\cdot}{C}H{-}CH_2 \qquad \cdot CH_2{-}CH{-}CH_2$$
$$\;\;|\qquad\quad\;\;| \qquad\qquad\;\;\;|\quad\;\;|$$
$$OH\qquad\quad OH \qquad\qquad OH\;\;OH$$
$$\text{(I)}\qquad\qquad\qquad\qquad\text{(II)}$$

five protons, and the latter three, which are expected (by analogy with the coupling constants for C_1- and C_2-protons in similar environments; see Table 1) to give the same coupling and hence a sextet and a quartet, respectively.

The greater concentration of radical (I) than (II) is in accordance with the finding that, in an olefin $CH_2{=}CHX$, the methylene group is normally more reactive than the substituted carbon atom towards free-radical addition.

(d) *Phenol and quinol.* Phenol gave the phenoxyl radical[13] (coupling constants: o-H 6·4; m-H 1·7; p-H 9·7 gauss), and quinol gave the semiquinone radical[7] (coupling constant 2·4 gauss). The effective abstraction of hydrogen from OH rather than from CH is here favoured by the resonance stabilisation in the radicals formed.

Coupling Constants.—The coupling constants obtained for the radicals formed by abstraction of hydrogen are set out in Table 1. The probable error in the data is 5%.

The coupling produced by a C_1-proton is influenced by the environment, as is apparent from examination of the data in Table 2.

[12] Merz and Waters, *J.*, 1949, S 15.
[13] Stone and Waters, *Proc. Chem. Soc.*, 1962, 253.

TABLE 1.

Coupling constants of radicals.

		Coupling constants (gauss)		
Alcohol	Type of spectrum	C_1–H	C_2–H	C_3–H
$CH_3 \cdot OH$	Triplet (1 : 2 : 1)	17·2		
$CH_3 \cdot CH_2 \cdot OH$	Two (1 : 1) quartets (1 : 3 : 3 : 1)	15·0	22·0	
$(CH_3)_2CH \cdot OH$	Septet (1 : 6 : 15 : 20 : 15 : 6 : 1)		20·0	
	and weak quartet (1 : 3 : 3 : 1)	22·0	22·0	
$(CH_3)_3C \cdot OH$	Three (1 : 2 : 1) septets (1 : 6 : 15 : 20 : 15 : 6 : 1)	21·3		1·3
$(CH_3)_2CH \cdot CH_2 \cdot OH$	Quartet (1 : 1 : 1 : 1)	12·7	20·0	
		20·0		
$(CH_2 \cdot OH)_2$	Triplet (1 : 2 : 1)	18·4		
$HO \cdot CH(CH_3) \cdot CH_2 \cdot OH$	Triplet (1 : 2 : 1)	(19·5) *		
$HO \cdot [CH_2]_3 \cdot OH$	Two (1 : 1) triplets (1 : 2 : 1)	16·0	19·0	
$[C(CH_3)_2 \cdot OH]_2$	Triplet (1 : 2 : 1)	22·4		
$C(CH_2 \cdot OH)_4$	Doublet (1 : 1)	16·3		
$CH_2 \colon CH \cdot CH_2 \cdot OH$	Sextet (1 : 5 : 10 : 10 : 5 : 1)	20·5	20·5	
	and quartet (1 : 3 : 3 : 1)	21·0	21·0	

* This result is approximate because the complexity of the spectrum made it difficult to determine the centres of the peaks.

TABLE 2.

Effects of substituents on the coupling constants of C_1-protons.

Proton environment	Substituents		Source	Coupling constant (gauss)
	R	R′		
$\cdot CHRR'$	H	$-CH(CH_3) \cdot OH$	$(CH_3)_2CH \cdot OH$	22·0
	H	$-C(CH_3)_2 \cdot OH$	$(CH_3)_3C \cdot OH$	21·3
	H	$-C(CH_3)(OH) \cdot C(CH_3)_2 \cdot OH$	$[C(CH_3)_2 \cdot OH]_2$	22·4
	H	$-CH(OH)-CH_2 \cdot OH$	$CH_2 \colon CH \cdot CH_2 \cdot OH$	21·0
	$-CH_2 \cdot OH$	$-CH_2 \cdot OH$	,,	20·5
$\cdot CHR \cdot OH$	H		$CH_3 \cdot OH$	17·2
	$-CH_3$		$CH_3 \cdot CH_2 \cdot OH$	15·0
	$-CH(CH_3)_2$		$(CH_3)_2CH \cdot CH_2 \cdot OH$	12·7
	$-CH_2 \cdot CH_2 \cdot OH$		$HO \cdot [CH_2]_3 \cdot OH$	16·0
	$-C(CH_2 \cdot OH)_3$		$C(CH_2 \cdot OH)_4$	16·3

Substitution of the hydroxyl group for hydrogen at the C_1-carbon appreciably reduces the coupling constant of the C_1-proton: the values of $\cdot CH_2 \cdot OH$ and $\cdot CH_3$ are 17·2 and 22 gauss, respectively. This may arise from reduction in the spin density on carbon due to the mesomeric effect of oxygen (*e.g.*, $\cdot CH_2 \cdot OH \longleftrightarrow {}^-CH_2 \cdot {}^+\overset{..}{O}H$).* The resulting stabilis-ation of the radical may underlie the greater ease of abstraction of hydrogen from α- than from β-carbon. Comparison of the coupling constants for the C_1-protons in methanol (17·2 gauss) and ethanol (15·0 gauss) shows that there is a small reduction when hydrogen is replaced by methyl.

The coupling constants of C_2-protons are hardly altered by the substitution of hydroxyl for hydrogen at the C_1-carbon; the small variations are probably within experimental error. Comparison of the coupling constants for the C_1-protons in pinacol and t-butyl alcohol with those of C_2-protons shows that the coupling of a C_2-proton is approximately equal to that of a C_1-proton when there is no hydroxyl group on the C_1-carbon. As discussed earlier, this supports the assignments made for the quartet from propan-2-ol and the sextet and quartet from allyl alcohol.

Conclusions.—The following conclusions are drawn:

(*a*) The hydroxyl radical abstracts a hydrogen atom from aliphatic alcohols, α-CH being rather more reactive than β-CH.

(*b*) Unsaturated alcohols may undergo either addition or abstraction, depending on their structure.

* We are indebted to a referee for this suggestion.

(*c*) The unpaired electron in the resulting radical is strongly coupled with both C_1- and C_2-protons, the extent of coupling being dependent on the nature of the adjacent groups.[2]

(*d*) Coupling with C_3-protons was observed in only one case, that of t-butyl alcohol. [This is unlikely to be exceptional, for we have also observed such coupling in the spectrum of $\cdot CH(CH_3) \cdot O \cdot CH_2 \cdot CH_3$, derived from ether.]

(*e*) Coupling with a proton on oxygen is normally too weak to be observed. There are indications of its occurrence in the spectrum from methanol, and that from propargyl alcohol has been interpreted in these terms.

EXPERIMENTAL

A Varian (100 kc. sec.$^{-1}$) V4500 electron spin resonance spectrometer was used. The flow system (Fig. 9) consisted of two concentric tubes carrying the reactant solutions, the inner one having four small holes at its end through which the inner solution was forced into the outer one, perpendicularly to the direction of flow. The dead-space was about 0·1 ml. and the maximum flow-rate was 5 ml. sec.$^{-1}$. In this way the reacting mixture entered the flattened section of an aqueous solution cell in the spectrometer within 0·02 sec. of mixing.
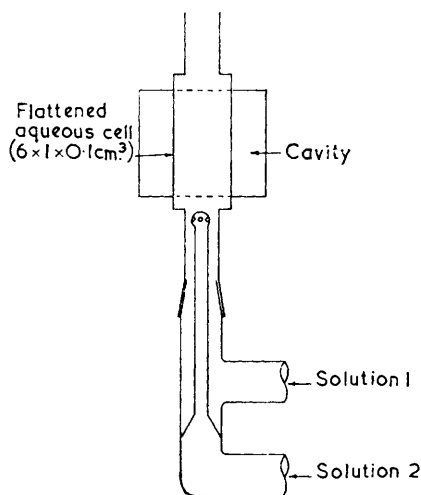

FIG. 9.   Flow system.

The spectrum of the hydroxyl radical was observed as follows. One reactant solution contained 15% titanous chloride solution (B.D.H; iron-free) (20 ml.) and concentrated sulphuric acid (14 ml.) in water (2 l.), and the second contained 100-vol. hydrogen peroxide (6 ml.) and concentrated sulphuric acid (14 ml.) in water (2 l.). The spectrum was scanned at least twice during the passage of 4 l. of solution through the cavity.

Organic radicals were observed by adding the appropriate alcohol to each of the reactants to make the solutions ∼m/10 with respect to the alcohol.

One experiment was carried out with a solution saturated with t-butyl hydroperoxide. In other experiments the concentration of either titanous chloride or hydrogen peroxide was varied while that of the other reactant was kept constant. The flow-rate could be reduced by means of an adjustable clip on the exit side of the cavity.

Experiments were also carried out with ceric sulphate (0·3 g./l.) in n-sulphuric acid as one reactant, and hydrogen peroxide (10 ml./l.; 100-vol.) and saturated solutions of t-butyl hydroperoxide and cumyl hydroperoxide, in n-sulphuric acid, successively, as the second reactant.

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