47. *Unstable Intermediates. Part II.*[1] *Photolysis of Hydrogen Peroxide in Solid Alcohols: Some Reactions of Hydroxyl Radicals.*

By J. F. Gibson, M. C. R. Symons, and M. G. Townsend.

When hydrogen peroxide, in dilute solution in alcohols at 77° K, is photolysed, characteristic changes in the visible and ultraviolet spectra are accompanied by intense electron-spin resonance signals containing marked hyperfine structure. Previous results [1, 2] have been extended by varying the irradiation conditions and the choice of solvent. In particular, the electron-spin resonance spectra recorded during the initial stages of photolysis and during warming-up are discussed. The hyperfine patterns, attributed to radicals derived from alcohols, can be interpreted in terms of α-hydrogen abstraction in certain cases. Possible explanations for the other spectra are presented and discussed in terms of the known reactivity of hydroxyl radicals.

Photolysis [1, 2, 3] of dilute solid solutions of hydrogen peroxide by 3650 Å light is a general method for producing trapped radicals which can then be studied in detail by ultraviolet and electron-spin resonance spectroscopy. The trapped radicals always arise through loss of hydrogen by the solvent or addition of hydroxyl radicals to double bonds. Results of those previous experiments are now summarised, and new results obtained from a wide range of saturated aliphatic alcohols are reported. The results are tabulated, and representative spectra reproduced in the Figures. During the initial stages of photolysis, except for very dilute solutions, a single line with a shoulder at low field strength is observed (Stage I). After a few minutes another spectrum appears, and after prolonged irradiation, this completely masks the former (Stage II). This new spectrum invariably contains considerable hyperfine structure. Finally, when the temperature of the glass is allowed to approach the softening point, the Stage II spectrum is lost, and two alternative spectra are observed (Stage III). Sometimes an asymmetric line similar to that at Stage I is recorded, and at others a single, relatively narrow symmetrical line is found. Further

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[1] Part I, Symons and Townsend, preceding paper.
[2] Gibson, Ingram, Symons, and Townsend, *Trans. Faraday Soc.*, 1957, **53**, 914.
[3] Ingram, Symons, and Townsend, *ibid.*, 1958, **54**, 409.

increase in temperature results in complete loss of signal. These changes, which are independent of the alcohol, are summarised in the Figures. A further complication appeared; the general appearance of the Stage II spectra seems to depend on the conditions, and at times the relatively simple spectra recorded earlier [2] are found to be considerably more complicated (see Fig. 4).

The experimental procedures were as previously described.[1] For some experiments a resonance cavity constructed for irradiation *in situ* was employed [4] which gave results identical with those obtained by periodically transferring the specimen from a Dewar flask containing liquid nitrogen into the cooled cavity.

Fujimoto and Ingram [4] repeated many of these experiments and largely confirmed our results. The few differences which do occur will be commented on as appropriate. Their interpretations, which are quite different from ours, will be discussed in Part III.[8]

RESULTS AND DISCUSSION

The results are presented in the Table and Figures and will be discussed in the following order:

(i) *Nature of the Changes occurring during Initial Photolysis, and Thermally after Photolysis* (*Stages* I—III).—Alcoholic solutions which are 0·1M or stronger in hydrogen peroxide will probably contain some clusters of hydrogen peroxide molecules. Such clusters will be increasingly important as the length of the hydrocarbon chain increases. On photolysis, such units would probably decompose according to the sequence

$$H_2O_2 + h\nu \longrightarrow 2{\cdot}OH$$
$${\cdot}OH + H_2O_2 \longrightarrow H_2O + HO_2{\cdot}$$

thus giving rise to $HO_2{\cdot}$ radicals. This is likely to occur more readily than the main reaction of hydrogen abstraction from the solvent, and since, at the temperatures employed, $HO_2{\cdot}$ radicals would not attack the solvent, the first radicals to be detected by electron-spin resonance would be $HO_2{\cdot}$. When such units are consumed, the major reaction becomes abstraction, by hydroxyl, of that hydrogen atom in the solvent molecule most susceptible to attack and, superimposed upon the small signal from $HO_2{\cdot}$ radicals (Stage I), the spectrum of the solvent radicals will appear (Stage II).

If, subsequently, the glass is allowed to soften sufficiently to permit migration of the solvent radicals (R·), then more $HO_2{\cdot}$ radicals would be formed, provided some hydrogen peroxide remains, and the single asymmetric line could again predominate:

$$R{\cdot} + H_2O_2 \longrightarrow RH + HO_2{\cdot}$$

If the warming-up is allowed to continue then oxygen formed during reaction, and any oxygen originally present, would also be liable to interact with all radicals:

$$R{\cdot} + O_2 \longrightarrow RO_2{\cdot}$$

and $$HO_2{\cdot} + O_2 \longrightarrow HO_4{\cdot}$$

or $${\cdot}OH + O_2 \longrightarrow HO_3{\cdot}$$

In the absence of excess of hydrogen peroxide, reaction with oxygen would be the only reaction likely to result in the formation of a different radical species (Stage III).

If these considerations concerning possible radical species are correct, then the electron-spin resonance spectra shown in Figs. 1*a* and 2*a* must be attributed to the $HO_2{\cdot}$ radical. The shape of this line is characteristic of radicals having a variation in *g*-value with orientation in the magnetic field. This means that the orbital containing the unpaired electron has axial symmetry. If the peak at $g = 2{\cdot}004$ is attributed to that extreme in which radicals are perpendicular to the field ($g_\perp$), then the shoulder at $g = 2{\cdot}024$ is due to radicals lying parallel with the field ($g_\parallel$). These values for $g_\parallel$ and $g_\perp$ may be compared

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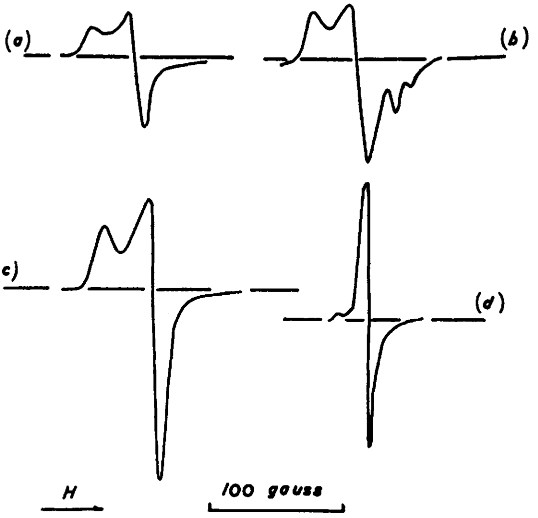
[4] Fujimoto and Ingram, *Trans. Faraday Soc.*, 1958, **54**, 1304.

with those obtained by Livingston *et al.*,[5] and attributed to $HO_2\cdot$, namely, $g_{\perp} = 2{\cdot}008$ and $g_{\parallel} = 2{\cdot}027$. The spread is almost identical and the slight difference in absolute value is probably within experimental error.

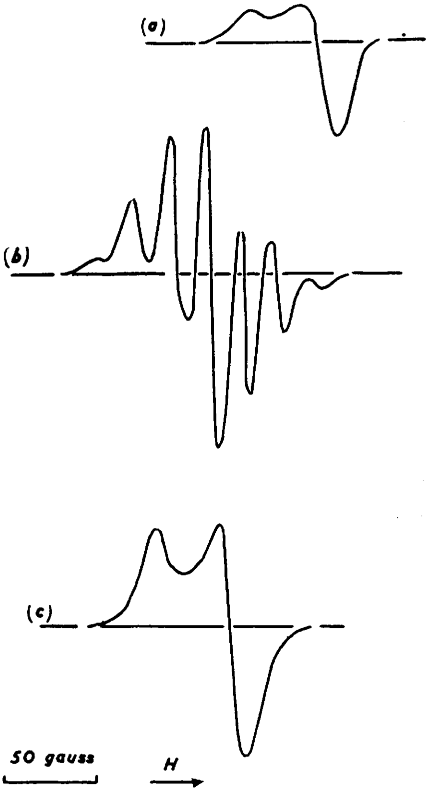
It is noteworthy that Livingston *et al.*[5] observed a yellow colour in solids thought to contain $HO_2\cdot$. We found that when a purple alcohol glass containing a large excess of hydrogen peroxide is allowed to warm under controlled conditions, the violet changes to yellow before complete loss of colour.[1]

FIG. 1. *Electron-spin resonance spectra from photolysed solutions of hydrogen peroxide in propanol.*



(*a*) After 3 min. (Stage I). (*b*) After 15 min. (Stage I and Stage II). (*c*) After partial softening and refreezing (*b*) (Stage III). (*d*) After further warming and refreezing (*c*) (Stage III).

FIG. 2. *Electron-spin resonance spectra from photolysed solutions of hydrogen peroxide in propan-2-ol.*



(*a*) After 5 min. (Stage I). (*b*) After 30 min. (Stage II). (*c*) After partial softening and refreezing (*b*) (Stage III).

Further support for the postulate that the asymmetric line is caused by $HO_2\cdot$ comes from the fact that when alcohols are irradiated with *X*-rays or high-energy electrons, electron-spin resonance and ultraviolet spectra are recorded which are generally very similar to those recorded here (Stage II) but an asymmetric single line has never been detected in these studies. Thus, hydrogen peroxide is an essential ingredient.

Comparison of the spectrum attributed to $HO_2\cdot$ with that found for its conjugate base, O_2^-, shows that these lines are very similar in form, but that the variation in *g*-value is very much greater in the case of superoxide.[6] For superoxide in the absence of asymmetric electric fields one would predict $g_{\parallel} = 4$ and $g_{\perp} = 0$, and the experimental values of $g_{\parallel} = 2{\cdot}175$ and $g_{\perp} = 2{\cdot}002$ show that strong asymmetric fields lift the degeneracy of the

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[5] Livingston, Ghormley, and Zeldes, *J. Chem. Phys.*, 1956, **24**, 483.

[6] Bennett, Ingram, Symons, George, and Griffith, *Phil. Mag.*, 1955, **46**, 443.

π orbitals, thus quenching spin–orbit coupling. In $HO_2\cdot$, the strong field of the proton splits the levels to an even greater extent, and hence the observed *g*-values are reasonable.

Little can be said about the nature of the single symmetric line often observed during warming-up. The ozonide ion, O_3^-, shows little or no variation in *g*-value, but the line is broad and the *g*-value of 2·012 is quite far from the average value of 2·004 found for alcohol radicals.[7] Further loss of symmetry would decrease spin–orbit coupling still further and therefore there seems no inconsistency in this sense, with the theory outlined above, that the single line is caused by addition of oxygen, and indeed, this postulate has often been made in other contexts. It has been suggested that this single line is to be associated with some sort of charge-transfer process whereby an electron passes from an alcohol radical to a neighbouring molecule.[4] It is not clear why such a process should give rise to a single narrow line, or why the transfer should occur when the solvent molecules have no low-lying vacant orbital. The further conclusion [4] that this process is only effective at 90° and not at 77° is not confirmed by our results since the specimen which gave rise to the spectrum recorded in Fig. 1*d* gave exactly the same spectrum when recorded at 77° and at 110° K.

Details of electron-spin resonance spectra obtained from irradiated solid solutions of hydrogen peroxide in various alcohols.

	No. of hyperfine lines	Hyperfine splitting constant (gauss)		No. of hyperfine lines	Hyperfine splitting constant (gauss)
MeOH	3	19	Bu^tOH	3	24
EtOH	5 (10, *a*, *c*)	22	*n*-Pentyl alcohol	7, *c*	20
Pr^nOH	5 (6, *b*)	22	*iso*Pentyl alcohol	7, 4, *c*	21, 21
Pr^iOH	7 (6, *a*)	20	*tert.*-Amyl alcohol	5, *c*	25
Bu^nOH	7, *c*	20	Allyl alcohol	4	13
Bu^iOH	8, *c*	23	*cyclo*Hexanol	6	20
Bu^sOH	6	21			

a = Occasionally observed. *b* = Ref. 4. *c* = Poorly resolved, therefore H.F.S. constant is an approximate value.

The phenomena discussed above, and illustrated in Figs. 1 and 2 for *n*- and *iso*-propyl alcohol, were also observed for other alcohols and seem to be quite general. The asymmetric line previously reported for ethanol [2] was a consequence of partial warming-up during measurement and is now attributed to $HO_2\cdot$.

(ii) *Position of Attack on the Alcohol Molecule as inferred from Electron-spin Resonance Spectra* (*Stage* II).—Unfortunately, in only a few cases can the Stage II electron spin resonance spectra be interpreted with some certainty. One might have expected that this technique would have given quite unambiguous results, as is often the case for complex aromatic radicals and radical ions in solution. This is not so, largely because rigid glasses have to be used, and hence dipolar interactions are considerable and give rise to broad lines. In mobile solution, these effects are averaged to zero, leaving only the isotropic interaction, which results in very narrow lines. This severe limitation means that with lines about 15 gauss wide at half-height and with hyperfine splitting constants of the order of 20 gauss, resolution is very poor, and small differences between different hydrogen atoms cannot be detected.

We have suggested [2] that the observed hyperfine patterns arise through interactions between unpaired electrons and the nuclei of α- or β-hydrogen atoms. This α–β rule will be assumed throughout this discussion and an attempt will be made to justify this assumption in Part III.[8]

The simplicity and apparent symmetry of derivative spectra can often be deceptive. For example, the spectrum recorded for the anthracene positive ion [9] contains 19 or 21

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[7] McLachlan, Symons, and Townsend, *J.*, in the press.

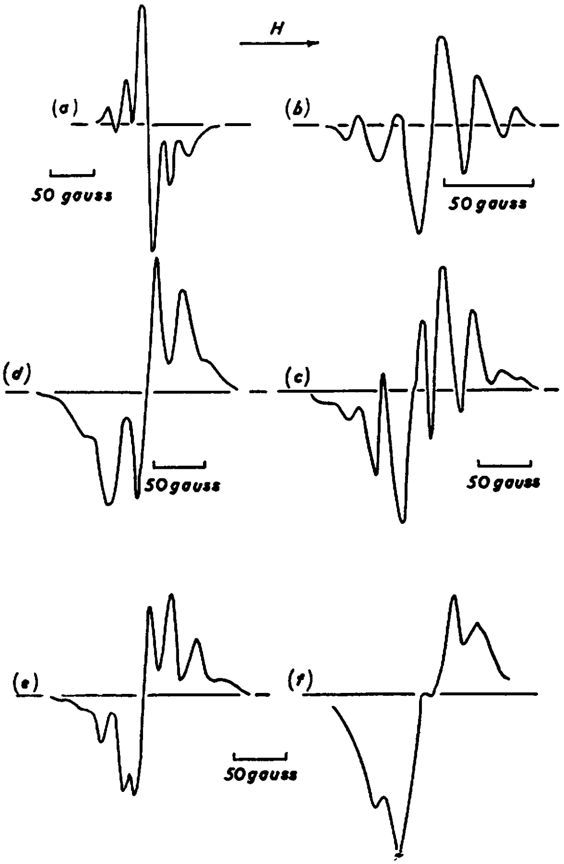
[8] Part III, following paper.

[9] Weissman, de Boer, and Conradi, *J. Chem. Phys.*, 1957, **26**, 963.

lines with apparently equal spacing for all lines. However, better resolution has shown that this is fortuitous, the new spectrum containing about 50 lines which are by no means evenly distributed.[10] All that can be done is to assume that the spectra are as simple as they appear, but this assumption may be far from the truth.

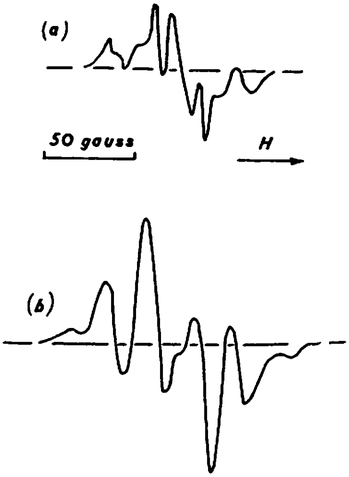
Methanol, ethanol, and propan-2-ol present reasonably well-resolved spectra of 3, 5, and 7 lines having an approximately gaussian distribution of intensities. The hyperfine splitting constants of 19, 22, and 20 are quite in accord with the postulate that α-hydrogen is removed in each case, giving, respectively, $\cdot CH_2\cdot OH$, $CH_3\cdot\dot{C}H\cdot OH$, and $(CH_3)_2\dot{C}\cdot OH$.[2, 8]

FIG. 3. *Electron-spin resonance spectra attributed to alcohol radicals.*



(*a*) Ethanol. (*b*) Propanol. (*c*) *iso*Butanol. (*d*) *tert.*-Amyl alcohol. (*e*) *iso*Pentyl alcohol. (*f*) *iso*Pentyl alcohol.

FIG. 4. *Alternative electron-spin resonance spectra for alcohol radicals.*



(*a*) Ethanol. (*b*) Propan-2-ol.

tert.-Butyl alcohol and *tert.*-amyl alcohol give 3 and 5 lines, and it is postulated that the predominating radicals are respectively $\dot{C}H_2\cdot CMe_2\cdot OH$ and $CH_3\cdot\dot{C}H\cdot CMe_2\cdot OH$.

From these conclusions one can deduce that α-hydrogen atoms are abstracted in preference to primary β-hydrogen atoms, and that in the absence of the former, secondary are abstracted in preference to primary hydrogen atoms.

From this stage onwards, however, interpretation of electron-spin resonance spectra is somewhat arbitrary. This can be illustrated by a consideration of the spectrum from propan-1-ol. We reported earlier an unsymmetrical five-line spectrum.[2] Further study

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[10] Carrington and Symons, *J.*, in the press.

has enabled us to obtain a quintet of far greater symmetry (Fig. 3*b*). Integration of this derivative shows that the line-intensity ratios are close to binomial distribution and that the hyperfine splitting constant is about 22. We suggested that the 5-line spectrum was built from a single central line and a symmetrical quartet. The better resolution and greater symmetry of the spectrum (Fig. 3*b*) render this interpretation untenable. Alger, Anderson, and Webb [11] obtained a spectrum very similar to ours after bombarding solid propan-1-ol with *X*-rays or high-energy electrons. These spectra were reproducible and were quite similar when observed at 77° or 90° K. The spectrum shown in Fig. 1*b* represents a halfway stage between Stage I and Stage II.

In contrast, Fujimoto and Ingram [4] found that a six-line spectrum results when hydrogen peroxide is photolysed in rigid propanol, sometimes accompanied by a single line. The reason for these differences is not understood, so interpretation is speculative.

The most obvious parameter to vary is the point of attack, which could be on the α-, β-, γ-, or hydroxyl-hydrogen atoms, resulting in the radicals (I)—(IV). If one makes the simplifying assumption, justified in the case of ethanol, that α- and β-hydrogen atoms will have about equal splitting, then the first radical should give 4 lines, the second 7, the third 5, and the fourth 3.

$CH_3{\cdot}CH_2{\cdot}\dot{C}H{\cdot}OH$	$CH_3{\cdot}\dot{C}H{\cdot}CH_2{\cdot}OH$	$\dot{C}H_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}$
(I)	(II)	(III)	(IV)

Both in our experiments, and when high-energy radiation is used, an intense violet colour develops during irradiation. We have suggested that this colour is caused by radicals of structure $R_2\dot{C}{\cdot}OH$.[1] If this be accepted, then one must conclude that radical (I) is present at least in part. However, only radical (III) seems to fit in with the experimental result. It will be shown below that this is unlikely on chemical grounds, so at present we can find no reasonable explanation for this spectrum.

Before leaving the problem of the propan-1-ol radical, one should consider the types of spectra to be expected if α- and β-hydrogen atoms do not give nearly equal interaction. (The postulate that roughly equal interaction is to be expected will be considered in detail in Part III.[8] However, inspection of the data for methanol and propan-2-ol shows that differences will not be great and certainly one would not expect to find a factor as large as 2 involved.) For radical (I), it is possible that the β-hydrogen atoms would give a slightly different splitting from the remaining α-hydrogen atom. This state of affairs is illustrated in Fig. 5. When $a_1 = a_2$, a four-line spectrum results. If $a_1 > a_2$ a sextet (1 : 1 : 2 : 2 : 1 : 1) with unequal spacing would be found, but for small differences and broad lines, this would still appear as a badly resolved quartet. If $a_1 = 2a_2$ a sextet of equally spaced lines would be found, but this extreme difference has already been rejected. Again, if $a_2 = 2a_1$ a symmetrical quintet (1 : 2 : 2 : 2 : 1) would result, but this extreme is equally unlikely.

The difficulty encountered with propan-1-ol is also met with in the case of the higher normal primary alcohols. Thus for *n*-butanol, our spectrum appears to be either a 6- or a 7-line pattern with a strong central line superimposed. Alger *et al.*[11] obtained a 7-line spectrum, poorly resolved but apparently symmetrical, and Fujimoto and Ingram reported a 6-line spectrum.[4] We cannot offer any simple explanation of these spectra.

The *iso*-primary alcohols give patterns which are more susceptible to interpretation. The most probable points of attack are now the α- and the tertiary hydrogen atoms. For *iso*butanol the two radicals to be expected are $(CH_3)_2CH{\cdot}\dot{C}H{\cdot}OH$ and $(CH_3)_2\dot{C}{\cdot}CH_2OH$, which should give rise to 3 or 9 lines respectively, if all α- and β-hydrogen atoms are nearly equivalent. The spectrum (Fig. 3*c*) consists of eight poorly resolved lines. Accordingly, we postulate that the tertiary hydrogen atom has been attacked preferentially, but that for some reason, one of the eight β-hydrogen atoms is not interacting with the unpaired electron.

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[11] Alger, Anderson, and Webb, in the press.

It is interesting to compare this result with that of Alger *et al.*[11] who find a well-defined triplet, very similar to that obtained from methanol. It would seem reasonable to postulate that loss of α-hydrogen has occurred under these conditions.

In contrast, the spectrum obtained from *iso*pentyl alcohol after exposure to high-energy radiation[11] consists of 9 lines, which points strongly to the radical $(CH_3)_2\dot{C}{\cdot}CH_2{\cdot}CH_2{\cdot}OH$. Our spectrum of 7 lines (Fig. 3*e*) could well be part of the same 9-line pattern, since the intensity of the outermost lines in a 9-line spectrum from eight equivalent hydrogen atoms will only be 1/70th of that of the central line and could easily be lost in background noise. However, under some conditions the spectrum appears to be a very poorly resolved quartet (Fig. 3*f*), which is what one would expect for the radical $(CH_3)_2CH{\cdot}CH_2{\cdot}\dot{C}H{\cdot}OH$ resulting from attack on α-hydrogen. We are not certain yet what precise conditions are required to give these alternative spectra.

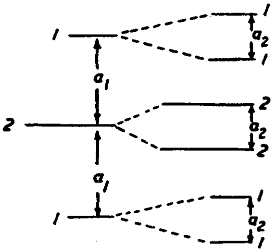

FIG. 5. *Hyperfine structure expected from two equivalent protons* (hyperfine splitting constant = a_1) *and one other proton* (hyperfine splitting constant = a_2).

sec.-Butyl alcohol gave a very poorly resolved sextet with a hyperfine splitting constant of about 22 gauss. It is tempting to assign the structure $CH_3{\cdot}CH_2{\cdot}\dot{C}Me{\cdot}OH$ to this radical, but the radical $CH_3{\cdot}\dot{C}H{\cdot}CHMe{\cdot}OH$ would also be expected to give six lines.

The spectra recorded in Fig. 4*a* and *b* are reproduced here to illustrate the fact that reproducibility is not as good as one would wish. As yet, we have found no systematic trends in variation of environment which will account for these differences. Occasionally some fault in instrumentation may cause these phenomena but if this is so, it has as yet escaped detection.

If the differences observed reflect real differences in the trapped radicals then there are two alternative explanations. One is that slight differences in environment can give rise to modifications in the interactions between protons and unpaired electrons in a given type of radical, and the other, that slight differences in experimental procedure can result in the formation of different radical species.

We do not yet propose to discuss the former explanation. The latter appears improbable on chemical grounds, but so little is known about reactions under these conditions that it ought to be considered. The spectrum obtained from ethanol (Fig. 4*a*) can be built up from two 5-line spectra having hyperfine-splitting constants of 22 and 25 gauss. The normal 5-line spectrum thought to be caused by $CH_3{\cdot}\dot{C}H{\cdot}OH$ radicals has a constant of 22 gauss: the other spectrum could then arise from the radical $\dot{C}H_2{\cdot}CH_2{\cdot}OH$.

Similarly the unusual propan-2-ol spectrum (Fig. 4*b*) can be obtained by superimposing a set of 4-lines having a hyperfine-splitting constant of 27 gauss upon the usual 7-line spectrum. This could be caused by $\dot{C}H_2{\cdot}CHMe{\cdot}OH$ radicals. We conclude that, if a considerable amount of β-attack occurred, one might well obtain spectra such as those in Fig. 4*a* and *b*. There are doubtless many other possible explanations, but if this interpretation were correct, one is at once faced with the difficult problem of understanding why attack is selective at one time and non-selective at others.

(iii) *General Observations on the Activity of Hydroxyl Radicals.*—In view of the preceding discussion it is advisable to turn to some other criterion to obtain information about the radicals resulting from attack by hydroxyl radicals on alcohols. Accordingly, the behaviour of hydroxyl radicals with respect to attack on hydrogen is briefly reviewed.

Important amongst the factors influencing relative rates of attack by radicals on various hydrogen atoms in a molecule are the stability of the displaced radical, the degree of bond breaking in the transition state, and the electrophilic or nucleophilic nature of the radical. The discrimination observed will also be a function of the temperature, increasing generally as the temperature is lowered.

The stability of the displaced radical will be important only if a considerable degree of C–H bond breaking has occurred before the transition state is reached. Comparison of the behaviour of methyl radicals on the one hand and chlorine atoms on the other has led to the conclusion [12] that only in the former case is the degree of bond breaking extensive. That means that when chlorine atoms attack hydrogen, the stability of the displaced radical is unimportant, and the overriding directive influence is the inductive effect of substituents. Chlorine atoms, with a high electron affinity, seek electron-rich centres and therefore selectively avoid α- and, to a less extent, β-hydrogen atoms in alkyl halides and carboxylic acids. The reverse is true for methyl radicals.

Hydroxyl radicals lie between these two extremes. Their electron-affinity is considerably smaller than that for chlorine atoms, whilst the proton affinity of hydroxide ions is much smaller than that for methyl negative ions.

The hydroxyl group in alcohols has a far weaker inductive effect than either chlorine or carboxyl and hence the tendency for electrophilic radicals to avoid α-hydrogen atoms will be less for alcohols than for alkyl halides or carboxylic acids.

All experimental data point to the conclusion that free radicals, whatever their nature, attack primary and secondary alcohols and ethers on α-hydrogen. Little is known about the reactions which occur between hydroxyl radicals and alcohols at room temperature, but, if one accepts the postulate that Fenton's reagent reacts as a source of hydroxyl radicals, then this reagent's reacting with propanol to give propionaldehyde establishes that α-attack is significant.[13] However, *tert.*-butylperoxy- and benzoylperoxy-radicals probably resemble hydroxyl radicals fairly closely, and both these reagents attack alcohols and ethers readily on α-hydrogen.[14,15] In the absence of α-hydrogen atoms, reaction is much slower.[14] (The conclusion that, in the absence of α-hydrogen, hydroxyl radicals attack hydroxyl-hydrogen [13] is not upheld by our results, which establish conclusively that, under our conditions, attack on β-hydrogen predominates.)

We conclude on chemical grounds that attack by hydroxyl radicals on primary and secondary alcohols will occur on α-hydrogen. If this is correct, then the uninterpreted electron-spin resonance spectra recorded must be due to radicals of type $R_2\dot{C}{\cdot}OH$ and there is some factor, so far overlooked, which would make this conclusion intelligible. The same conclusion was reached in Part I on spectroscopic grounds.[1]

When a tertiary hydrogen atom is present in the alkyl group as in the *iso*-primary alcohols, attack on this atom would be more favoured than on other primary or secondary hydrogen atoms because the C–H bond strength is relatively small and the displaced radical is greatly stabilised by the two methyl groups. Our results suggest that there is a rather fine balance between α-attack and attack on tertiary hydrogen: if this is correct, then one can again conclude that α-attack will predominate in the absence of tertiary hydrogen. These results can be compared with those of Kenyon and Symons who concluded that hydroxyl radicals attacked the anions of branched-chain carboxylic acids preferentially on tertiary hydrogen.[16]

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[12] Russell and Brown, *J. Amer. Chem. Soc.*, 1955, **77**, 4578.
[13] Merz and Waters, *J.*, 1949, 2427.
[14] Bartlett and Nazaki, *J. Amer. Chem. Soc.*, 1947, **69**, 2299.
[15] Urry, Stacey, Huyser, and Juveland, *ibid.*, 1953, **75**, 250; 1954, **76**, 450.
[16] Kenyon and Symons, *J.*, 1953, 3580.