

48. Unstable Intermediates. Part III.¹ Proton Interaction in Aliphatic Free Radicals.

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Values of hyperfine splitting constants obtained from electron-spin resonance spectra of aliphatic free radicals are correlated on the basis of certain simplifying assumptions. When radicals have been identified with reasonable certainty, good agreement is obtained: in other cases the observed splitting is of value for identification.

Interaction between unpaired electrons and β -hydrogen atoms is a function of the angle between the plane of the C-H bond and the nodal plane of the unpaired electron, and, if rotation is restricted, β -hydrogen atoms may cease to be equivalent. A variety of results is considered in terms of this principle.

An explanation is offered of the fact that, often, completely different reactions result in the final trapping of the same radicals. Some outstanding anomalies are discussed.

ALTHOUGH considerable attention has been given to the quantitative features of electron-spin resonance spectra obtained from stable aromatic radicals and radical ions, very little has been paid to the spectra of simple aliphatic free radicals. One reason for this is that the spectra of simple radicals trapped in solids are often difficult to interpret.¹ Indeed, since it is often not known what radicals have been trapped, the problem of interpretation becomes dependent upon identification, which may also be difficult.¹

Despite these difficulties, it is felt that many recent results can be correlated fairly accurately, provided some simplifying assumptions are made. The procedure rests upon the basic assumption that simple radicals such as $\cdot\text{CH}_3$, $\text{CH}_3\cdot\text{CH}_2\cdot$, $\cdot\text{CH}_2\cdot\text{OH}$, etc., have been trapped, and that the spectra do, in fact, relate to these radicals. This identification is rarely compelling but is generally reasonable, and will be accepted provisionally in order that certain quantitative aspects of these spectra may be examined.

The assumptions and calculations relating to hyperfine splitting constants are presented in Section I and the results compared with experimental values in Tables 2, 3, and 4. These results are then discussed. In Section II some aspects of hyperconjugation are considered, especially with regard to hindered rotation. In Section III some general remarks are made concerning outstanding anomalies in the field of radical-trapping.

I. *Symbols.*— a is the hyperfine splitting constant, *i.e.*, the separation (gauss) between hyperfine lines in the electron-spin resonance spectra; $a_{\alpha\text{H}}$ and $a_{\beta\text{H}}$ are its values for α - (as in $\cdot\text{CH}_3$) and β -hydrogen atoms (as in $\cdot\text{CMe}_3$), and a_{av} is the average of, and Δa the difference between, them. ρ_{C} is the unpaired electron density on trigonally-hybridised carbon (%); $X_{\alpha\text{H}} = a_{\alpha\text{H}}/\rho_{\text{C}}$ and $X_{\beta\text{H}} = a_{\beta\text{H}}/\rho_{\text{C}}$; $A_{\alpha\text{H}}$ and $A_{\beta\text{H}}$ are the delocalising powers of α - or β -hydrogen atoms; $\rho_{\text{C}} \cdot A_{\alpha\text{H}}^2$ is the unpaired electron density on each α -hydrogen atom; A_{Y} is the delocalising power of Y as in $\cdot\text{CH}_2\text{Y}$; $\theta = 90^\circ$ minus the angle between a β -C-H bond and the nodal plane of the unpaired electron.

Assumptions and Calculations.—It is first assumed that the hyperfine splitting constant is a measure of the unpaired electron density on hydrogen. The experimental value for hydrogen atoms is 502 gauss. If, then, a particular hydrogen atom gives a splitting of a gauss, the unpaired electron density on this hydrogen atom will be $a/5.02\%$.²

The second assumption is that both $a_{\alpha\text{H}}$ and $a_{\beta\text{H}}$ will be linearly proportional to ρ_{C} . This is equivalent to McConnell's equation $a_{\text{N}} = Q\rho_{\text{n}}$ for aromatic radicals,³ but represents a considerable and, as yet, unjustified extension to cases when ρ is large and both α - and β -hydrogen atoms interact with the unpaired electron.

¹ Gibson, Symons, and Townsend, preceding paper.

² Gibson, Ingram, Symons, and Townsend, *Trans. Faraday Soc.*, 1957, **53**, 914.

³ McConnell, *Ann. Rev. Phys. Chem.*, 1957, **8**, 116.

TABLE 1. *Alternative values for factors $A_{\alpha\text{H}}$, $A_{\beta\text{H}}$, $X_{\alpha\text{H}}$, and $X_{\beta\text{H}}$, derived from electron spin resonance spectra of methyl and tert.-butyl radicals.⁴*

Radical	Procedure	$A_{\alpha\text{H}}$	$X_{\alpha\text{H}}$	$A_{\beta\text{H}}$	$X_{\beta\text{H}}$
$\cdot\text{CH}_3$	(i)	0	0.26	—	—
	(ii)	0.062	0.31	—	—
	(iii)	-0.045	0.226	—	—
$\cdot\text{CMe}_3$	—	—	—	0.078	0.393

TABLE 2. *Estimated and experimental values of hyperfine splitting constants for the radicals $\cdot\text{CH}_2\text{Me}$ and $\cdot\text{CHMe}_2$ [by use of procedures (i), (ii), and (iii) outlined above].*

Radical	ρ_{C} (%)	$a_{\alpha\text{H}}$	$a_{\beta\text{H}}$	$a_{\alpha\text{v}}$ (est.)	$a_{\alpha\text{v}}$ (exp.)	Δa (est.)	Δa (exp.)
$\cdot\text{CH}_2\text{Me}$	(i) 81	21	31.8	27.5	26, ⁶ 24 ⁴	10.8	6 ⁴
	(ii) 73.6	22.8	28.8	26.4	—	6.0	Not resolved ⁶
	(iii) 87.4	19.8	34.3	28.5	—	14.5	—
$\cdot\text{CHMe}_2$	(i) 68.2	17.7	26.7	25.4	25.0 ⁴	9.0	Not resolved ⁴
	(ii) 65.4	20.3	25.7	25.0	—	5.4	—
	(iii) 70.3	15.8	27.6	26.0	—	11.8	—

TABLE 3. *Estimated and experimental values of hyperfine splitting constants for various radicals from alcohols.*

No.	Radical	ρ_{C}	$a_{\alpha\text{H}}$	$a_{\beta\text{H}}$	$a_{\alpha\text{v}}$	$a_{\alpha\text{xp}}^1$	Δa (est.)	N (est.)	N^1 (exp.)
1	$\cdot\text{CH}_2\cdot\text{OH}$	61.3	(19)	—	—	19	—	3	3 ^a
2	$\text{CH}_3\cdot\dot{\text{C}}\text{H}\cdot\text{OH}$	55.7	17.3	21.9	20.8	21	4.6	5	5
3	$\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$	75	23.3	29.5	26.4	25	6.2	5	5 ^b
4	$\cdot\text{CMe}_2\cdot\text{OH}$	50.8	—	20	—	20	—	7	7
5	$\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$	76.5	23.7	30.2	26	27	6.5	4	4 ^b
6	$\text{CH}_3\cdot\text{CH}_2\cdot\dot{\text{C}}\text{H}\cdot\text{OH}$	56.5	17.6	22.2	20.8	22	4.6	4	5
7	$\text{CH}_3\cdot\dot{\text{C}}\text{H}\cdot\text{CH}_2\cdot\text{OH}$	71.2	22.1	28	27	22	6.1	7	5
8	$\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$	75	23.3	29.5	26.4	22	6.2	5	5
9	$\text{Me}_2\dot{\text{C}}\cdot\text{CH}_2\cdot\text{OH}$	59.7	—	23.4	—	23	—	9	8
10	$\text{Me}\dot{\text{C}}(\text{OH})\text{Et}$	53	—	21	—	21	—	6	6
11	$\text{Me}\dot{\text{C}}\text{H}\cdot\text{CH}(\text{OH})\text{Me}$	67.6	21	26.6	25.5	21	5.6	6	6
12	$\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{OH}$	77.5	(24)	—	—	24	—	3	3 ^a
13	$\text{CH}_3\cdot\dot{\text{C}}\text{H}\cdot\text{CMe}_2\cdot\text{OH}$	68.7	21.5	27	25.5	25	5.5	5	5

^a Value assumed. ^b Experimental results may well be spurious.¹ N = No. of hyperfine lines.

TABLE 4. *Estimated values for A_{Y} in radicals $\text{R}_2\dot{\text{C}}\text{-Y}$.*

Y	OH	O ⁻	CN	CO ₂ Me	CO·NH ₂	CMe ₂ ·OH	CH ₃
A_{Y}	0.5	0.8	0.75	0.52	0.26	0.16	0.234

Accepting these postulates, we make the calculations as follows: From the value $a = 26$ for $\cdot\text{CH}_3$ ⁴ a figure for $A_{\alpha\text{H}}$ is estimated. Three alternative approaches can be made. (i) That $\rho_{\text{C}} = 100$, that is, that α -hydrogen effects no delocalisation, and therefore that $A_{\alpha\text{H}} = 0$ and $X_{\alpha\text{H}} = 0.26$. (ii) That α -hydrogen atoms effect a delocalisation, measured by the value of 26 gauss for a . On this basis, the unpaired electron density is 26/5.02% on each hydrogen atom, or 15.55% on all three. That means $\rho_{\text{C}} = 84.45$ and hence $A_{\alpha\text{H}} = 0.062$ and $X_{\alpha\text{H}} = 0.31$. (iii). In view of the postulate that positive spin on carbon gives rise to negative spin on α -hydrogen atoms, (ii) may be false, and it might be more correct to say that the spin on α -hydrogen atoms is -15.55, and hence that $\rho_{\text{C}} = 115.55\%$. On this basis, $A_{\alpha\text{H}} = -0.045$ and $X_{\alpha\text{H}} = 0.226$.

From the value $a = 23$ for $\cdot\text{CMe}_3$ ⁴ and the assumption that positive spin on carbon gives rise to positive spin on β -hydrogen atoms, the unpaired electron density is 23/5.02% on each β -hydrogen or 41.3% on all nine β -hydrogen atoms. Hence, $\rho_{\text{C}} = 58.7$, $A_{\beta\text{H}} = 0.078$, and $a_{\beta\text{H}} = 0.393$. These results can now be used to estimate $a_{\alpha\text{H}}$ and $a_{\beta\text{H}}$ in the radicals $\dot{\text{C}}\text{H}_2\text{Me}$ and $\dot{\text{C}}\text{HMe}_2$. For $\dot{\text{C}}\text{H}_2\text{Me}$ the total unpaired electron density of 100% can

⁴ Matheson and Smaller, *J. Chem. Phys.*, 1958, **28**, 1169.

be equated to the amount on carbon, ρ_C , that on α -hydrogens, $2A_{\alpha H}\rho_C$, and that on methyl, $3A_{\beta H}\rho_C$: *i.e.*, $100 = \rho_C + 2A_{\alpha H}\rho_C + 3A_{\beta H}\rho_C$, whence $\rho_C = 81, 73.6, \text{ or } 87.4\%$ for procedures (i), (ii), and (iii) respectively. From these values for ρ_C , $a_{\alpha H}$, and $a_{\beta H}$ have been calculated and are given in Table 2 together with values for a_{av} and Δa .

Similarly, ρ_C for the radical $\cdot\text{CHMe}_2$ can be calculated from the equation $100 = \rho_C + A_{\alpha H}\rho_C + 6A_{\beta H}\rho_C$. The results obtained again depend upon the procedure used, as do the estimates for $a_{\alpha H}$, $a_{\beta H}$, a_{av} , and Δa (Table 2).

The results are compared with values reported for these radicals.^{4,6} It is apparent that procedure (ii) gives by far the most satisfactory agreement with experiment. Indeed, since Matheson and Smaller⁴ claim to have obtained approximate values for the individual lines from α - and β -hydrogen atoms in $\dot{\text{C}}\text{H}_2\text{Me}$, and record a value of 6 for Δa , one can postulate that for values of Δa much greater than 6, some resolution would be apparent. Certainly, values greater than 10 should give resolved spectra, and can accordingly be rejected. For the present, therefore, only results obtained by procedure (ii) will be reported for further estimations. Anticipating, one can say that procedure (ii) gives far closer agreement with experiment than the alternatives in all cases tested so far, procedure (i) being superior to procedure (iii).

The dearth of experimental results renders the task of interpreting spectra for more complex radicals difficult. For radicals derived from normal alkanes, such as $\text{CH}_3\cdot\dot{\text{C}}\text{H}\cdot\text{CH}_2\text{R}$ and $\text{R}\cdot\text{CH}_2\cdot\dot{\text{C}}\text{H}\cdot\text{CH}_2\text{R}'$, on a first approximation one can expect all β -hydrogen atoms to be equivalent. The delocalising effect of the β -alkyl groups is hard to estimate, but two extremes can be considered: (a) that the effect is zero, and (b) that the effect is equal to that of β -hydrogen.

Assumption (a) gives, by procedure (ii):

$$100 = \rho_C + 0.062\rho_C + 5 \times 0.078\rho_C$$

for $\text{CH}_3\cdot\dot{\text{C}}\text{H}\cdot\text{CH}_2\text{R}$, whence $\rho_C = 68.9$ and therefore $a_{av} = 26.3$ and $\Delta a = 5.7$. Hence a poorly resolved 7-line spectrum having $a \approx 26.3$ should be observed. Alger *et al.*⁷ report a 7-line spectrum, $a = 27$, for radicals formed by high-energy radiation on the lower normal alkanes.

Similarly, for $\text{R}\cdot\text{CH}_2\cdot\dot{\text{C}}\text{H}\cdot\text{CH}_2\text{R}'$, $a_{av} = 27.4$ and $\Delta a = 6.0$. Hence a poorly resolved 6-line spectrum would be expected. In fact, the spectra obtained from higher alkanes after high-energy irradiation are complicated by the superposition of a set of relatively narrow lines on the central portion of the spectrum, and little can be said regarding the hyperfine splitting constants.⁷

Alternative (b) would mean that the parameters used for $\dot{\text{C}}\text{HMe}_2$ should be used. Hence $\rho_C = 65.4\%$, $a_{\alpha H} = 20.3$, and $a_{\beta H} = 25.7$. Since, however, there are now only five β -hydrogen atoms, $a_{av} = 24.8$. The value estimated by procedure (a) is thus closer to experiment, but the difference is not very large, so that no firm conclusions regarding hyperconjugation by β -alkyl groups can be drawn (see below).

The only unsaturated hydrocarbon radical whose spectrum is known is allyl, $\text{CH}_2\cdot\dot{\text{C}}\text{H}\cdot\text{CH}_2$. Matheson and Smaller⁴ report a value of 15.5 for the hyperfine splitting constant derived from the quintet ascribed to this radical. If the assumption were made that the unpaired electron was equally divided between the terminal carbons and had zero density elsewhere, calculations with procedure (ii) lead to $a_H = 13.8$ for the quintet predicted. The experimental value is appreciably higher, and the discrepancy can be understood in terms of the postulate that there is a small negative spin-density on the central carbon atom. Use of $a = 15.5$ gives $\rho_C = 50$, and hence the net spin-density on the methylene groups is 112.4%. This leads to a value of -12.4% on the central carbon atom, which can be compared with a recent theoretical estimate of -10.6% .⁵ On this

⁵ McConnell and Chesnut, *J. Chem. Phys.*, 1958, **28**, 107.

⁶ Gordy and McCormick, *J. Amer. Chem. Soc.*, 1956, **78**, 3243.

⁷ Alger, Anderson, and Webb, in the press.

basis, the central hydrogen atom should give rise to a splitting of about 3.8 gauss; this would appear as added broadening in the spectrum.

Turning to radicals of type $R_2\dot{C}Y$, we can, by using the above values [Table 1 (ii)], estimate the "delocalising power" of groups Y. The most extensive series of experimental results are for the aliphatic alcohols ($Y = OH$), the results being summarised in Part II.

Radicals derived from Alcohols.—From the value $a = 19$ for $\cdot CH_2\cdot OH$, $a_{\alpha H} = 19 = \rho_O \times 0.31$, whence $\rho_O = 61.3\%$. Hence from $100 = \rho_O = 2 \times 0.062 \times \rho_O + A_{OH} \times \rho_O$, one gets $A_{OH} = 0.50$. By using this value, together with the values for $a_{\alpha H}$ and $a_{\beta H}$ recorded in Table 2, the results shown in Table 3 (Nos. 1, 2, and 4) have been calculated. Agreement with experiment is well within experimental error and Δa for the radical from ethanol (No. 2) is so small that one would expect a fairly symmetrical 5-line spectrum.

In view of the uncertainty in the identification of the radicals¹ derived from propan-1-ol and higher alcohols the results cannot be used to test further the suitability of the procedure outlined above. However, the agreement found is such that one can postulate that any marked deviation from a_{av} estimated for a certain radical can be taken as a strong indication that the postulated radical is not, in fact, the correct one.

The experimental result for $\cdot CH_2\cdot CMe_2\cdot OH$ ($a = 24$) derived from *tert.*-butyl alcohol, though only approximate, can be used to obtain a rough value for the group $-CMe_2\cdot OH$. It turns out that $A \approx 0.16$, and the agreement with experiment found when this value is used to estimate a_{av} for $Me\dot{C}H\cdot CMe_2\cdot OH$ (Table 3, No. 13) indicates that this value is satisfactory. If one assumes that this delocalising power is equally shared between the β -methyl groups and β -hydroxyl, then $A_{\beta Me} \approx A_{\beta OH} \approx 0.053$. This result for β -methyl is less than that for β -hydrogen (0.078) and is probably of the right order of magnitude.

By using these figures, the results in Table 3 (Nos. 3, 5, 7, 8, 9, 11, 12) have been derived. For radicals formed by loss of α -hydrogen the largest estimated value is 21 gauss, whilst when β - or γ -hydrogen is lost the minimum value is 24, and the usual value between 26 and 27 gauss. In Part I we attempted to identify radicals by a consideration of the number of lines in the electron-spin resonance spectrum. In several instances, notably for propan-1-ol, this criterion proved unsatisfactory. If, however, the magnitude of a can be used as an added criterion, selection of alternative radicals is often easier. For example, our value of 22 gauss for propan-1-ol is only compatible with structure No. 6 (Table 3); both Nos. 7 and 8 require values for a far larger than the experimental value. Fujimoto and Ingram⁸ found 6 lines for radicals from propan-1-ol, with $a_{av} \approx 20$. Again, this value is too small for radicals formed by attack on β - or γ -hydrogen.

[The average value of 20 gauss is measured directly from the derivative curve presented.⁸ However, a reconstruction of the experimental curve is also given, consisting of a set of 4 lines, each split into a triplet. From the derivative curve, we estimate $a(4\text{-lines}) \approx 23$ and $a(3\text{-lines}) \approx 15$. However, the authors attribute this spectrum to the radical $CH_3\cdot\dot{C}H\cdot CH_2\cdot OH$, and quote $a_{CH_3} = 29$ and $a_{OH} = 20$. They conclude that the α -hydrogen atom gives no detectable interaction. From these quoted values, $a_{av} = 25.4$, which is certainly possible for the radical depicted. We cannot discover which set of data is correct since we invariably obtain a 5-line spectrum from propan-1-ol radicals.]

The 6-line spectrum from butan-2-ol was assigned to either radical No. 10 or No. 11.¹ The experimental value of 21 for a , however, fits well with No. 10 and eliminates No. 11.

In Part II we recorded examples of complex spectra sometimes detected for ethanol and propan-2-ol radicals. It was pointed out that one way of building up these spectra was to superimpose spectra of 5 lines ($a \approx 25$) and 4 lines ($a \approx 27$) respectively upon the normal spectra. These results are in close agreement with those expected for radicals formed by attack on β -hydrogen (Nos. 3 and 5 respectively).

Another result from the field of alcohol radicals which can now be treated quantitatively

⁸ Fujimoto and Ingram, *Trans. Faraday Soc.*, 1958, **54**, 1304.

is the 4-line spectrum from radicals formed by attack of hydroxyl radicals on allyl alcohol. We have already noted that the relatively small value for a (about 13 gauss) is best understood if the radical $\text{CH}_2\cdot\text{CH}\cdot\dot{\text{C}}\text{H}\cdot\text{OH}$ is formed by attack on allylic hydrogen.² Since a symmetrical 4-line spectrum is obtained, $a_{\alpha\text{H}} \approx a_{\gamma\text{H}}$ and therefore $\rho_{\alpha\text{C}} = \rho_{\gamma\text{C}} = \rho_{\text{C}}$. Proceeding as for the allyl radical and using $a_{\alpha\text{v}} = 13$, we get $13 = 0.31\rho_{\text{C}}$, whence $\rho_{\text{C}} = 42$. The total electron density on the outer carbon atoms and attached atoms is then equal to $42 \times 2.686 = 112.7$, and therefore the electron density on the central C-H group is 12.7%. This value being used, the hyperfine splitting constant for the central hydrogen is found to be 3.7 gauss. The doublet splitting caused by this interaction would be too small to show in our spectra.

Other Radicals.—Table 4 gives some values for A_{Y} , Y being attached directly to the carbon atom carrying the unpaired electron. The value for $-\text{O}^-$ is taken from $a = 16$ for the triplet obtained from $\cdot\text{CH}_2\cdot\text{O}^-$.⁷ That $-\text{O}^-$ is more effective than $-\text{OH}$ is not surprising, since the extreme structures $\cdot\bar{\text{C}}\text{H}_2\text{-O}\cdot$ and $\cdot\bar{\text{C}}\text{H}_2\text{-}\dot{\text{O}}\text{H}^+$ only involve charge separation in the latter case.

The values for CO_2Me and CN are derived from results reported for the radicals $\text{HO}\cdot\text{CH}_2\cdot\dot{\text{C}}\text{Me}\cdot\text{CO}_2\text{Me}$ and $\text{HO}\cdot\text{CH}_2\cdot\dot{\text{C}}\text{Me}\cdot\text{CN}$ respectively.⁹ The result for $-\text{CO}_2\text{Me}$ is only slightly greater than that for $-\text{OH}$, which is unexpected, since this group is able to effect delocalisation by means of structures such as (I). The value for A_{CN} can be used to predict a value for $a_{\alpha\text{v}}$, for radicals from polyacrylonitrile, $\text{R}\cdot\text{CH}_2\cdot\dot{\text{C}}\text{H}\cdot\text{CN}$. This gives $a_{\alpha\text{v}} = 18.1$ and $\Delta a = 4.2$. Although we have only obtained a single broad line from radicals from polyacrylonitrile, Abraham, Ovenall, and Whiffen¹⁰ report a 7-line spectrum with $a = 18.5$. It is not easy to understand why 7 lines should be observed, but the value for a is very close to the predicted value.

The figure for $-\text{CO}\cdot\text{NH}_2$ is very tentative. It was obtained from data quoted by Luck and Gordy¹¹ for the triplet and quintet which were observed after acetamide and propionamide had been exposed to X-radiation. If one postulates that the radicals responsible for these spectra are $\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ and $\text{CH}_3\cdot\dot{\text{C}}\text{H}\cdot\text{CO}\cdot\text{NH}_2$ respectively, then this value results in both instances.

A variety of results is available relating to radicals formed by high-energy irradiation of amino-acids. Waring¹² has made a careful study of α -aminoisobutyric acid and presents convincing evidence that the main radical produced is $\text{Me}_2\dot{\text{C}}\cdot\text{CO}_2^-$ (or $\text{Me}_2\dot{\text{C}}\cdot\text{CO}_2\text{H}$). Single-crystal studies show that the hyperfine splitting constant is not quite isotropic and give an average value of 23.5 gauss. Using this value, we get $A_{\text{CO}_2^-}$ (or $A_{\text{CO}_2\text{H}}$) ≈ 0.2 . If we assume that the same type of break-up occurs with other amino-acids, the 5-line spectrum from alanine ($a_{\alpha\text{v}} \approx 25$) and the triplet from glycine ($a \approx 20$) can be assigned to the radicals $\text{CH}_3\cdot\dot{\text{C}}\text{H}\cdot\text{CO}_2^-$ and $\cdot\text{CH}_2\cdot\text{CO}_2^-$ respectively. Using $A_{\text{CO}_2^-} = 0.2$, we get $a_{\alpha\text{v}} = 25$ for the former and $a = 23.4$ for the latter. Whilst the former result is compatible with experiment, the latter is far too large. It seems possible that in this case a different radical is involved.

Discussion.—The interaction which occurs between an unpaired electron in a p -orbital on trigonally hybridised carbon and protons bonded to this carbon has been discussed fully. The results obtained from aromatic radicals and radical ions in dilute fluid solution, under conditions such that all dipolar interactions would average to zero, show conclusively that contact interaction (whereby an unpaired electron is left in a 1s-state on hydrogen) is of considerable importance.

McConnell⁵ has been able, by use of the equation $a_{\text{N}} = Q\rho_{\text{n}}$ (where a_{n} is the hyperfine

⁹ Ingram, Symons, and Townsend, *Trans. Faraday Soc.*, 1958, **54**, 409.

¹⁰ Abraham, Ovenall, and Whiffen, *Arch. Sci.*, 1957, **10**, 84.

¹¹ Luck and Gordy, *J. Amer. Chem. Soc.*, 1956, **78**, 3240.

¹² Waring, personal communication.

splitting constant and ρ_n the unpaired electron density on $C_{(n)}$, to correlate many results and to obtain important information regarding ρ_n . Various theoretical and experimental values for Q have been proposed.^{5,13} McConnell favours the numerical value of 22.5 obtained from the benzene negative ion.⁵ We have found that an average value of 31 gauss gives a satisfactory fit for data from a number of aromatic positive and negative ions.¹⁴

If, as in (i) above, one assumes that $\rho_n = 1$ for $\cdot\text{CH}_3$ then $Q = 26$, a result which is remarkably close to the value derived from aromatic radicals and radical-ions. However, somewhat better agreement between experimental and estimated values is obtained if one allows for the fact that α -hydrogen atoms can delocalise the unpaired electron. That means that in the radical $\cdot\text{CH}_3$, ρ_n is not taken as unity but as some smaller value, depending upon the delocalising power of α -hydrogen atoms [see process (ii) above]. On this basis, an estimate of the hyperfine splitting constant for the planar radical $\text{R}_2\dot{\text{C}}\text{H}$ gives $a_{\alpha\text{H}} \approx 30$ gauss if it is assumed that the R groups do not interact. One conclusion that can be drawn is that $a_{\alpha\text{H}} \leq 30$ gauss in any radical having an unpaired electron in a p -orbit on trigonally hybridised carbon.

This conclusion is not true if the radical is pyramidal, but theoretical calculations by Karplus¹⁵ have shown that a small divergence from planarity would make very little difference, and that even in the extreme case in which tetrahedral configuration is retained, only a small increase in a would result.

Another conclusion is that α -hydrogen atoms are bound to interact strongly with the unpaired electron. For saturated radicals of the type discussed above, this interaction would probably give a value for $a_{\alpha\text{H}}$ greater than 15 gauss, and hence the assumption that in radicals of structure $\text{CH}_3\cdot\dot{\text{C}}\text{H}\cdot[\text{CH}_2]_n\cdot\text{OH}$ the α -hydrogen atom will not contribute to the observed spectrum seems to be unjustified.⁸ However, in some circumstances β -hydrogen atoms may not interact appreciably: this is discussed in Section II.

The results reported by Matheson and Smaller⁴ for $\cdot\text{CH}_3$ and $\cdot\text{CMe}_3$, used in the above manner, make it clear that $a_{\alpha\text{H}}$ and $a_{\beta\text{H}}$ will generally be so nearly equal that, because of the breadth of the individual lines, the measured spectrum will be an unresolved superposition of the lines from α - and β -hydrogen atoms and will closely resemble the spectrum to be expected from a radical in which α - and β -hydrogen atoms are equivalent. Several workers have been loth to accept this coincidence of near equality and have, instead, postulated the existence of radicals in which the hydrogen atoms are all completely equivalent. For example, Gordy *et al.*⁶ have suggested that, because of the symmetry of the sextet obtained from $\cdot\text{CH}_2\text{Me}$, a type of rapid intramolecular exchange of hydrogen or internal hydrogen bridging occurs. Matheson and Smaller's results⁴ show that this postulate is not required, and indeed there is strong experimental evidence against it. Thus McNesby, Drew and Gordon¹⁶ have shown that, even at high temperatures (365—506°), hydrogen atoms cannot be transferred intramolecularly in the n -butyl radical. A rapid equilibration at 72° K is therefore out of the question.

Another example is the ion C_2H_4^+ , which Gordy and his co-workers have frequently postulated in order to explain a 5-line spectrum ($a \approx 20$) which is observed during high-energy irradiation of certain organic compounds. For instance, Luck and Gordy¹¹ suggest that this radical-ion is formed during X -irradiation of solid ethanol. Their spectrum is almost identical with ours,¹ and we have presented strong evidence in favour of the radical $\text{CH}_3\cdot\dot{\text{C}}\text{H}\cdot\text{OH}$. It is difficult to see how C_2H_4^+ could be formed under the very mild conditions used in our experiments. Another argument against C_2H_4^+ is that the experimental value of about 21 for a is too large. This value for a corresponds to $X_{\alpha\text{H}} = 0.42$. Since all the results so far obtained for neutral, positive, and negative radicals give values between 0.22 and 0.31 for $X_{\alpha\text{H}}$, this value is excessively large and hence

¹³ Weissman, *J. Chem. Phys.*, 1954, **22**, 1378.

¹⁴ Carrington and Symons, *J.*, in the press.

¹⁵ Karplus, to be published.

¹⁶ McNesby, Drew, and Gordon, *J. Chem. Phys.*, 1956, **24**, 1260.

one can conclude that the spectrum is not that of $C_2H_4^+$. Bersohn¹⁷ has calculated a value of 8.4 gauss for a . Using the value $X_{\alpha H} = 0.31$ calculated above, we would predict $\rho_O = 44.4\%$ on each carbon atom, and hence that $a \approx 13.7$ for $C_2H_4^+$.

It has been assumed that in saturated radicals, only α - and β -hydrogen atoms interact with the unpaired electron. If β -methyl groups can release electrons significantly then there will be some contribution from γ -hydrogen atoms. However, on using the value $A_{\beta Me} \approx 0.053$ estimated above it is apparent that γ -hydrogen interaction will be an order of magnitude smaller than that from α - and β -hydrogen atoms. If, for steric reasons, hydrogen from another molecule or another portion of the same molecule is forced close in to the orbit of the unpaired electron, it might interact specifically and hence give rise to detectable splitting. However, no evidence of this process has yet been presented.

II. It is usually assumed that β -hydrogen atoms attached to a particular carbon atom give equal splitting; *i.e.*, they interact equally with the unpaired electron. This is only possible if rotation about the carbon-carbon bond is rapid. If, for some reason, rotation is restricted, such β -hydrogen atoms might no longer be equivalent, and I attempted to explain the curious 9-line spectrum obtained from poly(methyl methacrylate) in terms of this principle.⁹

This principle is assumed in many instances. For example, β -hydrogen interaction is not observed and never postulated for unsubstituted aromatic radical-ions. This is because all the hydrogen atoms lie in the nodal plane of the π -orbital containing the unpaired electron, and hence overlap between this and the C-H bonding orbital is negligible. A similar example is the central hydrogen atom of the radical from allyl alcohol considered earlier. This is in the nodal plane of the π -orbital containing the unpaired electron and therefore cannot interact by a hyperconjugation process.

There are other less clear-cut examples. The hydroxyl hydrogen in alcohol radicals of type $R_2\dot{C}\cdot OH$ is effectively a β -hydrogen and would surely interact in the usual way in the general case. However, there is considerable evidence that interaction is very weak. Thus the radical derived from methoxide gives a spectrum which is almost identical with that from radicals from methanol, and ethanol deuterated on the hydroxyl group gives a spectrum identical with non-deuterated ethanol.⁷ Our calculations suggest that the hydroxyl group has a large delocalising power. This probably arises through overlap between a fully occupied p - π oxygen orbital and the half-filled p -orbital on carbon. In order for this overlap to be large, the O-H bond must be constrained to lie in the nodal plane of the molecular orbital thus formed, and hence will not interact strongly.

A similar argument goes some way to explaining why the electron-spin resonance spectrum of $HO_2\cdot$ is not a doublet.¹ If one accepts that the extreme structure $\cdot O - O \begin{array}{l} \diagup \\ H \end{array}$ is an important contributor to the actual structure, then the main interaction between the unpaired electron and the proton should be by hyperconjugation. However, once again, in order to obtain efficient overlap with the filled p - π oxygen orbital, the hydrogen must lie in the nodal plane of the unpaired electron, thus removing the possibility of hyperconjugation.

The value $A_{OH} = 0.5$ being taken as a measure of the unpaired-electron density on the OH group, an approximate value for splitting to be expected from hydroxyl-hydrogen due to configurational interaction can be obtained. For example, the radical from propan-2-ol has $\rho_O = 50.8$ and hence $\rho_{OH} = 25.4$. If $a_{OH} \approx a_{\alpha H} = 0.31$, then $a_{OH} \approx 7.9$ gauss. A splitting of this magnitude would be on the verge of detection, and is probably an overestimate. (By the same argument, the doublet splitting for $\cdot OH$ should be about 30 gauss. Matheson and Smaller¹⁸ observed a doublet having $a = 10$ gauss after exposing ice and hydrogen peroxide to γ -rays. This is only detectable at 4° K and may well be due to hydroxyl radicals. If this is the case then our estimate of 7.9 for a_{OH} in $Me_2\dot{C}\cdot OH$ is too large.)

¹⁷ Bersohn, *J. Chem. Phys.*, 1956, **24**, 1066.

¹⁸ Matheson and Smaller, *ibid.*, 1955, **23**, 521.

No calculations concerning the way in which a for a given β -hydrogen atom will vary with θ have yet been published. Earlier, we assumed that if a C-H bond was fixed in a direction perpendicular to the nodal plane of the unpaired electron then it would give a splitting equal to that of a free β -hydrogen atom.⁹ It was also assumed that the interaction from a C-H bond at 30° to the plane would be negligible. These assumptions were arbitrary, and may be incorrect. On a semi-intuitive basis one might guess that the interaction would follow a $\cos^2 \theta$ law. If that were so, then, the interaction for a hydrogen lying at 90° to the nodal plane ($\theta = 0$) being taken as 1, the relative values for $\theta = 30^\circ$, 60° , and 90° will be 0.75, 0.25, and zero. In order to relate these relative values to experiment a value for a "free" hydrogen atom is required. It can be shown that if the three hydrogen atoms in a methyl group make angles θ_1 , θ_2 , and θ_3 to the normal, then $\cos^2 \theta_1 + \cos^2 \theta_2 + \cos^2 \theta_3 = 1.5$. Thus the net interaction for three equally interacting β -hydrogen atoms is 1.5, which gives a value of 0.5 for each.

If this argument is true, then the interpretation of the 9-line spectrum for poly(methyl methacrylate)⁹ requires revision. The spectrum, assigned to the radical $R\cdot\text{CH}_2\cdot\dot{\text{C}}\text{Me}\cdot\text{CO}_2\text{Me}$, consists of 5 lines ($a = 21$) together with 4 lines ($a = 21$) which are somewhat weaker. The splitting between adjacent lines is thus 10.5. In order to interpret this spectrum, two structures were proposed, one having the group R at 90° to the plane (which contains the methyl and methylene carbon atoms together with the methoxycarbonyl group) and the other having one of the C-H bonds at 90° to the plane. In each case the methyl group is considered to be freely rotating, and hence $a_{\text{Me}} = 21$. However, if the $\cos^2 \theta$ dependence is even approximately correct, these structures would not combine to give the required spectrum. The former has two equivalent hydrogen atoms at 30° to the plane ($\theta = 60^\circ$). Relative to the average value of 21, the hyperfine splitting constant will be $21 \times 0.25/0.5 = 10.5$. Therefore each of the four lines from the methyl group will be split into three, giving a final spectrum of nine lines, $a = 10.5$ with relative intensities 1, 2, 4, 6, 6, 6, 4, 2, 1. The number of lines and the splitting are correct, but the relative intensities are wrong, since in the experimental curve the ratios are approximately 3, 2, 12, 6, 18, 6, 12, 2, 3.

The latter structure can be rejected since one of the two methylene-hydrogen atoms (H_1) will have $a_1 = 21 \times 1/0.5 = 42$, and the other (H_2) will have $a_2 = 21 \times 0.25/0.5 = 10.5$. This will give a spectrum of 12 lines having $a = 10.5$.

A model of this radical reveals, not only that rotation about the C-C bond will be extremely difficult, but also that the least hindered conformation will be one in which the bulky R group is at 90° to the plane. This structure alone is not satisfactory, as shown above. However, if one allows a twist of 15° to either side of this symmetrical arrangement, then two other mutually equivalent structures will also contribute, in which H_1 is at 15° and H_2 at 45° to the plane (or *vice versa*); H_1 will now give a negligible splitting, since $a_1 = 21 \cos^2 75^\circ/0.5 = 2.8$. H_2 will have $a_2 = 21 \cos^2 45^\circ/0.5 = 21$. These structures will therefore give rise to a simple 5-line spectrum having $a = 21$. If each position is of equal importance, the final spectrum will consist of 9 lines having relative intensities 3, 2, 12, 6, 18, 6, 12, 2, 3. This result is very close indeed to the experimental spectrum.

It is tempting to apply this concept of hindered rotation to some of the simple radicals studied in Part II. In general, the probability that a β -hydrogen atom will not give an averaged interaction will decrease in the order tertiary > secondary > primary, for two reasons. First, the other groups are certain to be more bulky than hydrogen, and secondly, the amount of twist required to obtain equivalence decreases in this order. A single C-H bond must be twisted through 90° to pass from maximum to minimum interaction. In contrast, a methyl group needs to be rotated through only 30° .

We conclude that a methyl group is least likely to display differences due to hindered rotation. An attempt has been made to explain the 6-line spectrum sometimes observed for radicals from propan-2-ol¹ in terms of this principle of hindered rotation. The value $a = 22$ is assigned to six hydrogen atoms and $a = 9$ to the seventh.⁸ If our reasoning is

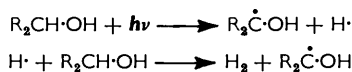
even approximately correct, even if the rotation of a methyl group was hindered in this way, it is extremely hard to understand why one hydrogen atom should have its interaction reduced so drastically whilst the other two still give an averaged interaction. It is suggested⁸ that this process is important at 77° K but insignificant at 110° K, at which temperature the normal 7-line spectrum for propan-2-ol is obtained. However, we have observed the 7-line spectrum at 77° K.

One radical in which restricted rotation should play an important part is that derived from cyclohexanol. It is certainly possible to build up the observed 6-line spectrum² by use of the above principle on the basis that the radical is formed by loss of an α -hydrogen atom. However, the observed spectrum is so poorly resolved that relative line intensities cannot be measured and therefore detailed discussion is not warranted. The alternative, that attack is on γ - or δ -hydrogen, would certainly explain the presence of 6 lines, but the observed splitting of 20 gauss is at least 5 gauss too small for this postulate.

III. *Secondary Radical Reactions in Solids.*—Intense electron-spin resonance spectra are often obtained from organic solids after exposure to high-energy radiation, and these spectra are often remarkably simple. This simplicity is at first sight surprising because, in general, two different paramagnetic species are to be expected, and their superimposed spectra would normally give a complex pattern.

It is often suggested, by analogy with the better understood behaviour of ionic crystals, that electrons, detached during the primary process, are trapped elsewhere in the solid. Two difficulties arise: first, the trapped electrons should give rise to an electron-spin resonance signal, and secondly, a radical positive ion rather than a neutral radical is the second product. It is possible that the electron-spin resonance spectrum from the trapped electrons is broad and escapes detection, but it is by no means clear why this should be. We have obtained spectra with line-widths (between points of maximum slope) of the order of 4 gauss from glasses formed by freezing blue solutions of alkali metals in ammonia,¹⁹ and it is hard to understand what features in simple organic solids would be able to increase this width so drastically.

The remarkable similarity between spectra obtained from neutral radicals formed by abstraction of hydrogen by hydroxyl radicals and radicals formed from the same organic compounds by high-energy radiation leaves little doubt that they are derived from identical radicals. The spectra obtained from methanol, ethanol, propan-1-ol, and propan-2-ol, for example, are all very similar whatever method is used.^{2,7} Since hydroxyl radicals are able to abstract hydrogen from alcohols at 77°,^{2,20} it is reasonable to postulate that other highly reactive radicals will also be able to do so. On this basis, one can formulate the reaction for alcohols as follows:



Reactions such as these may occur before the radicals have lost their excess of energy possessed at the time of formation, in which case the final products will be close neighbours. If this is so, an explanation can be found for a remarkable difference in the optical properties of alcohol glasses containing trapped alcohol radicals. As noted earlier,²⁰ when solutions of hydrogen peroxide in primary and secondary alcohols are irradiated a violet colour is observed due to an absorption band of low intensity with a maximum absorption at about 5000 Å. Alger *et al.*⁷ find very similar visible spectra to ours, but there is one marked difference. Colours formed during high-energy irradiation are rapidly bleached by visible light, but similar colours obtained by peroxide photolysis are unaffected by visible light. Both procedures give paramagnetic glasses displaying nearly identical electron-spin resonance spectra. The photobleached glasses still give the same spectra, not markedly

¹⁹ Clark and Symons, to be published.

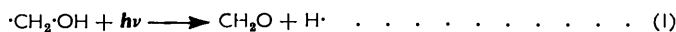
²⁰ Symons and Townsend, Part I, *J.*, 1959, 263.

diminished in intensity, and, because of this, Alger *et al.*⁷ justifiably conclude that the radical which gives rise to the electron-spin resonance spectrum is *not* the species responsible for the violet colour. However, for a variety of reasons, we have concluded the reverse, namely, that free radicals having the general structure $R_2\dot{C}\cdot OH$ are responsible for both the electron-spin resonance and the visible spectra.²⁰

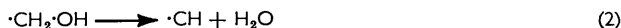
We have already postulated²⁰ that if radicals are formed in pairs, those in each pair may sometimes be so close together that the net magnetic field experienced by either radical is equal to the applied field plus a small increment from the neighbouring radical. This extra field will be a function of the distance between the paired radicals and the orientation of the pairs relative to the direction of the applied field. Since both these parameters are certain to vary over a wide range this interaction could broaden the resonance signal beyond the limits of detection.

Such magnetic interaction would not appreciably alter the visible and ultraviolet spectra of the radicals concerned. A situation could therefore arise in which a large number of radicals, giving rise to an intense violet colour, are paired off in such a way that no electron-spin resonance spectrum can be detected. At the same time a relatively small number of radicals are envisaged as being trapped singly so that no modification of the applied field occurs. The effect of these radicals will therefore be cumulative and a detectable electron-spin resonance spectrum should result. Finally, since most of these radicals are paired closely together, excitation by visible light could so dispose the radicals that recombination or disproportionation takes place: this would result in a great decrease in visible absorption but the electron-spin resonance absorption would be unaffected or become better resolved. The small specimens used by Alger *et al.*⁷ are sometimes so deeply coloured that they appear black, and yet the intensity of the electron-spin resonance spectrum is such that on a comparable scale, our specimens would probably seem colourless. Accordingly, it is postulated that radicals produced by hydroxyl-radical attack are not sufficiently close to interact magnetically. This theory is speculative but does seem to account for results which otherwise appear to be mutually contradictory.

Two other examples in which light excitation may lead to further reaction will be considered. The first is also drawn from the work of Alger *et al.*⁷ When an irradiated methanol glass is exposed to intense ultraviolet light the triplet attributed to $\cdot CH_2\cdot OH$ is lost, and a doublet with a splitting of 136 gauss appears instead. No explanation of this phenomenon has been offered. It seems likely that the original radicals are undergoing photolysis, and two modes of decomposition seem reasonable:



or



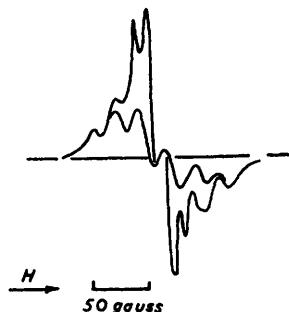
We would not expect that hydrogen atoms would be trapped under these conditions, but rather, that they would attack methanol to re-form the radical $\cdot CH_2\cdot OH$. Accordingly, it is suggested that the radical $\cdot CH$ is the species giving rise to the doublet. The splitting of 136 gauss is surprisingly large, but is not out of the question since the structure of this intermediate is very different from the radicals so far considered. The doublet is remarkable also because it is asymmetric, one band being much broader than the other. Recently McGarvey²¹ has applied a theory proposed by McConnell²² to explain a similar phenomenon found for solutions of copper chelates. This theory is based upon the supposition that the complex is tumbling, the asymmetry in line widths being a function of the rate of tumbling and the anisotropy of the resonance. The $\cdot CH$ radical might well be small enough to be moving in this way even in a solid at low temperature, in which case the asymmetry in hyperfine lines could be explained by the same theory.

²¹ McGarvey, *J. Phys. Chem.*, 1957, **61**, 1232.

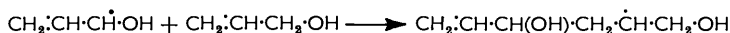
²² McConnell, *J. Chem. Phys.*, 1956, **25**, 709.

The other example of a light-induced secondary reaction is drawn from the effect of prolonged irradiation (3650 Å) upon the electron-spin resonance spectrum of radicals from allyl alcohol, $\text{CH}_2\text{:CH}\cdot\text{CH}\cdot\text{OH}$. The normal spectrum is a quartet having $a \approx 13$ gauss. However, on prolonged irradiation further lines appear on the edges with a splitting of about 24 gauss. A typical spectrum is shown in the Figure, together with a postulated 6-line spectrum, having $a \approx 24$ (broken line). The radical $\text{CH}_2\text{:CH}\cdot\text{CH}\cdot\text{OH}$ is yellow²⁰

First derivative of the electron-spin resonance spectrum from photolysed solid solutions of hydrogen peroxide in allyl alcohol, after prolonged irradiation.



and hence will certainly absorb in the 3650 Å region. It is postulated that light excitation renders the radical sufficiently reactive to be able to add to a neighbouring alcohol molecule:



(the alternative of attack on allylic hydrogen would lead to no net change). We would predict a spectrum of 6 lines for this radical, and estimate $a_{av} \approx 25.5$.

Fujimoto and Ingram⁸ have also observed this phenomenon, but suggest that the new lines which appear on the edges of the original spectrum are part of a superimposed 5-line spectrum. According to our measurements, this spectrum would have $a_{av} \approx 30$ gauss, which is very large. They suggest⁸ that the species responsible is a diradical formulated as



We cannot understand why a light-induced approach of radicals should stop, when a minute continuation would give a stable molecule. However, although the proposed structure is somewhat obscure, the unpaired electrons still appear to be in molecular orbitals covering the whole of each molecule, in which case a 7-line spectrum having $a \approx 13$ should result (provided that the diradical nature of the species was such that it would in fact give rise to an isotropic spectrum having a g -value of 2.00, and no zero-field splitting).

Conclusion.—Many of the concepts considered are undoubtedly extreme oversimplifications of the truth. Nevertheless it is hoped that, at least in some instances, they may lead towards a better understanding of a complex subject.

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