Recent Applications of Electron Spin Resonance in Chemistry *

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Summary

Free radicals, which are molecular fragments having odd, unpaired electrons, may be detected by observing transitions between the energy states corresponding to the parallel and anti-parallel orientations of the unpaired electron in a magnetic field. This is the technique of Electron Spin Resonance. Interaction of the unpaired electron with other magnetic nuclei in the radical, such as protons, produces e.s.r. spectra having considerable hyperfine structure. Analysis of the hyperfine structure often allows identification of the radical and gives information about the unpaired spin density distribution. The study of oriented radicals, trapped in the lattices of single crystals, gives additional information about their structure. Electron resonance has been used to investigate free radicals produced by the photolysis of chemical systems by visible and ultra-violet radiation, particularly in low temperature glasses. Occluded radicals and high energy radiation damage in polymers have been studied. The technique has also been applied to kinetic measurements involving shortlived free radicals. Examples illustrating these applications of e.s.r. in chemistry are discussed.

Before we start our discussion of its applications, let us briefly remind ourselves about the principles of electron spin resonance (or e.s.r.).

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A free electron has a magnetic moment. The measurable components of the moment in the direction of an applied magnetic field are $g\beta s$, where s is the spin quantum number with the values $\pm \frac{1}{2}$, β is the Bohr magneton and g is a factor, analogous to the spectroscopic splitting factor, which has the value 2.0023 for the free electron. In the magnetic field H the magnetic moment of the electron will be aligned parallel or anti-parallel to the magnetic field and the two energy levels as a function of field are shown in Fig. 1.

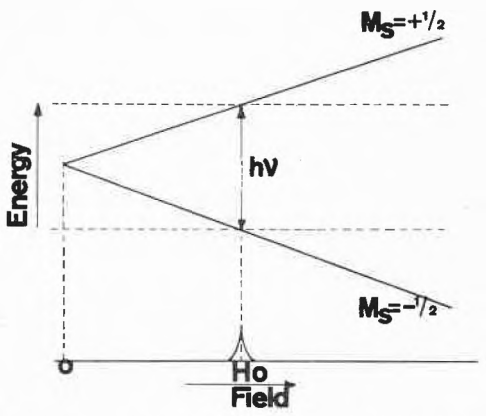


Fig. 1. Energy levels of an electron in a magnetic field

The energy difference between the two levels at a given field H_0 is $g\beta H_0$. If electromagnetic radiation of frequency ν such that

$$h\nu = g\beta H_0$$

is supplied to a system of free electrons, transitions between the two electron energy levels will be induced. Because of the Boltzmann population distribution between the two levels the absorption of radiation quanta by electrons in the lower level will exceed spontaneous emission from the upper level and there will be a net absorption of radiation energy. This is the phenomenon of electron spin resonance.

A free radical may be defined as a molecular fragment having an odd number of electrons and since the odd electron will be unpaired in its orbital the radical will be paramagnetic having a magnetic moment by virtue of the magnetic moment of this electron. Such radical species, like the methyl radical, are usually reactive chemically but they can frequently be stabilized under suitable conditions for study by e.s.r. and other techniques.

In free radicals, the orbital angular momentum of the unpaired electron orbital is nearly quenched so that, as a first approximation, the unpaired electron may be considered as "free". If therefore, a sample containing free radicals is placed in a magnetic field the magnetic moments of the unpaired electrons will align themselves parallel and antiparallel to the field with energy levels as in Fig. 1. Thus if electromagnetic radiation of frequency $g\beta H_0/h$ is supplied to the sample there will be a net absorption of energy and a single absorption line spectrum will be obtained. The single line e.s.r. spectrum from charred carbon samples is well-known and shows that they contain free radicals. In practice, with a field of 3200 gauss resonance occurs in the microwave region at about 9000 Mc/s. As a matter of experimental convenience it is usual to keep the microwave frequency constant and to vary the magnetic field in order to obtain the resonance condition. The spectra are normally recorded as the first derivative of the absorption line with respect to the field.

If we consider radicals containing a nucleus with a magnetic moment, for example the proton in the free radical $(CO_2H)\dot{C}H(CO_2H)$ obtained by irradiating malonic acid,[1] we find that the electron energy levels are more complex since the proton, which has a spin of ½, also has a magnetic moment which is parallel or antiparallel to the magnetic field. From the spin Hamiltonian, developed by ABRAGAM and PRYCE,[2] we deduce the energy level scheme shown in Fig. 2. M_s is the magnetic quantum number of the electron having values $\pm$ ½ and M_I for the proton is also $\pm$ ½. The selection rules for the transitions are:

$$\Delta M_s = \pm 1$$
$$\Delta M_I = 0$$

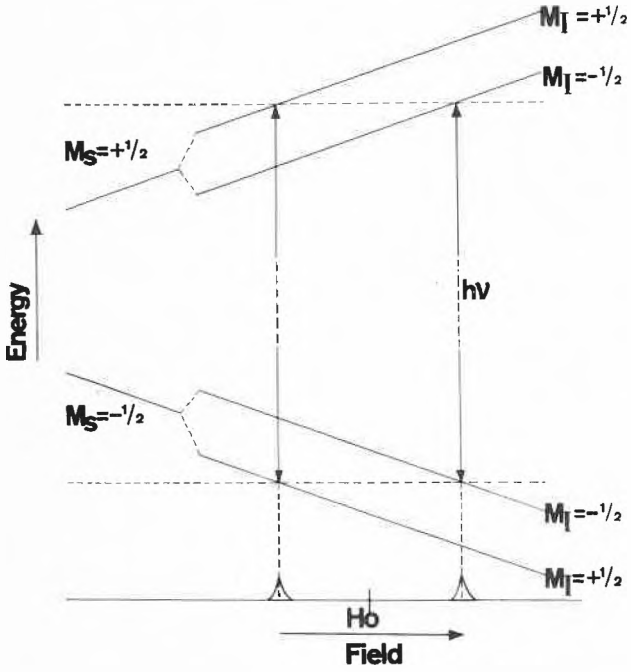


Fig. 2. Energy levels of an electron interacting with one proton in a magnetic field

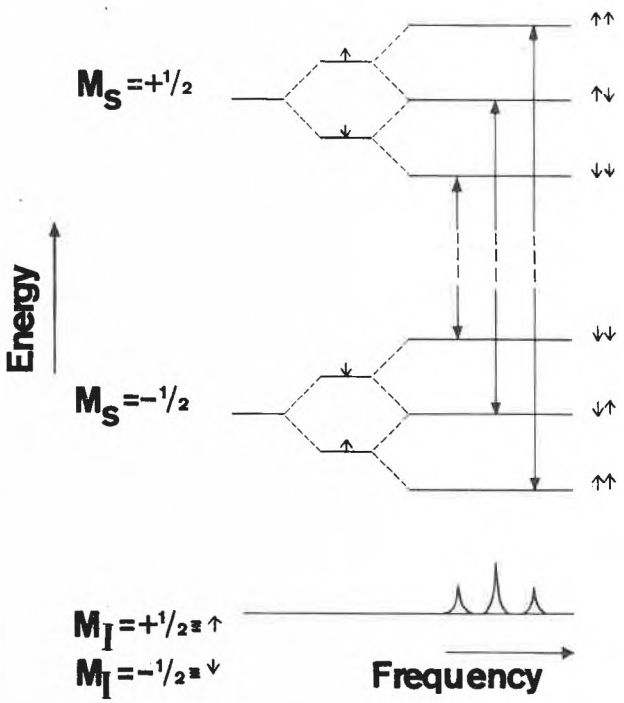


Fig. 3. Energy levels of an electron interacting with two equivalent protons in a fixed magnetic field

[1] H.M. MCCONNELL, C. HELLER, T. COLE and R.W. FESSENDEN, *J. Amer. Chem. Soc. 82* (1960) 766.
[2] A. ABRAGAM and M.H.L. PRYCE, *Proc. Roy. Soc. A 205* (1951) 135.

We therefore obtain two transitions, as shown, and two absorption lines of equal intensity are observed, the spectrum being said to show hyperfine structure. The separation between the hyperfine lines, or "splitting" which is usually measured in gauss, is important since the magnitude of the splitting depends on the unpaired electron density at the magnetic nucleus.

Turning to radicals containing two equivalent protons, for example dichlor-*p*-benzosemiquinone, the energy level diagram is shown in Fig. 3.

The effect of two protons is to split each of the original electronic energy levels into three hyperfine levels. As the protons are equivalent there are two combinations of $(+\frac{1}{2}, -\frac{1}{2})$ for their magnetic quantum numbers with the result that the middle level of each group of hyperfine levels is degenerate. Applying the selection rules we find a spectrum of three equally spaced lines with twice the intensity for the transition between the doubly degenerate levels. Continuing this analysis it can be shown that radicals with three equivalent protons will give a four line spectrum with relative intensities of 1:3:3:1 and in the general case n equivalent protons produce a spectrum of $n+1$ equally spaced lines with a binominal distribution of intensities. In Fig. 4 we see the five line spectrum from the four equivalent protons in *p*-benzosemiquinone. The lines have intensities of 1:4:6:4:1 within experimental error.

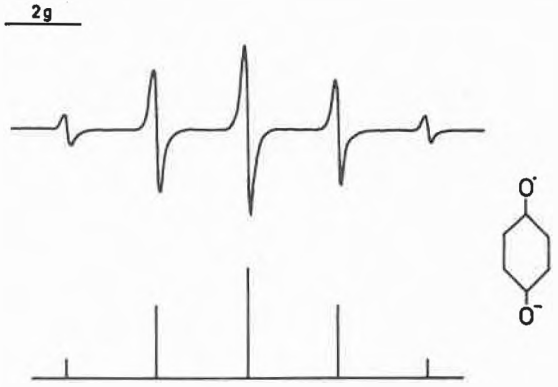


Fig. 4. First derivative e.s.r. spectrum of *p*-benzosemiquinone in alkaline solution

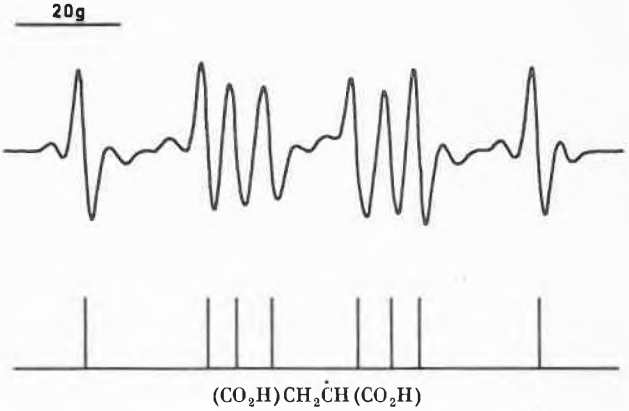
If the unpaired electron couples with non-equivalent protons, each proton will have its own coupling constant and in general n non-equivalent protons will produce a spectrum with 2^n hyperfine lines.

Fig. 5 shows the spectrum from the radical

$$(CO_2H)CH_2\dot{C}H(CO_2H)$$

in irradiated succinic acid.[3] The three hydrogens couple unequally giving an eight line spectrum, the splittings from the carboxyl hydrogens being too small to be detected.

[3] C. Heller and H. M. McConnell, *J. Chem. Physics 32* (1960) 1535. D. Pooley and D. H. Whiffen, *Mol. Physics 4* (1961) 81.



$(CO_2H)CH_2\dot{C}H(CO_2H)$

Fig. 5. First derivative spectrum of the radical $(CO_2H)CH_2\dot{C}H(CO_2H)$ in γ-irradiated succinic acid

Hyperfine structure is also produced by nuclei having spins greater than ½. Any nucleus with a spin I has $2I+1$ allowed energy levels in a magnetic field and transitions having $\Delta M_I = 0$ between the two sets of levels corresponding to $M_s = \frac{1}{2}$ and $M_s = -\frac{1}{2}$ results in $2I+1$ hyperfine lines with equal intensities. The deuteron which has a spin of 1, gives rise to a triplet hyperfine structure. This can be of practical importance since the splitting due to a particular proton can be identified by deuterium substitution in the free radical, changing the hyperfine doublet due to the proton into a triplet.

From these examples it is clear that the hyperfine structure of e.s.r. spectra tells us with which magnetic nuclei the unpaired electron couples and from this information we may often deduce the nature and structure of the radical involved. Furthermore it gives us details of the probability distribution of the unpaired electron. Fermi[4] showed that the isotropic splitting from a magnetic nucleus is proportional to $\psi^2(0)$, the probability density of the unpaired electron at the nucleus and this is non-zero only for s wave functions. For example the hyperfine splitting for the hydrogen atom having a $1s$ electron orbital is 509 gauss[5] so that the percentage $1s$ character of the unpaired electron orbital at a particular hydrogen in a free radical is given by the ratio $A/5.09$ where A is the observed proton splitting.

Free Radicals in Solution

A rich application of the e.s.r. technique has been the study of the radical ions of aromatic hydrocarbons in solution. The electron affinity of many hydrocarbons is such that in contact with alkali-metal in an inert solvent, such as dimethoxy-ethane, negative ions are formed

$$M + Na \rightarrow M^- + Na^+$$

The negative ions, having unpaired electrons, are paramagnetic and generally show complex hyperfine structure in their spectra, the naphthalene negative ion being

[4] E. Fermi, *Z. Physik 60* (1930) 320.

[5] C. K. Jen, S. N. Foner, E. L. Cochran and V. A. Bowers, *Physic. Rev. 104* (1956) 846.

typical. By symmetry there are two sets of four equivalent protons in naphthalene, each of which will give rise to five hyperfine lines making a total of 5×5 or 25 lines. All twenty five lines have been resolved and this proton interaction accounts for the number and intensity distribution of the hyperfine spectrum, but it is rather surprising that any hyperfine structure should be seen at all since the unpaired electron is in a π-orbital which has a nodal plane through the molecule and hence no interaction with the hydrogen nuclei, which are in the plane, seems possible. Theoretical calculations[6] show that some mixing of the π-orbital with the σ-bonding electron system by an atomic exchange coupling mechanism is allowed (known as "configuration interaction") resulting in a finite probility for finding the electron in the region of the ring hydrogen atoms. The negative ions of a large number of aromatic hydrocarbons have been studied and are of importance because the proton hyperfine splitting A is related to unpaired electron density φ on the adjacent carbon atom by the relation proposed by McConnell[6]

$$A = \varphi Q \, .$$

Q is a constant having the value 22.5 gauss which is obtained from the benzene negative ion[7] for which the unpaired electron is symmetrically distributed round the ring. This relationship has been tested for many hydrocarbons[8] and has been found to be generally applicable with variations in Q up to 28 gauss. Thus from the measured proton splittings of the e.s.r. spectra the distribution of the unpaired electron orbital on the carbon skeleton of the molecule can be derived.

[6] H.M.McConnell, *J. Chem. Physics 24* (1956) 632 and 764.
[7] S.I.Weissman, T.R.Tuttle and E. de Boer, *J. Physic. Chem. 61* (1957) 28.
[8] A.Carrington, F.Dravnieks and M.C.R.Symons, *J. Chem. Soc. 1959*, 947.

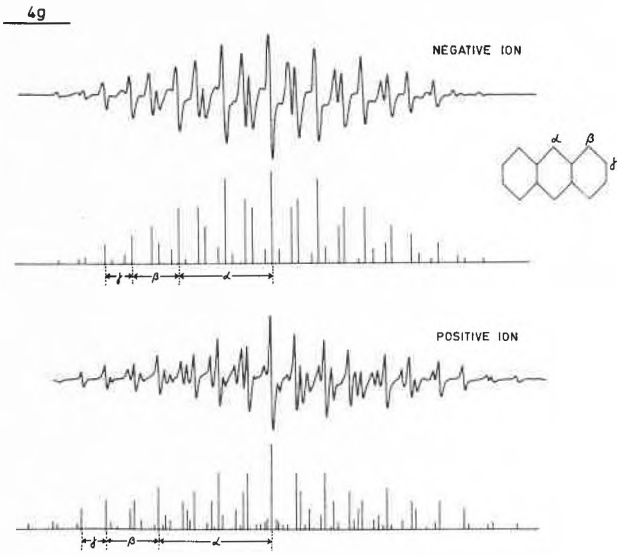


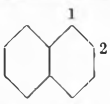
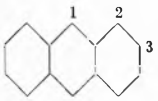
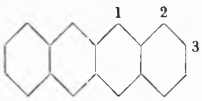
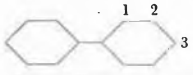
Fig. 6. Electron resonance spectra of the negative and positive ions of anthracene

When the hydrocarbons are dissolved in sulphuric acid very similar hyperfine spectra are obtained and in Fig. 6 we see the anthracene spectrum. These spectra are attributed to the positive ions formed by loss of one electron in sulphuric acid. Evidence for this assignment is the marked similiarity between the pairs of spectra for different hydrocarbons. Theoretically the positive and negative ion spectra should be identical[9] and the e.s.r. results show the electron distribution to be very similar in both ions.

The unpaired electron density distribution given by such measurements is very detailed information about a particular electron orbital and this may be compared

[9] S.I.Weissman, E. de Boer and J.J.Conradi, *J. Chem. Physics 26* (1957) 963.

Table 1: Comparison of theoretical unpaired electron densities with experimental values derived from the relation $A = \varphi Q$, for hydrocarbon radical-ions

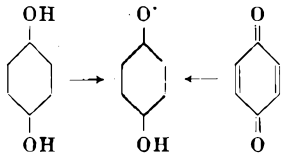
Radical ion		Unpaired electron density on ring carbons	carbon 1	carbon 2	carbon 3	Reference
	− ve	(m) *	0.213	0.079		11
		(c)	0.181	0.069		
	− ve	(m)	0.242	0.119	0.068	8
		(c)	0.192	0.096	0.047	
	+ ve	(m)	0.289	0.135	0.061	8
		(c)	0.192	0.096	0.047	
	− ve	(m)	0.185	0.065	0.051	8
		(c)	0.148	0.056	0.034	
	+ ve	(m)	0.220	0.074	0.045	8
		(c)	0.147	0.056	0.034	
	− ve	(m)	0.109	0.017	0.218	11
		(c)	0.090	0.020	0.158	

* (m) = measured (c) = calculated.

with the results of theoretical calculations. In table 1 are listed some typical results given by molecular orbital theory calculations and we see that the agreement with the electron resonance results is quite statisfactory.

The e.s.r. spectra of substituted aromatic systems, such as 9,10-dimethylanthracene positive and negative ions in which the methyl hydrogens also give hyperfine splitting, have been accounted for by molecular orbital theory[10]. Recently the spectra of nitrogen heterocyclic radical ions such as pyrazine have been investigated[11] and a linear relation, similar to McConnell's for proton splittings, was found between the nitrogen splitting and the unpaired electron density on the nitrogen atom with a value of 25 gauss for the proportionality constant Q_N.

Another class of free radicals extensively studied in solution is the semiquinone type. Para-benzosemiquinone is easily produced by oxidation of hydroquinone or reduction of quinone.



In alkaline solution the semiquinone ion $\dot{O}\text{–}C_6H_4\text{–}O^-$ is observed and this radical, with four equivalent protons, has a well-resolved five line spectrum with a splitting of 2.37 gauss which is shown in Fig. 4. The unpaired electron in semiquinone occupies a π-orbital and the observed hyperfine structure is a result of σ–π configurational interaction as in the hydrocarbon ions. Because of the ease with which radicals are formed this type of compound has proved very convenient for studying the effects of side-groups in substituted semiquinones, such as the dimethyl *p*-benzosemiquinones, and the observed methyl hydrogen splittings are in satisfactory agreement with molecular orbital calculations.[12]

Free Radicals in Crystals

The coupling between the unpaired electron and a magnetic nucleus has isotropic (or Fermi) and anisotropic contributions. In solutions the anisotropic part is averaged to zero by tumbling motion of the molecules with the result that the hyperfine splitting constant of the nucleus is scalar. In a system of oriented radicals the variation of hyperfine splitting with change of the orientation of the radicals in the magnetic field can be studied. By high energy irradiation of single crystals of simple organic and inorganic materials, free radicals are produced which are trapped in the crystal lattice with essentially the same orientations of the parent molecules from which they are formed. McConnell and his co-workers[1] examined the free radicals in X-irradiated crystals of malonic acid—$(CO_2H)CH_2(CO_2H)$. The stable radical left after annealing the crystal is $(CO_2H)\dot{C}H(CO_2H)$, formed by loss of a hydrogen atom. The hyperfine structure due to the hydrogen attached to the central carbon consists of two lines, with a splitting which varies as a periodic function of angle as the crystal is rotated in the magnetic field. From the three sets of data obtained by measuring the splitting at small intervals during rotation of a crystal about three mutually perpendicular axes, which are usually chosen according to the symmetry of the crystal, the hyperfine coupling tensor of the magnetic nucleus may be derived.[13] From the measured tensor the hyperfine splitting for any given direction of the magnetic field with respect to the three chosen axes can be calculated. With the appropriate algebraic manipulation the diagonalized coupling tensor (that is, with zero off-diagonal elements) can be derived from the measured tensor and for malonic acid the diagonalized hydrogen coupling tensor was found to be:

$$\begin{vmatrix} 10.7 & 0 & 0 \\ 0 & 22.0 & 0 \\ 0 & 0 & 33.0 \end{vmatrix}$$

where 10.7, 22.0, 33.0 are the principal values of the tensor expressed in gauss. The maximum and minimum hyperfine splittings are given by the principal values 10.7 and 33.0. Since the direction cosines of the principal values referred to the axes of rotation of the crystal are also derived by diagonalization, their directions may be related to the known crystal structure of malonic acid and it was found that the direction of the principal value 10.7 gauss was parallel to the internal bisector of the angle between the methylene hydrogens in $(CO_2H)CH_2(CO_2H)$ while the direction of the value 22.0 gauss was normal to the plane of the three carbon atoms, both within experimental error. These are the directions expected for the $\dot{C}$–H bond and the carbon $2p$ orbital if the central carbon atom in the radical $(CO_2H)\dot{C}H(CO_2H)$ assumes sp^2 hybridization. Detailed theoretical calculations by McConnell and Strathdee[14] for an sp^2 hybridized free radical carbon $>$CH with the electron confined predominantly to the carbon $2p$ orbital showed that the large anistropy in the coupling can be explained by the dipole-dipole interaction between the magnetic moments of the proton and the electron. They predicted the smallest and intermediate principal values of the coupling tensor to be parallel to the $\dot{C}$–H bond and to the carbon $2p$ orbital, with values of 7.5 gauss and 24.6 gauss which are in satisfactory accord with experiment.

Examination of a γ-irradiated crystal of succinic acid[3] showed an eight-line spectrum (Fig. 5) indicating coupling of the electron with three non-equivalent hydro-

[10] J.R. Bolton, A. Carrington and A.D. McLachlan, *Mol. Physics* 5 (1962) 31.
[11] A. Carrington and J. dos Santos-Veiga, *Mol. Physics* 5 (1962) 21.
[12] R. Bersohn, *J. Chem. Physics* 24 (1956) 1066.
[13] D.H. Whiffen, *Free Radicals in Biological Systems*, Academic Press, 1961, p. 227.
[14] H.M. McConnell and J. Strathdee, *Mol. Physics* 2 (1959) 159.

gens in the radical $(CO_2H)CH_2\dot{C}H(CO_2H)$. Coupling tensors for each hydrogen were obtained. One tensor was found with principal values almost identical with those obtained for the malonic acid radical and this clearly belongs to the hydrogen attached to the free radical carbon (or α-hydrogen). The coupling tensors of the two methylene hydrogens (or β-hydrogens) were much less anisotropic because the larger distance between the β-protons and the carbon $2p$ orbital makes the dipole-dipole interaction less important. McCONNELL and HELLER[3] suggested that β-hydrogen splittings varied with the orientation of the methylene group with respect to the free radical carbon according to the expression $B\cos^2\vartheta$, where B is a constant and ϑ is the angle between the carbon $2p$ orbital and the C–H_β bond both projected on to the plane normal to the H_2C–$\dot{C}H$ bond. Using the isotropic β-hydrogen splittings (the average of the three principal values of each tensor) of 35.6 gauss and 28.6 gauss for succinic acid, B was found to be 42.8 gauss and a 5° twist of the plane of the carbon atoms $-CH_2-\dot{C}H-CO_2H$ from the symmetrical position with respect to the methylene group accounted for the difference in the two β-couplings.

Confirmation of the $B\cos^2\vartheta$ relationship was provided by the radical $CH_3\dot{C}HCO_2H$ formed in irradiated crystals of alanine.[15] At room temperature the methyl group is rotating making the three β-hydrogens equivalent with an splitting of 25.0 gauss. When the crystal is cooled down to 77 °K however, the rotation of the methyl group is quenched with the three β-hydrogens in non-equivalent crystallographic positions and with three separate hyperfine couplings which may be fitted to the $B\cos^2\vartheta$ expression with the value 49.3 gauss for B.

The radical $(CO_2H)CH_2CH_2\dot{C}H(CO_2H)$ was found in irradiated glutaric acid[16] and the eight line spectrum obtained showed that γ-hydrogen couplings from the extra methylene group are too small to be resolved in this type of radical. The detailed results for this crystal were similar to those for the succinic acid.

The examples we have considered of free radicals in solution and in crystals illustrate the considerable detail that may be obtained about the orbital of the unpaired electron. This is of great importance in theoretical chemistry since it provides a practical means of checking calculations and we have already noted the success of molecular orbital theory in explaining the spectra of aromatic ion-radicals in solution. This work is also very valuable in building up a background of well-established results which can be applied to other chemical systems where interpretation of the e.s.r. data is not unambiguous. For example, in polycrystalline or amorphous samples where the free radicals are randomly oriented, the spectra obtained are the average over all the random radical positions and if the hyperfine splittings have large anisotropies much detail may be blurred out in the average spectrum. Identification of radicals in such circumstances may be difficult and often requires isotopic labelling for confirmation.

[15] A. HORSFIELD, J. R. MORTON and D. H. WHIFFEN, *Mol. Physics 2* (1959) 159. I. MIYAGAWA and K. ITOH, *J. Chem. Physics 36* (1962) 2157.

[16] A. HORSFIELD, J. R. MORTON and D. H. WHIFFEN, *Mol. Physics 4* (1961) 169.

Free Radicals Trapped at Low Temperature

A number of highly reactive radicals, such as hydrogen atoms and NH_2 radicals, have been stabilized at low temperatures. One method used is to freeze the products of a gas discharge on to a sapphire rod[17] cooled to liquid helium temperatures which can then be inserted into a microwave cavity at low temperature. In this way the doublet spectrum of hydrogen atoms from a hydrogen discharge was observed and the hyperfine splitting of about 509 gauss measured.[5] The expected triplet hyperfine structure from the ^{14}N nucleus (with a spin of 1) was observed[18] with nitrogen atoms trapped by the same technique. NH_2 radicals were obtained by ultra violet photolysis of ammonia[19] in a matrix of solid argon at 4.2 °K. The well resolved nine-line spectrum obtained from the NH_2 radicals which are not regularly oriented in the argon matrix shows that their rotational motion is not quenched even at 4.2 °K.

Radicals have been obtained by ultra violet irradiation of compounds in rigid glassy solvents at higher temperature (~77 °K) in which the radical fragments separate and become trapped—in random orientations—after dissociation of the photolysed molecule. INGRAM *et al.*[20] obtained electron resonance spectra from u. v. irradiated compounds such as benzyl chloride in hydrocarbon glasses but radical yields are often low and the spectra complicated because of reaction between the primary radicals and solvent molecules. Where the primary radicals can react readily with the surrounding solvent molecules, large concentrations of secondary free radicals can be built up. For this purpose hydrogen peroxide is very convenient since it can be decomposed with 3650 Å radiation from a mercury lamp to give primary OH radicals which readily diffuse in a glass and produce secondary radicals by hydrogen abstraction.

Photolysis of a solution of hydrogen peroxide in isopropyl alcohol at 110 °K leads to free radical formation and an e.s.r. spectrum consisting of seven lines with a hyperfine splitting of 20 gauss and an approximate intensity distribution of 1:6:15:20:15:6:1 is observed.[21] This is undoubtedly due to the radical $(CH_3)_2\dot{C}OH$ which

[17] C. K. JEN, S. N. FONER, E. L. COCHRAN and V. A. BOWERS, *Physic. Rev. 112* (1958) 1169.

[18] T. COLE, J. T. HARDING, J. R. PELLAM and D. M. YOST, *J. Chem. Physics 27* (1957) 593.

[19] S. N. FONER, E. L. COCHRAN, V. A. BOWERS and C. K. JEN, *Physic. Rev. Letters 1* (1958) 91.

[20] D. J. E. INGRAM, W. G. HODGSON, C. A. PARKER and W. T. REES, *Nature 176* (1955) 1227.

[21] J. F. GIBSON, D. J. E. INGRAM, M. C. R. SYMONS and M. G. TOWNSEND, *Trans. Faraday Soc. 53* (1957) 914.

has six equivalent hydrogens from the two rotating methyl groups. The methyl hydrogens are β-hydrogens with essentially isotropic couplings so that a well-resolved seven line spectrum would be expected in a glass. The small hydroxyl-hydrogen splitting, which is likely to have considerable anisotropy,[13] is not resolved however and is probably responsible for the line widths of about 10 gauss. The reaction is thus:

$$H_2O_2 \xrightarrow{h\nu} OH + OH$$

$$OH + \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CHOH \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!\dot{C}OH + H_2O$$

Other radicals formed from alcohols in this manner have been reported[21] but the blurring of spectra by the anisotropy of the hyperfine splittings makes absolute identification of radicals difficult. The four line spectrum from a glass of allyl alcohol containing hydrogen peroxide[22] was attributed to the $CH_2{=}CH{-}\dot{C}HOH$ radical in which the α- and γ-hydrogens were considered equivalent and responsible for the four line spectrum, the β-hydrogen splitting being unresolved. A recent study[23] of oriented allyl-type radicals in a crystal of glutaconic acid suggests that this interpretation is correct for in the radical $(CO_2H)CH{=}CH{-}\dot{C}H(CO_2H)$ the α- and γ-hydrogens are equivalent. The isotropic splitting of 12.9 gauss derived from the coupling tensors is in good agreement with the splitting of 12 gauss measured for the allyl alcohol radical while the β-hydrogen splitting in the crystal is small (4 gauss) and such a small splitting would not be observed from radicals randomly oriented in a glass.

Ayscough and Thomson[24] have systematically examined a number of γ-irradiated glasses of alkyl halides at 77 °K and they showed that the primary effect of γ-rays is to form the parent alkyl radicals and this is in agreement with the results from radiolysis experiments at room temperature using product analysis techniques. They confirmed that careful analysis of the spectra from glasses is required not only because of α-hydrogen couplings but also because of the possible variation in β-hydrogen couplings from rigid methylene groups with orientation according to the $B\cos^2\vartheta$ expression.

It was observed by Alga, Anderson and Webb[25] that the triplet spectrum of $\dot{C}H_2OH$, formed by γ-irradiation of methyl alcohol at 77 °K, disappears under u. v. irradiation and is replaced by a doublet with a splitting of 130 gauss. Deuterium substitution proved this to be a hydrogen coupling and the large splitting indicates about 25% hydrogen 1*s* character for the unpaired electron orbital and it was shown by Symons *et al.*[26] who detected the spectrum in several different chemical systems that this is the formyl radical:

$$CH_2OH \xrightarrow{h\nu} CHO + H_2$$

A σ-orbital for the unpaired electron with a high unpaired electron density at the proton is predicted for the formyl radical and the large proton splitting observed by electron resonance confirms this.

Free Radicals in Polymers

The importance of free radicals in polymerization reactions is well-known. It is unfortunate that the steady-state concentrations of the propagating radicals during polymerization reactions are small and not easily detected by e.s.r. However the trapping technique at low temperature can be used to build up measurable radical concentrations, as in the photochemical studies we have discussed, and Ingram, Symons and Townsend[27] have examined radicals derived from various monomers in u. v.-irradiated glasses containing hydrogen peroxide.

With acrylonitrite a single broad line was obtained and the radical could not be identified but with methyl methacrylate and methacrylonitrile identical six-line spectra were observed and these are thought to be due to the radicals

$$HOCH_2\dot{C}(CH_3)(CO_2CH_3) \quad \text{and} \quad HOCH_2\dot{C}(CH_3)(CN)$$

formed by addition of hydroxyl radicals to the monomers, in which the five β-hydrogens are nearly equivalent. These radicals can initiate polymerization for on warming up the acrylonitrile glass, polymer is precipitated. It is a property of some polymer systems that

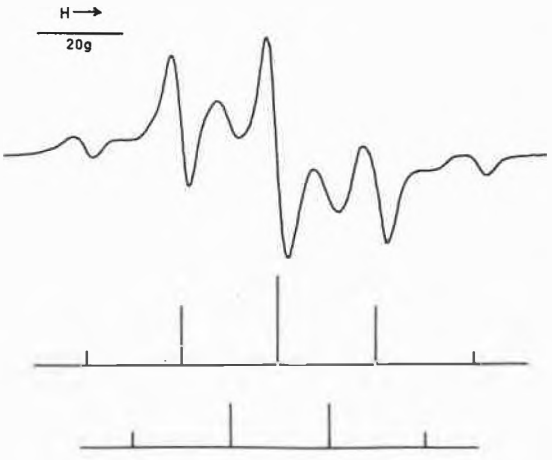
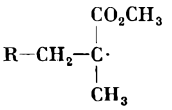


Fig. 7. First derivative spectrum of γ-irradiated polymethyl methacrylate

[22] M. Fugimoto and D. J. E. Ingram, *Trans. Faraday Soc. 54* (1958) 1304.
[23] C. Heller and T. Cole, *J. Chem. Physics 37* (1962) 243.
[24] P. B. Ayscough and C. Thomson, *Trans. Faraday Soc. 58* (1962) 1477.
[25] R. S. Alger, T. H. Anderson and L. A. Webb, *J. Chem. Physics 30* (1959) 695.
[26] J. A. Brivati, N. Keen and M. C. R. Symons, *J. Chem. Soc. 1962*, 237.
[27] D. J. E. Ingram, M. C. R. Symons and M. G. Townsend, *Trans. Faraday Soc. 54* (1958) 409.

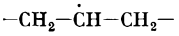
self-trapping of the free radicals occurs. During the heterogeneous polymerization of acrylonitrile the polymer is precipitated from solution and some of the propagating radical-chains become trapped in the solid polymer leading to enhanced free radical concentrations as high as 10^{17} per gram. The spectrum from polyacrylonitrile is a single broad line.[27] When occluded radicals in polymethyl methacrylate are examined however hyperfine structure is obtained,[27] as shown in Fig. 7.

These are two overlapping patterns of five and four lines with approximate intensity distributions of 1:4:6:4:1 and 1:3:3:1. Because exactly the same spectrum has been produced by γ-irradiation of the polymer[28] it has been argued that one radical is involved, which is



and that the two spectral patterns are due to two different geometrical configurations of the methylene group with respect to the p orbital of the free radical carbon. If one methylene hydrogen is in the nodal plane of the carbon p orbital there will effectively be four β-hydrogens producing the five line spectrum while if both methylene hydrogens are equally inclined to the nodal plane they will couple significantly less with the unpaired electron than the three methyl-hydrogens so that a spectrum of four broad lines results. WHIFFEN and his coworkers[29] suggested that the overlapping spectra are due to two different configurations of the methyl group which is non-rotating. BRESLER *et al.*[30] showed that on heating the irradiated sample, the quintet disappears faster than the quartet, suggesting that two different radicals are present. Clearly more work is needed before this well-known spectrum is thoroughly understood.

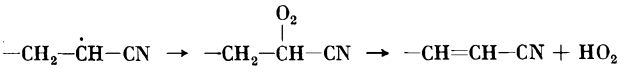
When polyethylene is γ-irradiated in vacuum a six-line spectrum obtains[31] with approximately a binominal intensity distribution and a hyperfine splitting of about 26 gauss. The most likely radical is



formed by loss of a hydrogen atom during irradiation. This interpretation assumes that the α- and β-hydrogens couple equally with the unpaired electron which means that all four β-hydrogens must be equally inclined to the carbon p orbital. Although single crystals of polymers, in which better resolution of the spectrum of the oriented radicals would be obtained, are not available for study some orientation of the long-chain molecules has been achieved by stretching the samples. When the stretched polyethylene samples were arranged with the direction of stretch perpendicular to the magnetic field it was found that the polymer molecules were sufficiently oriented for the difference between the α-hydrogen and the four β-hydrogens to become observable and a spectrum of five doublets was obtained,[31] with a doublet splitting of 13 gauss.

It has been suggested by LAWTON, BALWIT and POWELL[32] that these radicals occur in pairs, the hydrogen atom ejected from the first radical during irradiation abstracting hydrogen from another polymer molecule nearby leaving two adjacent radicals in a favourable position for crosslinking which occurs readily in irradiated polyethylene. A second radical in irradiated polythene with a five line spectrum,[32] which is more readily formed at low temperatures, is probably $R-CH_2-\dot{C}H_2$ formed by chain scission.

The effect of oxygen on free radicals in irradiated polymers is readily shown by e.s.r. Admission of oxygen in polyacrylonitrile leads to disappearance of the signal from the trapped radicals by a diffusion controlled process,[33] attributed to the formation of peroxy-radicals which then split off mobile HO_2 radicals which undergo destruction.



In contrast the radicals in polymers such as low density polyethylene[29] and teflon[34] (in which the radical $-CF_2-\dot{C}F-CF_2-$ is formed) are stabilized by forming peroxy radicals and recently CARRINGTON and STEIN[35] have demonstrated the formation of peroxy-radicals in polymethyl methacrylate irradiated with low X-ray doses although at high doses (> 1 Mrad.) the familiar 5 + 4 line spectrum which we have already discussed predominates.

High energy irradiation damage in polymers is of importance because of the possibility of producing crosslinking as in polyethylene and also because of the possibility of producing graft co-polymers by initiating polymerization of a second monomer at radical sites in an irradiated "host" polymer.[36] Electron spin resonance is clearly invaluable in such investigations.

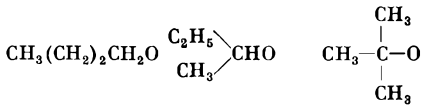
Kinetic studies

It is well established that many chemical reactions proceed with mechanisms involving free radical intermediates. It would be very useful to apply electron resonance techniques to kinetic studies since it would be possible to identify the radical intermediates from their hyperfine spectra and also to follow the reaction

[28] E. E. SCHNEIDER, M. J. DAY and G. STEIN, *Nature 168* (1951) 645.
[29] R. J. ABRAHAM, H. W. MELVILLE, D. W. OVENALL and D. H. WHIFFEN, *Trans. Faraday Soc. 54* (1958) 409.
[30] S. E. BRESLER, E. N. KAZBEKOR and E. M. SAMINSKII, *Vysokomolekularnye Soedinenia 1* (1959) 132.
[31] D. LIBBY, M. G. ORMEROD and A. CHARLESBY, *Polymer 1* (1960) 212.
[32] E. J. LAWTON, J. S. BALWIT and R. S. POWELL, *J. Chem. Physics 33* (1960) 395.
[33] C. H. BAMFORD, A. D. JENKINS, M. C. R. SYMONS and M. G. TOWNSEND, *J. Polymer Sci. 34* (1959) 181.
[34] H. N. REXROAD and W. GORDY, *J. Chem. Physics 30* (1959) 399.
[35] A. CARRINGTON and G. STEIN, *Nature 193* (1962) 976.
[36] A. CHAPIRO, *Ind. Plastiques Mod.* (Paris) 9/2 (1957) 34.

kinetics by monitoring the free radical concentrations. There are, however, two difficulties in doing this. The steady-state radical concentrations are often too low for detection by e.s.r. Secondly the line width of short-lived radicals is of the order of $1/2{,}8 \cdot 10^6 \Delta t$ gauss where Δt is the average lifetime—and if Δt is very short the spectral lines may be too broad to be detected. Despite these difficulties useful measurements are possible, as illustrated by the work of LANDGRAF and PIETTE[37] on the photolysis of alkyl hydroperoxides.

Normal-, secondary- and teriary-butyl hydroperoxides were photolysed with ultra-violet light. The irradiation was performed with the samples in the microwave cavity through slots in the walls so that the formation and decay of radicals could be monitored by means of the e.s.r. signal intensity. By working at low temperatures (175 °K to 273 °K) the rate of recombination of the free radicals was slowed down sufficiently to give large steady-state concentrations. The spectra were observed to be a triplet from the normal compound and a doublet from the secondary, both having splittings of about three gauss, and a single line from the tertiary hydroperoxide. This indicates the u.v. irradiation produces largely the alkoxy radicals:



Because the unpaired electron is largely localized on the oxygen atom only α-hydrogen interactions are observed. The technique of LANDGRAF and PIETTE was to cut off the radiation and follow the decay of the spectra with time. The decay curves fitted a scheme of second order kinetics with rate constants of the order of 10^5 litre/mole sec for recombination of the radicals. Measurement of rate constants at different temperatures gave an Arrhenius plot from which activation energies of about 4 Kcal/mole were obtained in agreement with results obtained by other workers using analytical techniques.

An analogous technique was used by FESSENDEN and SCHULER[38] who studied the radiolysis of liquid hydrocarbons by irradiation with 2.5 MeV electrons which were injected into the sample cavity through an axial hole through one of the magnet hole pieces. A well-resolved twelve line spectrum from liquid ethane is undoubtedly due to the ethyl radical $CH_3\dot{C}H_2$ since coupling of the unpaired electron with one group of three equivalent hydrogens and with another group two equivalent hydrogens were clearly shown in the hyperfine structure. A second order rate constant of 4×10^9 litre/mole sec was obtained for the recombination of radicals, and the activation energy was found to be negligible.

The recombination of oxygen atoms, which have a characteristic hyperfine spectrum,[39] was investigated using e.s.r. by KRONGELB and STRANDBERG.[40] They measured the concentration of oxygen atoms in the gas phase in a side-arm tube attached to a flow tube fed from an oxygen discharge at about 1 mm pressure. The oxygen atom concentration at any point in the side-arm depended on a balance between diffusion of oxygen atoms from the main gas stream and recombination of the atoms. It was found that the oxygen atom concentration decreased exponentially along the side-arm indicating a first order recombination on the surface of the tube and this conclusion was checked by varying the gas pressure and the tube diameter. Independant data obtained by switching off the discharge and following the decay of oxygen atoms at one point in the tube allowed both the oxygen atom diffusion coefficient and the rate of recombination of atoms to be evaluated. Results in agreement with non-resonance methods were obtained. In a second experiment the discharge gases were passed directly through a quartz tube in the cavity using high flow rates for which diffusion to the walls was of secondary importance. The oxygen atom concentration was measured at different distances along the flow tube from the discharge. In this case the dominant reaction was recombination of the atoms in third-body collisions as indicated by the second-order kinetics, with oxygen molecules as third bodies.

$$O + O + O_2 \longrightarrow O_2 + O_2$$

The rate constant found for this reaction was 5×10^9 litre^2/mole^2 sec. This result, which was obtained by observing the oxygen atom concentration directly, suggests that other atom recombination reactions could be usefully studied by e.s.r.

The flow technique can be conveniently used with solutions. If the reactants are rapidly brought together in a mixing chamber and passed through a tube in the microwave cavity, the free radical concentration at different stages of the reaction can easily be monitored by varying the rate of flow of the reaction mixture. In this way radicals with life times as short as 5 milliseconds can be measured. YAMAZAKI, MASON and PIETTE[41] used such a flow system to investigate the oxidation of hydroquinone and ascorbic acid by the enzyme peroxidase in the presence of hydrogen peroxide and by measuring the rate of formation of radicals as a function of substrate, enzyme and peroxide concentrations they were able to confirm the kinetic scheme of SAUNDERS and MANN.[42]

The triplet state

Molecules in the triplet state, having two unpaired electrons, are paramagnetic and should therefor be observable by electron spin resonance. For a long time the triplet state remained undetected by e.s.r., the reason

[37] W.C. LANDGRAF and L.H. PIETTE, *J. Chem. Physics 32* (1960) 1107.
[38] R.W. FESSENDEN and R.H. SCHULER, *J. Chem. Physics 33* (1960) 935.
[39] E.B. RAWSON and R. BERINGER, *Physic. Rev. 88* (1952) 677.
[40] S. KRONGELB and M.W.P. STRANDBERG, *J. Chem. Physics 31* (1959) 1196.
[41] I. YAMAZAKI, H.S. MASON and L.H. PIETTE, *J. Biol. Chem. 235* (1960) 2444.
[42] B.C. SAUNDERS and P.J.G. MANN, *J. Chem. Soc.* (1940) 769.

being that the large dipole-dipole interaction between the two unpaired electrons lifts the degeneracy of the three sub-levels of the triplet state in zero field, giving a zero-field splitting, and the resulting anisotropy of the magnetic splitting in high fields is so large that in any system of randomly oriented molecules, the average electron resonance absorption line for transitions between adjacent triplet sub-levels, having $\Delta M_s = \pm 1$, is too broad to be detected. HUTCHINSON and MANGUM[43] used a system of oriented naphthalene molecules, incorporated in a single crystal of durene, and when the crystal was irradiated in the microwave cavity with ultra violet light at 77°K the triplet state signal was observed. VAN DER WAALS and DE GROOT[44] found that transitions between highest and lowest sub-levels of the triplet state, having $\Delta M_s = \pm 2$, are much less anisotropic and they were able to detect these transitions for naphthalene and other hydrocarbons in a glass at 77°K, while MCDOWELL *et al.*[45] were able to demonstrate energy transfer from the triplet state of benzophenone to that of naphthalene in a similar way. So far, however, there have been few triplet state measurements using electron resonance and more work in this field is to be expected.

[43] C. A. HUTCHINSON and B. W. MANGUM, *J. Chem. Physics 29* (1958) 952, and *34* (1961) 908.

[44] J. H. VAN DER WAALS and M. S. DE GROOT, *Mol. Physics 2* (1959) 233, and *3* (1960) 190.

[45] J. B. FARMER, C. L. GARDNER and C. A. MCDOWELL, *J. Chem. Physics 34* (1961) 1058.

Conclusion

Electron spin resonance will detect free radicals and its valuble feature is that it will detect small concentrations of paramagnetic radicals (as few as 10^{12} radicals in favourable cases) in the bulk of the diamagnetic chemical sample. Interaction between the unpaired electron and magnetic nuclei encompassed by its orbital gives rise to hyperfine structure which often serves to identify the radical and to characterise its electronic structure. The examples considered here illustrate the diverse applications of the technique. There are many other examples, among which may be mentioned the studies of colour centres in alkali halides, impurities in semiconductors and transition metal ions in crystals and in solution. Electron spin resonance has clearly become an established tool in chemistry and we may anticipate that its potentialities will be fully exploited in the future.