ELECTRON SPIN RESONANCE of STABLE FREE RADICALS

When the spin of an unpaired electron changes orientation in a magnetic field, the energy absorbed is a clue to the nature of the molecule (or fragment). By measuring field strength and the frequency of radiation causing the flip, chemists can use this relatively new phenomenon to identify radicals, measure coupling between electronic and nuclear spins and determine the influence of surrounding material. The author is Eugene Higgins professor of physical chemistry at Princeton University.

By John Turkevich

Electron spin resonance is a relatively new phenomenon in physics and chemistry while free radicals are substances long familiar to organic chemists. Electron spin resonance, discovered by the Soviet physicist Zavoiski in 1945, is the absorption of radiation in a magnetic field of certain definite strength by materials having unpaired electrons. The absorption has the characteristics of a resonance phenomenon because the differences in the energy levels of the unpaired electron or electrons due to the Zeeman splitting are sharp. This splitting is given by $g\beta H$ where g is the gyromagnetic ratio (equal to 2.0023 for "spin only" case), β the value of the Bohr magneton, and H the intensity of the magnetic field. On the other hand, this energy difference is equal to $h\nu$ where h is Planck's constant and ν is the frequency of the absorbed radiation. Equating these two conditions, we obtain the resonance condition in conventional units of $F = 2.80\ H$, with F being given in megacycles and H in oersteds. Such resonance absorption is observed in many chemical systems, transition metal ions, rare earth and actinide ions, conduction electrons, charred materials, radiation damaged materials, and the free radicals of the organic chemist. Not only can free radicals be detected with high sensitivity by electron spin resonance, but various aspects of this resonance absorption have given the chemist a powerful tool for the elucidation of the structure of organic molecules and of the mechanism of chemical reactions.

Free radicals are substances characterized by the presence of unpaired electrons. Stable free radicals are rare chemical species representing at most a tenth of a percent of all known stable chemical compounds. The million known compounds of organic chemistry and thousands of compounds of inorganic chemistry normally have an even number of electrons. Free radicals are usually considered to be compounds containing carbon atoms. Their existence was postulated in the first half of the nineteenth century when the chemistry of carbon compounds was formulated. At that time they were merely visualized as groupings of carbon, hydrogen, oxygen, or nitrogen atoms which behaved as units in organic chemical reactions much in the same way as atoms of chlorine, sodium, phosphorus, etc., behaved in inorganic reactions. This view was firmly established by the classical research of Liebig and Wohler on the benzoyl radical (1832). These German chemists showed that the essence of the oil of bitter almond consisted of benzaldehyde and that this material could be transformed into a variety of related compounds—benzoic acid, benzoyl chloride, benzoyl bromide, benzoin, benzoyl cyanide, benzoyl iodide, benzamide, ethyl benzoate—all containing a grouping of C_7H_5O which remained unchanged in the transformations and was called the benzoyl radical. This suggested that the reactions of organic chemistry are merely reshufflings of complex units of a number of atoms just as the reactions of inorganic chemistry are

reshufflings of individual atoms. The question then arose: Can these radicals be isolated in pure form just as atoms are isolated as elements? Attempts to isolate free radicals at the various centers of organic chemistry were unsuccessful during the nineteenth century. However, the concept of a radical was firmly established in the formalism of organic chemistry.

The search for free radicals was essentially abandoned when, in 1900, Moses Gomberg at the University of Michigan unexpectedly prepared the first free radical. Gomberg set out to prepare what was envisaged as an inert chemical-hexaphenyl ethane, $(C_6H_5)_3C-C(C_6H_5)_3$. Instead he obtained a highly reactive material which he proved by both chemical and physical methods to be the first example of the long-sought-for free radical $(C_6H_5)_3C-$. Its most marked property was its reactivity with oxygen. Unusual physical properties were the variation of its optical extinction coefficient and molecular weight with concentration of the hexaphenyl ethane in solution. Gomberg correctly interpreted these properties as due to the dissociation of the hexaphenyl ethane into two triphenyl methyl radicals in which the central carbon atom had a valency of three instead of the usual four. Though in this particular case the dissociation was only thirteen percent, soon afterwards other compounds were synthesized in which one or more of the fifteen hydrogen atoms of the triphenyl methyl were replaced by other groups such as CH_3, CH_3O, C_6H_5, F, Cl, NO_2, etc. These replacements had varying effect on the degree of dissociation of the free radical. Other free radicals containing monovalent oxygen and divalent nitrogen were also discovered and characterized. Organic chemists theorized concerning the nature of structural factors which determined the dissociation of a complex organic molecule into free radicals, and concerning the specific role free radicals played in chemical reactions. These speculations were sufficiently extensive to become chapters in treatises of organic chemistry.

In 1925, G. N. Lewis of the University of California, concerned as he was with the electronic formulation of valence, pointed out that free radicals must contain an unpaired electron and therefore should be paramagnetic. Static magnetic susceptibility measurements became an important tool for investigating free radicals. In 1928, F. Paneth used a mirror technique to show the transient existence of the long elusive methyl radical CH_3. Vapor of tetramethyl lead was passed in a hydrogen stream through a heated portion of a tube and produced, by dissociation, the methyl free radical which could be detected downstream by its ability to remove a thin cold film of lead previously deposited on the sides of the vessel. Disappearance of such a film was used as a criterion for the presence of free radicals, and the conditions of flow and temperature for such a disappearance permitted the characterization of the lifetime of the unstable free radicals. In the thirties and forties of this century optical and mass spectroscopic techniques were also developed for the study of free radicals. At the same time the role of free radicals in the chemical reactions was recognized.

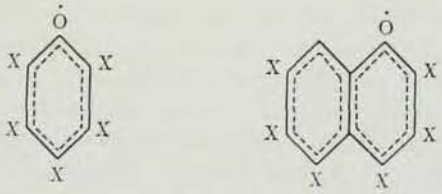
Since most compounds have an even number of electrons, chemical transformations as ordinarily observed involve an overall two-electron transfer process. However, a more careful analysis of the velocity of many reactions, particularly those of explosions, oxidation, polymerization, and biochemical processes, indicated that unstable free radicals must be the intermediates and that the two-electron transfer step previously postulated may be, in fact, a succession of one-electron transfer steps detectable if the means of detection is sufficiently sensitive. The exceptionally high sensitivity and the wealth of information provided by electron spin resonance makes this the technique of choice to obtain detailed information about the electronic structure of free radicals and to uncover a new world of chemical compounds—compounds whose lifetimes span the range from milliseconds to minutes, whereas the chemist previously had been concerned with molecules whose lifetimes in the pure state and shielded from radiation, were infinite.

Free radicals can be either stable or unstable. As a rule, stable free radicals are organic molecules of rather complicated structure which can be classified on the basis of the anomalous valence of one of their constituent atoms. Gomberg's triphenyl methyl $(C_6H_5)_3C$ is characteristic of trivalent-carbon-atom free radicals. Other radicals of this class can be made by replacing either the phenyl group C_6H_5 with other aromatic fragments, such as diphenyl $C_{12}H_9$, naphthyl $C_{10}H_9$, etc., or the hydrogens of these fragments with other atoms or groups. The number of such free radicals is limited by the patience of the synthetic chemist. Since the triphenyl methyl free radicals react with the oxygen of the air, they must be handled in an inert atmosphere. An interesting set of free radicals containing trivalent carbon are the anion free radicals (positively charged) or cation free radicals (negatively charged). An example of the anion free radical is the substance produced when anthracene reacts with potassium metal. Electron transfer

takes place, giving a positive potassium ion and a negative radical ion. The free electron transferred from the potassium atom joins the pool of the so-called "π" electrons located on each of the carbon atoms of the anthracene radical. Pi electrons are electrons not directly involved in the binding of the carbon atoms either to other carbon atoms or to hydrogen atoms. A π electron on one carbon atom may exchange with π electrons on other carbon atoms, thus becoming a member of a pool of delocalized π electrons.

A positive free radical can be made by reacting perylene with sulfuric acid. An electron is transferred to the sulfuric acid from the pool of π electrons of the perylene, making the latter a free radical with a positive charge.

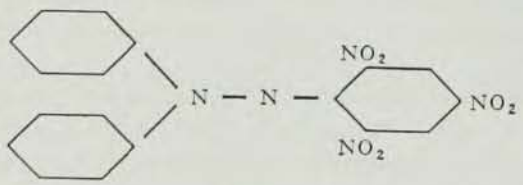
Free radicals containing monovalent oxygen are the phenoxyls or the naphthoxyls which are derived from phenols or naphthols, having the general formula:



where the X's may be hydrogen or other substituents such as CH_3, OCH_3, Cl, NO_2, etc. The hexagons are a conventional representation of an aromatic system with carbon atoms at the apices. The dotted orbits within hexagons represent the π electron system. Free radicals can also be obtained having monovalent sulfur in structures analogous to those producing monovalent oxygen free radicals.

Free radicals containing divalent nitrogen are derived from $R_2N{-}NR$ (the hydrazyls), the $R_2\dot{N}$, and the R_2NO (the azotosyl radicals); R is usually a C_6H_5 group in which one or more of the hydrogens is replaced by CH_3, OCH_3, Cl, NO_2, etc., groups.

The free radical par excellence for ESR studies has been DPPH diphenyl picryl hydrazyl,



This divalent nitrogen radical is readily made, and is completely dissociated in the solid state. It does not react chemically with oxygen at room temperature. It was discovered in 1922 by S. Goldschmidt. Its paramagnetic behavior and its ability to catalyze the ortho-para hydrogen conversion (into molecules with spins one or zero) were investigated in 1941 by Turkevich and Selwood. Measurements of its dielectric constant by Turkevich, Oesper, and C. P. Smyth in 1942 indicated the delocalization of the electron in the molecule. In 1950, its ESR resonance was determined by C. H. Townes and Turkevich in a communication appearing simultaneously with that of the Bell Telephone Laboratory results of A. N. Holden, C. Kittel, F. R. Merritt, and W. A. Yager. The ready availability of this radical, its stability, and the sharpness of its ESR resonance have made DPPH the favorite radical for study of ESR phenomena. In the subsequent discussion of the various features of the ESR techniques, it will be used as the main example.

One of the great advantages of the ESR technique is the number of observables that can be measured and these in turn used to characterize the free-radical system.

The sensitivity of detection is high. If the ESR spectrometer is operated in the *X*-band (9000 Mc/s) where most free-radical investigations are carried out, the limit is 10^{12} spins with a line width of one gauss and with a signal-to-noise ratio of five to one. The broader the resonance line, the more difficult it is to identify it in the noise. An amount as small as 10^{-9} *g* of DPPH has been detected. In *Q* band spectrometers (36 000 Mc/s) the limit of detection drops to 10^9 spins. A method of further decreasing the limit of detection is to scan through the resonance region repeatedly and to store the information in a digital computer. Since noise is random in character, any spurious peaks will be eliminated, and one can then detect signals much weaker than the overall noise.

The position of the lines in the ESR systems with unpaired electrons is determined by the *g* factor which, for a free atom, is given by

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)},$$

where *L*, *S*, and *J* are respectively the orbit, spin, and total quantum numbers. The "spin only" case gives a *g* equal to 2.000 and, when radiation field effects are considered, a *g* of 2.0023. The experimentally observed values for free radicals are just slightly above this value. For DPPH it is 2.0036. The deviation from the theoretical value is attributed to the spin-orbit interaction and the

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influence of excited states. The calculation of this configurational interaction is complicated but can be represented in approximate form by

$$g \cong 2\left[1 - \frac{\lambda}{\Delta}\right]$$

where Δ is the energy separation to the nearest upper excited state and λ is the spin-orbit energy. For organic free radicals, $\lambda < 0$ and Δ is large. The result is that g for free radicals is greater than two and differs from 2.0023, the value for the free electron, by two or three units in the third place if the free radical contains only light atoms such as H, O, C, D, N. For radicals containing heavier atoms such as S, which have a larger spin-orbit coupling constant, the g value differs from that of the free electron by two units in the second decimal place. Since the value of the g factor can be determined with great accuracy, the effects of substituents on the value of the g factor have been determined. Thus, introducing oxygen in the free radical (with a λ equal to 152 cm^{-1}) increases the value of the g factor of the free radical, while introducing a methyl group CH_3 (with λ for carbon of 28 cm^{-1}) decreases the value of the g. The g factor also varies with the temperature of measurement and the orientation of the free radical in the magnetic field.

Hyperfine structure appears in dilute solutions of free radicals, and is due to the interaction of the unpaired electron with whatever nuclei possess nuclear magnetic moments. If the spin of the nucleus is equal to I in a fixed magnetic field, it can assume $2I + 1$ orientations and consequently possess $2I + 1$ different energy sublevels. Since the orientations of the nuclei remain unchanged during an electronic transition, the nuclear interaction produces a hyperfine structure of $2I + 1$ lines with a constant separation between the lines. In free radicals, the unpaired electron moves in a highly delocalized orbit which may embrace a number of nuclei possessing magnetic moments. Each one of these nuclei will interact with the unpaired electron to produce a hyperfine splitting. The final spectrum can be quite complicated. Most free radicals, however, show one of two types of interactions. In one type the interaction with one nucleus of spin I_1 is much larger than that with another nucleus of spin I_2. The hyperfine structure will consist of $2I_1 + 1$ well separated lines due to the strong interaction, while each of these is split into $2I_2 + 1$ super-hyperfine lines due to the weaker nuclear interaction.

In the second case, the interaction is equally strong with n identical nuclei of spin I. This results in a hyperfine structure of $2nI + 1$ lines with a maximum at the center and a symmetrical intensity of lines about the center. If the nuclei are equivalent protons, the hyperfine structure will consist of $n + 1$ equally spaced lines with an intensity distribution which follows the law of binomial coefficients.

DPPH in dilute solution shows a structure of five lines with a ratio of intensities of 1:2:3:2:1, indicating approximately equal interaction of the unpaired electron with the two nitrogen atoms with a splitting of 8.9 oersteds. A more careful analysis of the hyperfine structure showed that the two atoms of nitrogen are not equivalent, having two splitting constants $a_1 = 9.35$ and $a_2 = 7.85$.

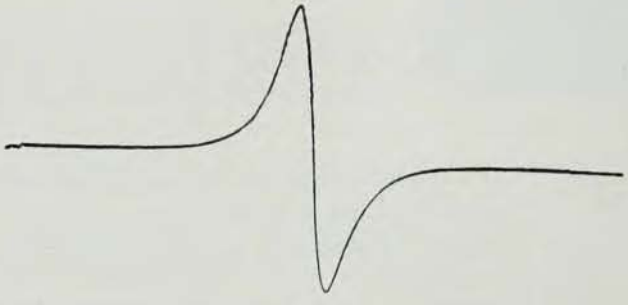

Fig. 1. Electron-spin-resonance spectrum of a saturated solution of diphenyl picryl hydrazyl in tetrahydrofurane. The single line is due to exchange interaction between the unpaired electrons of neighboring molecules.

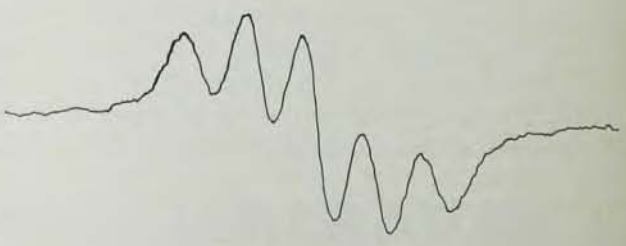

Fig. 2. Electron-spin-resonance spectrum of diphenyl picryl hydrazyl in a tetrahydrofurane solution obtained by diluting a saturated solution a thousand times. The five peaks of the hyperfine structure are due to nuclear spin interaction of the two nitrogen atoms.

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If a carefully dehydrated and degassed solution of 10^{-3} mole DPPH in a liter of tetrahydro furan is measured, a large number of lines are found on each of the five nitrogen hyperfine lines. This super-hyperfine structure is due to the weaker interaction of the protons of the phenyl groups and the picryl group with the unpaired electrons.

The distance between the hyperfine lines, in wave numbers, or the hyperfine splitting constant, characterizes the degree of interaction of the electron with the nuclei having a magnetic moment. The constant can be interpreted as an averaged local field produced by the nucleus at the locale of the unpaired electron. This is possible only if the unpaired electron is located in an atomic s orbit or a molecular σ orbit since only in these orbits is the density of electrons not equal to zero at the nucleus. Fermi calculated this constant, which is isotropic, as

$$a_i = \frac{8\pi}{3h}\gamma\gamma_i\ \beta\beta_i \left|\ \psi(0)\ \right|^2,$$

where γ and γ_i are the gyromagnetic ratio of the electron and the ith nucleus, β and β_i are the electron and nuclear Bohr magnetons, and $|\psi(0)|^2$ is the density of the unpaired electron at the position of the ith nucleus. If the electron is in a pure p orbit, its eigenfunction has a node at the nucleus and $|\psi(0)|^2 = 0$; there will be no isotropic hyperfine splitting. If, however, there is an admixture of s orbit in the p orbit, this will produce a splitting and the magnitude of this splitting will be a measure of the s character of the p orbit.

One of the unexpected results in the study of the ESR of the free radicals was finding a hyperfine structure associated with the protons in the free radical. This was mentioned previously in the super hyperfine structure of carefully prepared solutions of DPPH. The effect is best brought out in the case of triphenyl methyl, a free radical that should show only one ESR line since its unpaired electron is in a p orbit or an sp orbit around the carbon nucleus, which has no nuclear moment. Actually over a hundred lines are observed. This complicated structure of lines is undoubtedly due to the interaction of the unpaired electron with three para protons, six meta protons and six ortho protons. Ortho, meta, and para positions in a benzene ring are positions on the next carbon atom, the carbon atom once removed, and the carbon atom twice removed from the ring carbon atom on which the main substituent is located.

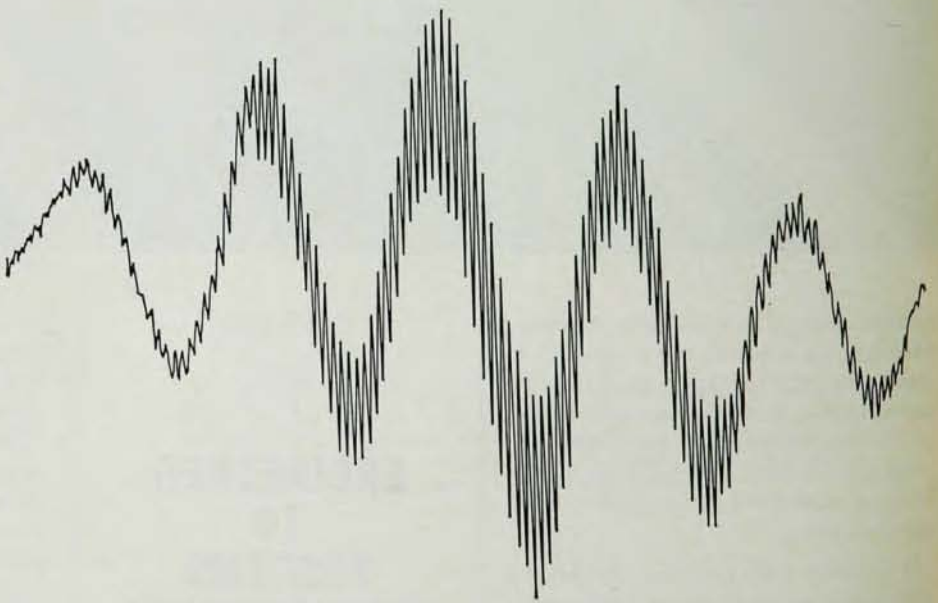


Fig. 3. Electron-spin-resonance spectrum of diphenyl picryl hydrazyl in de-aerated dilute tetrahydrofurane solution obtained by diluting the saturated solution a hundred times. The concentration of the free radical was further decreased by heating the solution. The superfine structure is due to nuclear-spin interaction with protons on the benzene rings.

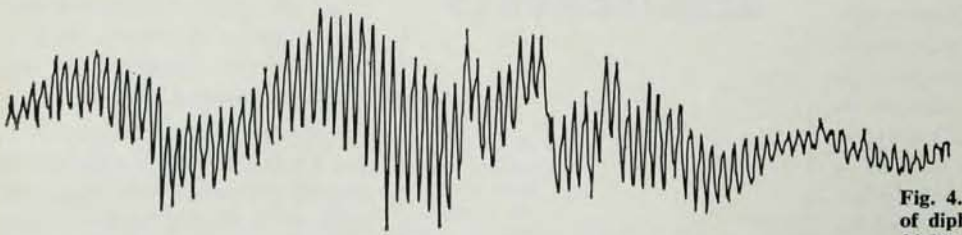
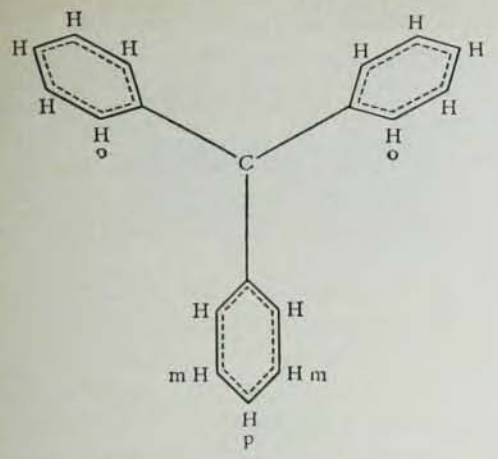


Fig. 4. Electron-spin-resonance spectrum of diphenyl picryl hydrazyl in de-aerated highly dilute 6 x 10^{-4}M tetrahydrofurane solution.



It was well established by valence theory that the unpaired electron was a p electron and was situated in the carbon atoms of the rings. The explanation for the interaction with the protons was found in a configurational interaction which had been previously invoked to explain the hyperfine structure of the Mn(II) ion and for the deviation of the g value from the "free-electron" value of 2.0023. The configurational interaction consisted of including in the wave function of the system not only the ground state of the system but also the excited states whose electronic configuration retains the same spin and orbital moment characteristic of the ground state. Thus, in the C–H bond of the aromatic compound, the ground state is $\sigma_B^2\pi$, where σ_B is a bonding σ orbit holding the carbon atom to the H atom, while π is the orbit of the unpaired electron. The excited state is $\sigma_B\pi\sigma_A$, where σ_A is an antibonding orbit breaking this bond between the C and H orbits and thus producing a spin density on both σ_A and σ_B orbits.

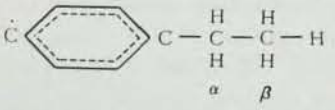
McConnell has shown that the magnitude of the splitting of the proton a_H must be proportional to the spin density ρ_c of the unpaired electron in the π orbit of the carbon atom neighboring the hydrogen atom,

$$a_H = Q\rho_c^\pi = \lambda^2 Q_H \rho_c^\pi,$$

where Q_H is the magnitude of the splitting of the electronic level of a pure s electron at a hydrogen atom (512 oersteds) and λ^2 is the probability of the excited configuration. Theoretical calculations of Q give a value equal to 23 oersteds. Thus, by observing the hyperfine interaction, the spin density in the carbon atoms of the free radicals can be calculated. This theoretical approach was subjected to two refinements—one of negative spin density and another of hyperconjugation.

The McConnell formula implies that the total breadth of the hyperfine structure should not exceed 23 oersteds. However, many cases were observed in which this value was exceeded. McConnell and Chestnut interpreted this to indicate that certain carbon atoms in the radical had negative spin density. An unpaired electron situated in some π orbit can interact not only with σ electrons of the C–H bond but also with the other π electrons of the same radical. This π–π interaction implies that the unpaired electron may occupy other molecular orbits of higher or lower energy and this may bring about a negative spin density. A positive value of the spin density at a given point in a molecule indicates that the spin of an unpaired electron at that point has the same direction as the total electron spin of the radical, while a negative value of the spin density indicates that the direction of spin at that point is in the opposite direction. Furthermore, it was shown that this type of configurational interaction gives a sign of spin density for the protons of a sign opposite to that of the carbon atom.

Hyperconjugation was another refinement that had to be introduced into the theory of hyperfine splitting in order to account for splittings produced by protons which are not directly attached to the carbon atoms of the aromatic rings of the free radical (such as the α and β protons in the figure).



A configurational interaction had to be invoked in which the π orbit of the unpaired electron in the carbon of the ring interacts with a pair of s orbits of the C–H bond of the same pseudosymmetry as the π orbit.

The spin densities of many free radicals have been measured and the results so obtained have been compared with quantum-mechanical calculations based on models of varying complexity. An overall concordance has been found. The resulting data have indicated to the organic chemist how various substituents influence the spin density of various atoms of a complex molecule. Evidence is accumulating to indicate that the most reactive carbon atom in a molecule is one in which the spin density is the greatest.

The width of the resonance line can be used as a measure of the interaction of the free radical with its surroundings. The natural width of the ESR line $\Delta\nu \cong \frac{\Delta E}{\hbar} = \frac{1}{\tau}$ where τ is the relaxation time. If τ is very short, the line is too broad to be observed experimentally. If τ is very long, the ESR

signal is again difficult to observe because of the saturation of the excited state. Ward and Weissman obtained, from the line width of the free radical immersed in an excess of its parent, the second-order rate constant of 10^6 l/g-atom/sec for the exchange reaction between the radical and the parent,

$$[\text{naphthalene}]^- + \text{naphthalene} \longrightarrow \text{naphthalene} + [\text{naphthalene}]^-.$$

Actually the width of the ESR line is considerably greater than the natural width since the radical interacts with its surroundings and thus decreases the relaxation time. These interactions are determined by two processes, the spin-lattice interaction characterized by τ_1 and a spin-spin interaction characterized by τ_2. Thus $\Delta\nu = 1/\tau_1 + 1/\tau_2$, and either one or the other interaction will play the dominant role in a given case.

In solids, the spin-lattice relaxation can be considered as the interaction of the free radical with the ensemble of oscillators which represent the elastic vibrations of the lattice. The lattice is a huge reservoir of thermal energy. There are two mechanisms for such an interaction: (1) a direct resonance in which a quantum of excited spins is transferred to those oscillators whose energy-level differences match this energy ΔE, and (2) a two-phonon interaction in which a spin quantum disappears by virtue of the disappearance of a phonon (lattice vibration) of energy $h\nu_2$ and appearance of a phonon (lattice vibration) of $h\nu_1$ so that $\Delta E = h(\nu_2 - \nu_1)$. The relaxation time τ_1 is given by

$$\tau_1 = \frac{10^4 \Delta^M}{\lambda^2 H^4 \tau^N},$$

where for the resonance process M is equal to 4 and N is equal to 1, while for the two-phonon process M is equal to 6 and N to 7. In free radicals the value of Δ, the energy increment to the next excited state, is large, while λ, the spin orbit constant, is small, so that τ_1 is usually as long as several seconds. However, other specific effects permit transfer of magnetic energy to thermal energy. One such effect is the exchange interaction in solid DPPH, which is more important than the spin-orbit coupling and gives a value of 10^{-6} sec for τ_1. In solutions, there are the tumbling motions of the molecules and the chemical-exchange interactions, which play an important role in the spin-lattice relaxation.

The width of the electron-spin-resonance line usually is determined mainly by the spin-spin dipole interactions between the electrons and less so by those between the electrons and the nuclei in the system having a magnetic moment. If there are two paramagnetic particles at a distance r_i between them, then each of them will experience, in addition to the external magnetic field, a local field due to the other. This is given by

$$H_i = \mu_z \left\langle r_i^{-3} \right\rangle_{\text{av}} \left\langle 3 \cos^2 \theta_i - 1 \right\rangle_{\text{av}},$$

where μ_z is the z component of the magnetic moment of the paramagnetic particle. The external magnetic field along the z direction is H_0, and θ_i is the angle that the line joining the two particles makes with the H_0 direction. This results in a spread of magnetic field from H_0 to $H_0 \pm H_i$, and leads to the broadening of the resonance line. If the magnetic particles are identical, the rotating components μ_x and μ_y will produce a variable field of resonance frequency, leading to exchange of the orientation of moments, thus decreasing the lifetime of a given Zeeman state and producing a magnetodynamic line broadening. τ_2 depends on the concentration of the paramagnetic species and the line sharpens as the concentration decreases because the r_i increase. The magnetodynamic broadening also decreases with a decrease in concentration. The effect of temperature on these broadening effects is negligible.

Another spin-spin interaction is between the magnetic moment of the electron and that of the nuclei. In liquid systems this anisotropic broadening is removed by rapid isotropic rotation of the radical. However, if the frequency of rotation is not sufficiently great and is comparable to the width of the line, this type of interaction may widen out the hyperfine structure, particularly that of the outer components and lead to what is known as symmetrical broadening.

Magnetic nuclei of neighboring molecules can also produce a widening. This effect is averaged out if the frequency of the motion of these molecules relative to the radical is large compared to the frequency of the resonance radiation. This effect can be shown best by comparing the width of the line in solution with the width of the line in a rigid lattice, where the motions are retarded. Analysis of the temperature dependence of the width of line gives information about the nature of motion in a matrix. This has been particularly useful in studying the internal motion of segments of polymers.

An interesting effect of the interaction of free radicals with the solvent is the uniform variation of the width of the individual components of the hyperfine structure. This effect was explained by

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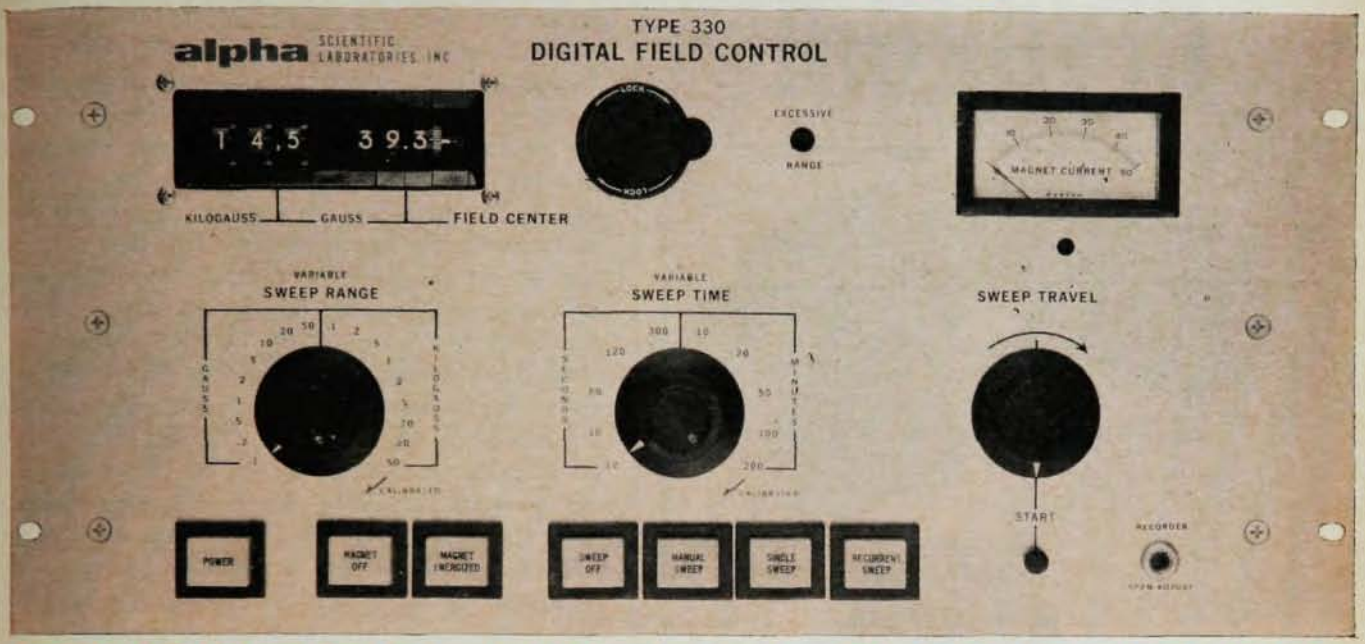

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DIAL ACCURACY: 0.1% or 10 gauss to 15 Kg; 0.3% to 25 Kg; 1% to 50 Kg

FIELD RANGE: true zero to 49,999.9 gauss (power source will provide a negative current to overcome residual magnetism)

SWEEP RANGES: continuously variable from 100 milligauss to 50 Kg, in 1-2-5 sequence with vernier (1% accuracy, 0.5% linearity)

SWEEP TIMES: continuously variable from 12 seconds to 200 minutes, in 1-2-5 sequence with vernier (3% accuracy, 0.5% linearity)

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McConnell in terms of the anisotropy of the g factor of the "solvated free radical" and the spin correlation time of its Brownian motion. An interesting consequence of the McConnell theory, confirmed experimentally, is the dependence of the width of the components of the hyperfine structure on the value of I_z, the nuclear magnetic quantum number. Asymmetric widening may also be due to the Brownian motion around the different axes of the molecule which brings about only a partial removal of the anisotropy of the hyperfine structure and a consequent dependence of the width of the individual components on the I_z values.

In classical organic chemistry electrons and protons were assumed to be fixed on certain atoms in the molecule. Modern organic chemistry envisages certain molecular situations in which not only the electrons are mobile (π electrons) but also protons can exchange. The width of the components of the hyperfine structure also depends on the frequency of delocalization of the electrons in the bond system of the radical. If, for instance, the radical contains two protons far removed from each other, and the frequency of delocalization is low, the hyperfine structure will appear as if due to one proton. However, at sufficiently high frequency of delocalization, the effect of the two protons will be seen in the spectrum. The magnitude of the splitting of these protons will be the lower limit of the frequency of delocalization.

Interorbital exchanges which produce negative spin densities also lead to a sharpening of the components of the hyperfine structure. The smaller the difference between the energy levels, the higher the frequency of this exchange and the narrower the line width. Furthermore, the greater the width of the individual lines, the more symmetrical the structure of the radical.

In general, weak electron spin-spin interactions lead to a widening of the resonance lines. However, a strong interaction, such as that produced at high concentration of the radical, leads to a drastic sharpening of the lines due to exchange forces as in DPPH. For, at distances between the radicals comparable to the size of the molecules themselves, the overlap of the orbits of the unpaired electrons leads to the averaging of the local fields and a consequent sharpening of the resonance line. The hyperfine structure disappears at concentrations at which the frequency of exchange, determined by the exchange integral divided by Planck's constant, is of the same order of magnitude as the hyperfine splitting constant.

I wish to thank Professor Y. Fujita for help in obtaining the spectra used in this article.