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Introduction

The Structure and Physical Properties

of Free Radicals

1·1 Introduction

Words have the common property of changing their meaning with use, and the terms used in chemistry are no exception. In fact, such changes are almost inevitable as our knowledge of the phenomena

that the words were coined to describe develops and grows. The term *radical* is a case in point, and, if we follow the changes in connotation that this word has undergone, we are led through the whole development of the ideas of theoretical organic chemistry.

Originally, the word *radical* was employed to designate a group of atoms that preserve their integrity and endure as a unit through a series of chemical reactions, a sense in which the word is still widely used today. During the first half of the nineteenth century, a number of such radicals were recognized as components of organic compounds, and attempts were made to isolate them in a free state, in a manner more or less analogous to the separation of metals from their salts. Several such endeavors, initially believed successful, later proved to have yielded dimers of the expected radicals. Nevertheless, the results obtained served as important additions to the expanding body of chemical knowledge. Thus Gay-Lussac in 1815 prepared cyanogen, the dimer of the cyanogen (cyano) radical CN, by heating mercuric cyanide, and so introduced this substance to chemistry.[1] Similarly, in 1842 Bunsen prepared the dimeric cacodyl from cacodyl chloride and zinc [2] via the reaction

$$2(CH_3)_2AsCl + Zn \rightarrow (CH_3)_2As\!-\!As(CH_3)_2 + ZnCl_2 \qquad (1)$$

Employing the analogous reaction of sodium with methyl and ethyl iodides, Wurtz in 1854 prepared gases with the empirical formulas CH_3 and C_2H_5.[3] Again, although subsequent work showed that the products were respectively, in fact, ethane and butane (admixed with ethane and ethylene), Wurtz's researches led to a new reaction which still bears his name and remains one of the (more moss-covered) cornerstones of elementary organic instruction.

At about the same time, similar presumed radicals were described by Frankland [4] as the result of heating ethyl iodide with zinc in a sealed tube. Again the experiment produced important results; for, on distilling the residue in his tubes, Frankland was led to the discovery of the spectacular class of organozinc compounds, a versatile group of reagents which found considerable synthetic use until superseded by the more tractable Grignard reagents some fifty years later.

[1] H. L. Gáy-Lussac, *Ann. chim.,* **95,** 172 (1815)
[2] R. H. Bunsen, *Ann. Chem Justus Liebigs,* **42,** 27 (1842).
[3] C. A. Wurtz, *Compt. rend.,* **40,** 1285 (1854).
[4] E. Frankland, *Ann.,* **71,** 171, 213 (1849).

Around 1860 two concepts entered chemistry which had a profound effect upon the search for organic free radicals. One was the vapor-density method of determining molecular weights, which conclusively identified earlier "radicals" as dimers. The second was the valence theory. Although this served to clarify the issue by identifying earlier postulated radicals as essentially derivatives of trivalent carbon, its success in interpreting the growing array of observations in organic chemistry solely in terms of structures involving tetravalent carbon really brought to a halt attempts to isolate or detect organic free radicals as such. In fact, by the end of the nineteenth century, although metal vapors were considered to be monatomic and high-temperature dissociations such as

$$I_2 \rightleftharpoons 2I \cdot \tag{2}$$

were recognized,[5] the majority of organic chemists were convinced that, except for such anomalies as carbon monoxide and the isocyanides, only compounds of tetravalent carbon were capable of existence.

This viewpoint was rather violently upset at the turn of the century by Gomberg's description of his attempts to prepare hexaphenylethane by treating solutions of triphenylmethyl chloride with silver powder or zinc dust.[6] The resulting yellow solutions reacted instantly with air, iodine, and a variety of other reagents, properties which he could only explain on the basis of dissociation of the hexaphenylethane into triphenylmethyl radicals, i.e.:

$$\phi_3C\text{---}C\phi_3 \rightleftharpoons 2\phi_3C \cdot \tag{3}$$

In short, the goal which had eluded numerous investigators a half century and more before had been achieved.

Once the initial scepticism of other workers was overcome, a number of laboratories turned to the problem of stable free radicals, and a large variety of such species were prepared, identified and their properties studied. However, because their structural requirements for existence are possessed by only rather complicated molecules, they have remained a rather esoteric branch of organic chemistry, considered in more detail in Chapter 10.

The development of the concept of the electron pair bond, beginning with Lewis's suggestions in 1916,[7] and elaborated by the devel-

[5] V. Meyer, *Ber.*, **13**, 394 (1880).

[6] M. Gomberg, *ibid.*, **33**, 3150 (1900); *J. Am. Chem. Soc.*, **22**, 757 (1900).

[7] G. N. Lewis *J. Am. Chem. Soc.*, **38**, 762 (1916).

opment of quantum mechanics, gave more specific meaning to the term *radical* or *free radical* (here used interchangeably). Thus the (then hypothetical) methyl radical

$$\overset{\displaystyle H}{\underset{\displaystyle \ddot{H}}{H\!:\!\ddot{C}\cdot}}$$
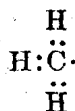
consisted of a carbon atom surrounded by three electron pairs and an additional unpaired or odd electron. By extension, any structure containing an atom with an unshared electron might be considered a radical, as may molecules containing two or more unpaired electrons (di- and polyradicals), and this definition of a *free radical as a molecule or atom with one or more unpaired electrons* will be employed here. As will be seen, although the largest number of radicals are those with an odd electron associated with a carbon atom, halogen atoms and radicals with odd electrons on O, N, P, S, and Si play important roles in many reactions. Finally we may note that, although most of the radicals with which we are concerned are electrically neutral, radical ions also exist and are sometimes important either as stable products or reactive intermediates in certain systems.

The next step in the development of the chemistry of free radicals, the establishment of the role of radicals as transient intermediates in chemical reactions, first received serious attention in quite a different branch of chemistry, the investigation of pyrolytic and photochemical reactions in the gas phase. This field became an increasingly active branch of physical chemistry in the 1920's, and the possibility of free radical intermediates in such processes was seriously suggested as early as 1925 by Taylor.[8] Nevertheless, a number of alternative hypotheses continued to be advanced to interpret experimental results,[9] and it was not until the publication of the work of Paneth and Hofeditz in 1929 [10] that conclusive evidence became available. These investigators, in an elegant series of experiments, studied the pyrolysis of tetramethyl lead under conditions of low pressure and rapid flow, in an apparatus shown schematically in Fig. 1·1. A carrier gas such as hydrogen, saturated with tetramethyl lead

[8] H. S. Taylor, *Trans. Faraday Soc.*, **21**, 560 (1925).

[9] For an interesting discussion of the early evolution of this field, cf. F. O. Rice and K. K. Rice, *The Aliphatic Free Radicals*, The Johns Hopkins Press, Baltimore, 1935, Chapter II.

[10] F. Paneth and W. Hofeditz, *Ber.*, **62**, 1335 (1929).

(contained in A at some predetermined temperature), passes through a quartz pyrolysis tube B at a pressure of 1–2 mm and a velocity of 10-15 meters/sec and through a trap C maintained at liquid nitrogen temperature   If B is heated strongly at some point a, the tetramethyl lead is completely decomposed, depositing a lead mirror at that point 'Once such a mirror is deposited (alternatively by heating a small piece of metal previously introduced into the tube) the significant part of the experiment may be performed. If the mirror at a is allowed to cool and the tube is now heated at a new point b, upstream from the first, a new mirror is deposited at b, and, simul-
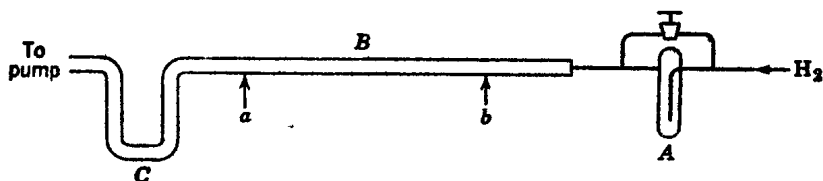

FIG. 1·1   Apparatus for the detection of methyl radicals in the pyrolysis of tetramethyl lead.[10]

taneously, the mirror at a disappears and tetramethyl lead collects in C. Evidently the pyrolysis yields reactive fragments which have very short lives, since the rate of removal of the mirror at a decreases as the distance between a and b is increased. These same fragments also remove mirrors of zinc and antimony, in the former case yielding dimethyl zinc as the product in C. These observations led the authors to conclude that the reactive intermediates being swept down the tube were methyl radicals formed by the reaction

$$(CH_3)_4Pb \rightarrow Pb + 4 \cdot CH_3 \tag{4}$$
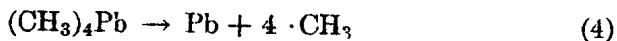
which rapidly combined to form ethane but still had half-lives of the order of 10^{-3} sec during which they could react with a cold metal mirror by the reverse of reaction 4.

Paneth's conclusions soon received additional experimental support, and, subsequently, the whole field of gas-phase radical reactions has had notable development. However, since it has recently been reviewed in detail [11] and lies outside of the proper scope of this book, gas-phase reactions will be mentioned here only when they

[11] E. W R. Steacie, *Atomic and Free Radical Reactions*, second edition, Reinhold Publishing Corp. New York. 1954

   A shorter discussion is given by W A. Waters, *The Chemistry of Free Radicals*, second edition, Oxford University Press, London.'1948

have direct bearing on similar radical processes in solution. Actually, as we will see, organic radical reactions comprise one of the fields of chemistry where a close parallel indeed exists between phenomena in the gas and liquid state. Such differences as arise are usually accounted for by concentration differences and the intrusion of heterogeneous processes on vessel walls in the gaseous state reactions.

The idea of free radicals (in the modern sense) as intermediates in liquid-phase reactions has had a largely independent and somewhat more recent development. The parallel between autoxidation of aldehydes and of sulfite ion was pointed out in 1927 by Bäckström,[12] who recognized the chain nature of both processes, and in 1934 postulated the aldehyde autoxidation as a free radical chain reaction.[13] Although this appears to be the first specific liquid-phase reaction involving a free radical chain to be identified, it is interesting that Staudinger had suggested in 1920 that polymerization processes might involve trivalent carbon,[14] and Haber and Willstätter had considered free radical chain mechanisms for a number of organic reactions in solution.[15] However, most of their schemes, like most of Nef's much earlier reaction mechanisms involving divalent carbon "radicals,"[16] have not survived subsequent detailed investigation.

In 1937 Hey and Waters published a most significant review,[17] interpreting a number of reactions, which had hitherto proved stumbling blocks in the development of the electronic theory of organic reactions, as being free radical processes. Among these were the reactions of aromatic nuclei with benzoyl peroxide, decompositions of aromatic diazonium salts as in the Gomberg-Bachmann reaction, and the "abnormal" addition of hydrogen bromide to olefins. At the same time and independently, Kharasch[18] proposed the present accepted free radical chain mechanism for the "abnormal" addition, a reaction first demonstrated by Kharasch and Mayo four years before.[19] Finally, in the same year, Flory[20] published a brilliant and

[12] H. L. J. Bäckström, *J. Am. Chem. Soc*, **49**, 1460 (1927).

[13] H. L. J. Bäckström, *Z physik. Chem,* **25B**, 99 (1934).

[14] H. Staudinger, *Ber*, **53**, 1073 (1920).

[15] F. Haber and R. Willstätter, *ibid*, **64**, 2844 (1931).

[16] J. U. Nef, *Ann*, **298**, 202 (1897).

[17] D. H. Hey and W. A. Waters, *Chem. Revs.*, **21**, 169 (1937).

[18] M. S. Kharasch, H. Engelmann, and F. R. Mayo, *J. Org. Chem.*, **2**, 288 (1937)

[19] M. S. Kharasch and F. R. Mayo, *J. Am. Chem. Soc.*, **55**, 2468 (1933).

[20] P. J. Flory, *ibid.*, **59**, 241 (1937)

prescient paper on the kinetics of vinyl polymerization, treated as a free radical chain reaction, and outlining the framework into which much subsequent work has been fitted.

Inevitably, the full significance of these publications was not immediately recognized, nor the conclusions everywhere accepted. Nevertheless, 1937 is a convenient date to mark the beginning of our present recognition of the role of free radicals as reactive intermediates in ordinary temperature, liquid-phase reactions, just as the publication of Rice and Rice's *The Aliphatic Free Radicals*[9] two years earlier marked a turning point in the study of free radicals in gas-phase photochemistry and pyrolysis.

Since 1937 knowledge of organic reactions involving free radicals has increased at a steadily accelerating pace. New synthetic methods such as radical addition reactions to double bonds have come into being, and old reactions of halogenation and autoxidation have been rendered more versatile and efficient by a recognition of their reaction paths.

In fact, whole new industries, notably that of vinyl polymerization, have arisen based upon free radical processes. Along with these developments has come a much more detailed understanding of the mechanism and characteristics of free radical reactions.

The balance of this and the next chapters will be devoted to an introductory survey of some of this knowledge. Subsequent chapters will consider the kinetics of radical processes in more detail and take up the specific properties of individual radical reactions. Actually, as we will see, in spite of the great volume of data now available, the whole subject of organic radical reactions is a rather closely integrated one, involving only a few types of reactions and rather a limited number of types of radical. Furthermore, because the species involved are, in general, uncharged, many of the complexities of polar reactions (effects of ionic strength, acidity and basicity, ionizing power of the media, etc.) are largely avoided. A happy consequence is that the tie-up between theory and experiment is often gratifyingly clear-cut and direct.

1·2   Magnetic Properties of Free Radicals

An organic free radical, like any other molecular species, has its own distinctive physical properties—molecular weight, absorption spectrum, dipole moment, melting point, etc. In addition, free radicals, as a class, have a group of characteristics due to a unique struc-

tural feature: the presence of one (or more) unpaired electrons. These characteristics are of great importance as means of detecting the presence of free radicals, quantitatively estimating their concentrations, and learning something of their structures.

Of the characteristics arising from the presence of unpaired electrons, the most significant are those affecting the magnetic properties of molecules, and, in fact, these are the only ones which provide a general tool for demonstrating the free radical nature of molecules:

1·2a   Magnetic Susceptibility

Since a number of comprehensive reviews are available,[21–24] the basis of magnetic susceptibility measurements need only be discussed briefly. When a substance is placed in a magnetic field of strength H, the resulting intensity of magnetization per unit volume, I, is given by the relation

$$I/H = \chi \tag{5}$$

where χ (also sometimes written as K or κ) is the magnetic susceptibility of the material per unit volume. Similarly, a molar susceptibility may be defined as

$$\chi_M = \chi M/\rho \tag{6}$$

where M is the molecular weight and ρ the density. Experimentally, it turns out that χ (and hence χ_M) may be either positive or negative. When χ is positive, a substance is *paramagnetic;* whereas if χ is negative, it is *diamagnetic.* In addition, a few materials such as iron, nickel, and certain alloys show extremely large positive susceptibilities and are known as *ferromagnetic.* In terms of the classical model, it is convenient to think that, in a magnetic field, the magnetic lines of force are concentrated within a paramagnetic substance and partially excluded from a diamagnetic one. Magnetic susceptibility is thus equivalent to electric susceptibility in electrical theory, which, in turn, is related to the dielectric constant.

From quantum mechanics and statistical mechanics, the molar sus-

[21] J. H. Van Vleck, *Electric and Magnetic Susceptibilities,* Oxford University Press, New York, 1932.

[22] E. C. Stoner, *Magnetism and Matter,* Methuen, London, 1932.

[23] P. W. Selwood, *Magnetochemistry,* Interscience Publishers, New York, 1943.

[24] L. Michaelis, *Technique of Organic Chemistry,* A. Weissberger, editor, Volume I, Interscience Publishers, New York, 1949, Chapter 29. This is probably the most useful account for the organic chemist.

ceptibility χ_M may be divided into two parts, which in most cases may be expressed in the form

$$\chi_M = N(\alpha_0 + \mu_M^2/3kT) \tag{7}$$

where N is Avagadro's number, k, Boltzmann's constant, α_0 the induced moment, and μ_M the permanent magnetic dipole moment of a single molecule. The quantity α_0 arises chiefly from electronic motion within a molecule. Since electrons are charged particles, imposition of a magnetic field distorts their motion and this change in motion produces a countermagnetic field. This consequence, in turn, decreases the effective magnetic field in the region of the molecule. The result is that χ_M is negative, and molecules without permanent magnetic dipole moments are diamagnetic.

In all cases of significance to us here, permanent magnetic dipole moments arise from electron spin.[25] With paired electrons, the net moment is zero, since the pairing is between electrons of opposite spins. However, for an unpaired electron this moment is not zero, and may be calculated from quantum theory to have the value $\sqrt{3}$ Bohr magnetons. As a consequence, since μ_M^2 is positive, χ_M will contain a positive term. In fact, since $N\mu_M^2/3kT$ has a value of 1260×10^{-6} cgs units at 20°C, and since the diamagnetic term for typical organic molecules is generally less than 10% of this, it appears that *paramagnetism is a unique property of free radicals*, a prediction first made by Lewis in 1923.[26] It should be noted that, provided other sources of magnetic moment can be neglected, the magnitude of the paramagnetic term in χ_M is independent of the molecule involved, but is temperature dependent, increasing as the temperature is lowered. In the case of molecules with more than one unpaired electron, μ_M is given, in Bohr magnetons and for n electrons, by the relation

$$\mu_M = \sqrt{n(n+2)} \tag{8}$$

providing that the electrons involved occupy orbitals which may interact with one another. However, if they are isolated, the expected relation is $\mu_M = n\sqrt{3}$.

[25] Two other sources of permanent magnetic dipoles may exist in molecules: angular momenta of the orbital electrons and nuclear spin. However, in organic molecules, the effect of the former appears to be "quenched" by the strong internal electric fields, and the moment due to the latter is less than $\frac{1}{1000}$ of that due to the spin of a free electron.

[26] G. N. Lewis, *Valence and Structure of Atoms and Molecules*, Chemical Catalog Co., New York, 1923, p. 148.

Finally, we may note that the ions of many transition-state metals may possess as many as several unpaired electrons. By our definition, such ions are properly free radicals, but they differ so in bond-forming properties from organic radicals that the definition is of little utility here. Nevertheless, studies of the magnetic properties of such ions and their coordination complexes have proved very valuable in connection with the determination of their structures.

The determination of the magnetic susceptibilities of molecules is most commonly carried out by investigating their behavior in inhomogeneous magnetic fields. A material placed in a magnetic field of strength H acquired a potential energy per unit volume.

$$E = \chi H^2/2 \tag{9}$$

Accordingly, if the field is inhomogeneous in some direction x, it follows that it will be acted upon by a force per unit volume

$$F = \chi H \, dH/dx \tag{10}$$

From eq. 10 it is evident that paramagnetic substances will be subject to a force drawing them into a magnetic field, whereas diamagnetic materials will be repelled, and, in fact, this distinction provides the original definition of the terms.

The simplest method of determining χ by measuring H is probably that of Gouy, first employed in 1889,[27] and shown schematically in Fig. 1·2. If a long sample of uniform cross section, A, is suspended between the poles of a powerful magnet, so that one end is in a uniform field of strength H, and the other lies essentially in field zero, the force acting upon the sample is given by

$$F = \chi H^2 A/2 \tag{11}$$

and may easily be determined by weighing the sample in the presence and absence of the magnetic field. In practice, a number of refinements are necessary, for example the use of a double-ended compensating tube, so that χ is always determined relative to some known standard, but the procedure is basically as described. For liquids, a thin-walled container may be employed, or the force may be determined by measuring the difference in level of the liquid in two arms of a U tube, one of which is placed in a magnetic field. This technique, originally developed by Quincke,[28] is shown schematically in Fig. 1·3: It has had a number of modifications and appears very well

[27] L. G. Gouy, *Compt. rend.,* **109**, 935 (1889).
[28] G. Quincke, *Ann. Physik,* **24**, 347 (1885); **34**, 401 (1888).

adapted for the study of solutions of stable organic radicals. It is quite sensitive, but temperature control becomes difficult if it is used at high or low temperatures.

Probably the most sensitive modification of the Gouy method is the Theorell balance. Here the sample is suspended horizontally as
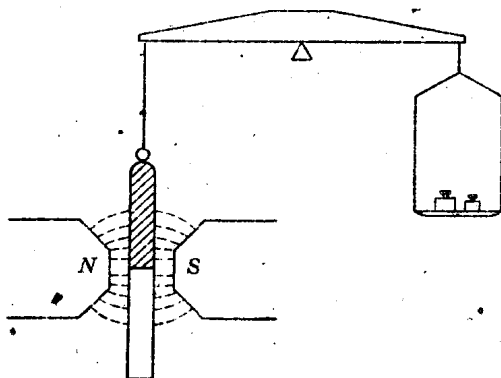

FIG. 1·2   Schematic diagram of Gouy balance for determining magnetic susceptibilities.

a pendulum in the magnetic field, and its displacement is measured with a microscope.[29] With such a device, displacing forces as small as 10^{-6} gram may be detected with samples of about 100 mg.

Although a number of measurements have been made on organic radicals in the solid state, the most important application of magnetic
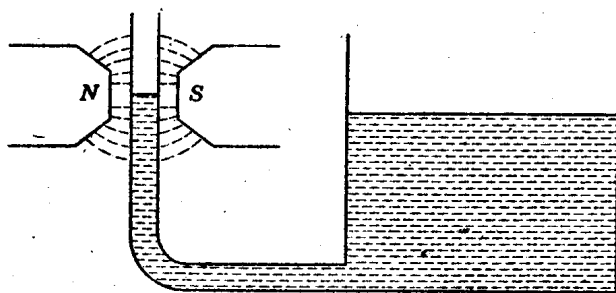

FIG. 1·3   Schematic diagram of Quincke technique for determining the magnetic susceptibility of liquids.

susceptibility measurements has been in the detection and quantitative estimation of free radicals in solution. Determination of the degree of dissociation of hexaphenylethane is a typical example of

[29] H. Theorell, *Arkiv Kemi, Mineral. Geol.*, **A16**, 1 (1943).

such an application and illustrates well the utility and limitations of
magnetic susceptibility measurements. The major problem in inter-
preting measurements in such a system is separating the paramag-
netic contribution of the radicals from the diamagnetic contribution
of all the components of the system. In principle, this might be done
by employing measurements over a temperature range and separating
out the temperature-dependent paramagnetic term, but this procedure
is not feasible in most systems since radical concentrations are also
temperature dependent. Accordingly, solvent diamagnetism is usually
corrected for, either by using a compensating-tube apparatus, or by
direct measurement in the same apparatus and some method of esti-
mating the diamagnetism of the other components (e.g., hexaphenyl-
ethane and the radicals themselves in the system mentioned).

Fortunately, diamagnetism proves to be a closely additive property,
and the diamagnetism of a molecule may be estimated by summing
the expected contributions of its atoms plus certain constitutional
corrections. The validity of this method was first established by
Pascal, and a table of such Pascal constants or atomic diamagnetic
increments are given in Table 1·1.

TABLE 1·1 ATOMIC DIAMAGNETIC INCREMENTS IN CGS UNITS ($\times 10^{-6}$)

(After Michaelis [24])

H	−2.93	S	−15.0
C	−6.00	Se	−23.0
N (open chain)	−5.57	P	−26.3
N (ring)	−4.61	As	−43
N (monoamides)	−1.52	Constitutional Corrections	
N (diamides, imides)	−2.11	C=C (aliphatic)	+5.5
O (single bond)	−4.61	C=C—C=C	+10.6
O (double bond)	−3.36	C≡C	+0.8
F	−11.5	C in aromatic ring	−0.24
Cl (bonded to C)	−17.0	C common to 2 aro-	
Br (bonded to C)	−26.5	matic rings	−3.1
I (bonded to C)	−40.5		

The accuracy of such an estimate may be increased by directly
measuring χ_M for a molecule of similar structure and then making
the necessary corrections (e.g., χ_M for hexaphenylethane should be
twice that for triphenylmethane less the value for two hydrogens).

An illustration of the actual magnitudes of the quantities involved
is given in the following, calculated from the data of Roy and Marvel

on the dissociation of 0.1 molar hexaphenylethane in benzene solution at 20° [30] employing the Quincke technique.

Calculated Diamagnetic Contributions	
Benzene	-0.668×10^{-6} cgs units
Solute	-0.037
χ (calculated)	-0.705
χ (observed)	-0.700 ± 0.002
Paramagnetic contribution	0.005 ± 0.002

The result corresponds to some 2% dissociation or to a radical concentration of 4×10^{-3} molar. Since the paramagnetic contribution is a small difference between large numbers, and approaches the accuracy with which they are known, it is evident that experimental error is considerable and one is nearing the capabilities of the technique. This sensitivity limit of 10^{-3} molar as we will see (Chapter 3 et seq.) lies far above the actual concentrations in many systems in which radical reactions are in progress, but greater sensitivity is sometimes possible. The most delicate measurement of organic radical concentrations by magnetic susceptibility measurements to date is that of Lewis, Calvin, and Kasha.[31] These workers demonstrated the paramagnetic properties of the phosphorescent state of fluoroscein using a modified Theorell balance, capable of determining approximately 2×10^{-8} moles of free radicals in a volume of 0.02 cc with an accuracy of $\pm 10\%$, i.e., detecting a 10^{-4} molar concentration.

1·2b Paramagnetic Resonance Spectra

The fact that paramagnetic substances may show characteristic absorption spectra when placed in a magnetic field provides a relatively new and potentially very valuable technique for detecting and studying organic free radicals, and recent reviews of the topic have been written by Wertz [32] and Fraenkel.[33] Compared with magnetic susceptibility measurements, the technique is more sensitive and may provide information concerning electronic structure. On the other hand, the apparatus is relatively elaborate, and as a test for free

[30] M. F. Roy and C. S. Marvel. *J. Am. Chem. Soc.*, **59**, 2620 (1937).
[31] G. N. Lewis, M. Calvin, and M. Kasha, *J. Chem. Phys.*, **17**, 804 (1949).
[32] J. E. Wertz, *Chem. Revs.*, **55**, 829 (1955).
[33] G. K. Fraenkel, *Ann. N. Y. Acad. Sci.*, **67**, 546 (1957).

radicals it may fail because, for various reasons, the radical may show no. absorption.

The theory of paramagnetic absorption spectra is complex, and, in fact, many of the features of spectral fine structure are not understood.· The qualitative basis of the theory, however, is as follows. An unpaired or free electron in a magnetic field is acted upon by a force which tends to orient its spin in relation to the field (this is the origin of the paramagnetic term in eq. 7). Two such orientations are possible, "with" or "against" the field, which differ in energy by an amount proportional to the external field. From quantum theory this difference amounts to

$$E = g\beta H \qquad (12)$$

where g is the spectroscopic splitting factor, 2.0023 for a free electron, and β the Bohr magneton, 0.927×10^{-20} ergs/gauss. The existence of such a phenomenon has long been known and is related to the Zeeman effect, or splitting of atomic spectral lines in a magnetic field. If such a system is exposed to electromagnetic radiation of appropriate frequency so that

$$h\nu = g\beta H \qquad (13)$$

electrons in the lower level may absorb energy and "flip over" to the higher state.

Substitution of numerical values into eq. 12 shows that, at any feasible field strength, the energy involved in the transition is very small, amounting to about 2.4 cal/mole at 9000 gauss. Indeed, the corresponding absorption would occur in the microwave region at 2.5×10^{10} cycles/sec, and necessarily the study of paramagnetic resonance spectra is normally carried out in this region, the first published observation being by Zavoisky in 1945.[34]

The required microwave and magnetic equipment for paramagnetic resonance work is necessarily elaborate,[32, 35, 36] and any description would be out of place here. However, the method consists essentially in placing a sample in a suitable microwave system which is also in a strong magnetic field, and determining the effect of the sample on the microwave power absorbed or reflected in the system. Since it is

[34] E. Zavoisky, *J. Phys. U.S.S.R.,* **9,** 211 (1945).

[35] B. Bleaney and K. W. H. Stevens, *Reports on Progress in Physics,* **46,** 107 (1953).

[36] J. M. Hirshon and G. K. Fraenkel, *Rev. Sci. Instruments,* **26,** 34 (1955).

more convenient to change magnetic field than microwave frequency, the resulting power absorption commonly is obtained as a function of field strength, and line widths are measured in gauss rather than frequency units. Samples may be introduced in thin-walled glass tubes of capillary size or larger, and the system under examination may be heated, cooled, or irradiated during examination without too much difficulty. A notable feature of this technique is the sensitivity. The theoretical quantity of radicals detectable by a suitably designed instrument has been calculated as 2×10^{-14} moles,[33, 37] and, experimentally, 5×10^{-11} moles of the stable radical diphenylpicrylhydrazyl have given observable spectra.[37] Since the sample employed was a solid, diluted with inert material to a volume of approximately 0.1 cc, this corresponds to a 5×10^{-7} molar radical concentration. By using larger samples, lower radical concentrations should be detectable, but the sensitivity of the method decreases with increasing width of the observed absorption bands.

Aside from the sensitivity of the method, paramagnetic resonance spectra have two other significant properties which add to their usefulness. First, the spectra observed are independent of the diamagnetic properties of the system, and thus require none of the corrections needed in magnetic susceptibility measurements. Second, although spectra of all radicals with a single odd electron have their band centers at approximately the same frequency at a given field strength (corresponding to that expected for a free electron), band widths vary widely, and, in addition, some radicals show hyperfine splitting to give a number of peaks. Evidently, in favorable cases these differences permit the identification of individual radicals. They also provide information on radical processes and structures.

Under suitable conditions, band widths may be correlated with radical lifetimes, the width in gauss being approximately $10^{-7}/\tau$, where τ is the lifetime in seconds. This provides a technique for measuring radical lifetimes in the range of 10^{-6} to 10^{-10} sec and has been used to determine the rate of reaction between the naphthalene radical ion and naphthalene,[38] and also of radical displacements occurring in molten sulfur (cf. Section 7·3c).

Hyperfine splitting appears usually to arise from interaction between the odd electron of a radical and neighboring atoms possessing nuclear magnetic moments. It thus gives information about the

[37] J. M. Hirshon, thesis, Columbia University, 1954.
[38] R. L. Ward and S. I. Weissman, *J. Am. Chem. Soc.*, **76**, 3612 (1954).