

CHARACTERISTIC HYDROGEN HYPERFINE COUPLINGS IN ALIPHATIC FREE RADICALS

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INTRODUCTION

Electron spin resonance has proved to be an excellent technique for studying free radicals. Early work¹ paid considerable attention to aromatic radicals, since many of these are comparatively stable in solution. Aliphatic radicals are mostly more reactive and dimerize to spin-paired molecules with high probability on each collision. Three techniques have been used to overcome this difficulty:

(a) The free radicals are trapped from the gas phase in solid matrices such as the solid inert gases². This method has limitations in that it is restricted to radicals which can be formed in moderate yield in the gas phase.

(b) The free radicals can be continuously generated inside the spectrometer³; this technique is of recent application and shows considerable promise.

(c) The free radicals can be generated by high energy radiation inside solid materials when diffusion is prevented and long lives may be obtained. In this case, the chemical nature of the free radicals must be inferred from the electron resonance spectra themselves.

Normally the same radicals are produced by γ -rays, X-rays, electrons, *etc.* With polycrystalline or amorphous solids, the lines in the spectra are very broad and the spectra in many cases have proved difficult to interpret. However, following the pioneer experiment of Uebersfeld and Erb⁴, recent work in this category has been done with single crystals, when the lines are narrower and interpretation is more certain. The present review is largely restricted to such work.

The reason for the broad-line spectra in polycrystalline samples lies in the variation of the hyperfine coupling, or, more strictly, the line separation, with the direction of the magnetic field with respect to the radical. In liquid systems (as in nuclear resonance), the anisotropy is accurately averaged to zero and only the isotropic term remains. In single triclinic crystals, the radicals are precisely oriented parallel to each other, and sharp hyperfine patterns are obtained with the coupling appropriate to the crystal orientation. If the crystal is rotated with respect to the magnetic field, a changed spectrum is obtained. With a number of orientations a complete investigation of the hyperfine coupling anisotropy can be made. For crystals of higher symmetry than triclinic, there may be a small number of possible radical orientations, but these are accurately related to each other by the symmetry operations of the host crystal.

The present author has reviewed the theory of such measurements elsewhere⁵, and the present review relates only to the results obtained. In particular, it will discuss the problem concerning the extent to which the hyperfine couplings can be transferable between radicals. It is especially when transferable features can be recognized that spectroscopy can be widely applied in organic chemistry. Solution ultra-violet spectroscopy, characteristic infra-red frequencies and chemical shifts in nuclear resonance all exemplify this approach.

In order to understand the following sections, it is necessary to appreciate that the hyperfine coupling of each nucleus to the electron spin may be expressed as a tensor A such that the term $S.A.I$ is included in the Hamiltonian. In the absence of large orbital contributions to the magnetic properties, A is expected to be a symmetric tensor. It can then be expressed in terms of three principal values and the three pieces of information required to specify the three mutually perpendicular directions for which these occur. The polarizability tensor of a molecule is somewhat analogous, although it is not necessary that the principal components of the hyperfine coupling should be positive. It is often convenient to discuss the average coupling, *i.e.* one-third of the sum of the principal values, separately. This is also called the isotropic component and is the quantity observed in solution measurements. It is related to the probability of the unpaired electron being at the nucleus in question. For hydrogen this is equivalent to the electron being in a $1s$ orbital, and one may say that the isotropic coupling* in Mc/sec divided by 1,420 is the extent to which the electron is in the $1s$ orbital: the factor 1,420 derives from the coupling of 1,420 Mc/sec for an H atom. It should be emphasized that this is the spin population in the orbital, which differs from the electron population. The latter quantity derives additively from electrons of either resolved spin, whereas the spin population is the occupancy by electrons of the same spin as the odd electron minus that of electrons of opposite spin. A negative spin population arises when the latter contribution predominates.

If the isotropic coupling is subtracted from the principal values, there remains the anisotropic contribution which consists, therefore, of three components whose sum is zero. These are dependent on the average of $(3 \cos^2 \theta - 1)/r^3$ where r is the distance from the unpaired electron to the nucleus in question and θ is the angle between this radius vector and the magnetic field. Because of the r^{-3} dependence, the anisotropy is largest when the nucleus is close to an important region of the wave function of the unpaired electron.

α -HYDROGEN ATOMS

The most important type of hydrogen atom for which characteristic coupling may be expected is the case for which the hydrogen is directly attached to the free radical carbon atom of an organic radical. The value of the isotropic coupling in the methyl radical^{2,6} and related radicals^{3,6} has shown that the typical value for such hydrogens, sometimes called α -hydrogens, is about ± 60 Mc/sec, and this value with a negative sign has been deduced indirectly from aromatic radicals. This numerical value is in the

* Couplings quoted in gauss should be multiplied by 2.8 to convert to Mc/sec.

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middle of the range for β -hydrogens (see below), and is of limited diagnostic importance. However, the single crystal studies have shown that the anisotropic contribution is very large, as indicated in *Table 1*. The anisotropy is fairly constant and in no other position is hydrogen expected to show nearly such a large anisotropy.

Table 1. α -Hydrogen hyperfine couplings

Host crystal	Radical	Hyperfine coupling		
		Isotropic	Anisotropic	
Malonic acid ⁷	$\text{H}_2\dot{\text{C}}\cdot\text{COOH}$	{ -59 -63	+29	+3 -26
Malonic acid ⁸	$\text{H}\dot{\text{C}}(\text{COOH})_2$	-60	+31	+4 -31
Succinic acid ^{9,10}	$\text{HOOC}\cdot\text{CH}_2\cdot\dot{\text{C}}\text{H}\cdot\text{COOH}$	-60	+30	+1 -32
Aspartic acid ¹¹	$\text{HOOC}\cdot\text{CH}_2\cdot\dot{\text{C}}\text{H}\cdot\text{COOH}$	-63	+24	+3 -27
Glutaric acid ¹²	$\text{HOOC}\cdot(\text{CH}_2)_2\cdot\dot{\text{C}}\text{H}\cdot\text{COOH}$	{ -56 -51	+30	+3 -32
Adipic acid ¹³	$\text{HOOC}\cdot(\text{CH}_2)_3\cdot\dot{\text{C}}\text{H}\cdot\text{COOH}$	-57	+29	+7 -37
Glycollic acid ¹⁴	$\text{HO}\dot{\text{C}}\text{H}\cdot\text{COOH}$	-57	+27	+2 -29
Potassium glycollate ¹⁵	$\text{HO}\cdot\dot{\text{C}}\text{H}\cdot\text{COO}^-$	-51	+28	+1 -29
Lithium glycollate ¹⁶	$\text{HO}\dot{\text{C}}\text{H}\cdot\text{COO}^-$	{ -50 -54	+27	+3 -29
α -Alanine ^{17,18}	$\text{H}_3\text{C}\cdot\dot{\text{C}}\text{H}\cdot\text{COOH}$	-55	+27	+3 -31
Glycine ^{5,19}	$\text{H}_3\text{N}^+\cdot\dot{\text{C}}\text{H}\cdot\text{COO}^-$	-62	+30	+5 -34
<i>N</i> -Acetylglycine ²⁰	$\text{H}_3\text{C}\cdot\text{CO}\cdot\text{NH}\cdot\dot{\text{C}}\text{H}\cdot\text{COOH}$	-51	+35	-4 -30
			+23	+3 -25

The size of this anisotropy is just that to be calculated²¹ if the unpaired electron is on a $2p$ orbital on the free radical carbon. The directions in which the particular principal values occur coincide with a radical orientation which is close to that of its parent molecule in the undamaged crystal.

β -HYDROGEN ATOMS

In contrast to the α -hydrogen couplings, the isotropic coupling of β -hydrogens is very variable. When the intermediate atom is carbon, so that the radical has the form $=\dot{\text{C}}-\text{CH}=\text{}$, the largest coupling yet observed is +122 Mc/sec in one of the chemically equivalent radicals from irradiated glutaric acid¹², and the smallest ± 8 Mc/sec in the radical $(\text{CH}_3)_2\dot{\text{C}}\cdot\text{CH}(\text{NH}_3^+)\cdot\text{COO}^-$ in irradiated valine²². It appears that this coupling is very dependent on the geometry of the radical being small when the hydrogen is in the nodal plane of the $2p$ orbital of the free radical carbon, and large if the hydrogen is far from this plane. This explanation is in agreement with theory^{23,24}, and also suggests that chemically equivalent hydrogens may be geometrically inequivalent and have different coupling constants. Thus the values 107 and 33 Mc/sec were found for the two β -hydrogens in the radical $\text{HOOC}\cdot(\text{CH}_2)_2\cdot\dot{\text{C}}\text{H}\cdot\text{COOH}$ in one of its forms in irradiated glutaric acid¹². In all cases the anisotropy is quite small; typical

are the values +8, -2 and -7 Mc/sec for one of the β -hydrogens¹⁰ in the radical $\text{HOOC}\cdot\text{CH}_2\cdot\dot{\text{C}}\text{H}\cdot\text{COOH}$. When single crystal spectra are available, α - and β -hydrogens are readily distinguished by the extent of the anisotropy.

Geometrical inequivalence cannot occur if the β -hydrogens are part of a methyl group which is rotating freely, or at least "tunnelling", at the temperature of observation. This condition is regularly fulfilled at room temperature and the coupling of the three hydrogens of a structure $\text{H}_3\text{C}-\dot{\text{C}}=$ is about +70 Mc/sec each. When two such methyl groups are present, the value is slightly lower, as in $(\text{CH}_3)_2\dot{\text{C}}\cdot\text{COOH}$ where the value²⁵ is +65 Mc/sec, when the radical is trapped in α -aminoisobutyric acid. The equivalence of the hydrogens means that sets of four equally-spaced lines of intensity ratio 1 : 3 : 3 : 1 are present and are easily identified. The rotation also partially averages the anisotropy which may be very small, being +4, -1 and -3 Mc/sec for this same radical. In such cases even polycrystalline spectra may be fairly well resolved.

CONCLUSION

Hydrogen atoms in more remote positions do not appear to couple, and it would seem that γ -hydrogens have a coupling less than 5 Mc/sec, at which value they would be lost in the line width. Coupling to hydrogen atoms in structures such as $\text{HO}-\dot{\text{C}}=$ have been measured¹⁴⁻¹⁶, and a number of nitrogen couplings are known^{19,22,26}. At present, there are insufficient number of cases for it to be possible to give typical values.

To summarize, it can be said that the typical hyperfine coupling tensor of α -hydrogen atoms is now well characterized, and that β -hydrogen tensors are certainly more variable and are the subject of much present work. Couplings to N, F, Cl, ¹³C and ¹⁷O remain to be studied systematically, but the work on H couplings in the last few years gives hope that some characteristic features may also be found for these nuclei. Such work is not only valuable for the insight it provides to the wave functions of the free radicals, but also for the help it should give to the radiation chemist and others who wish to identify radicals of uncertain structure.

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