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Electron Spin Resonance Studies on Gamma-Irradiated Ferrocene*

EIICHI SAITO

Chemistry Department, Brookhaven National Laboratory, Upton, New York and *Departement de Physico-Chimie, Service des Isotopes Stables, Centre d'Etudes Nucleaires de Saclay, France*

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The aim of this study was to determine the nature of the free radicals induced in ferrocene by ^{60}Co gamma rays. The irradiations were carried out on the powder at 77°K, the temperature at which crystals have burst into powder form, and on the single crystals at 193°K. At 77°K two radicals are formed, I and II; I transforms itself into a third radical, III, on annealing at temperatures above 145°K. In the single crystals irradiated at 193°K, only radicals II and III are formed. When the single crystals were not too damaged, the disappearance of the radical III with concommitant appearance of a fourth radical, IV, which presents a hyperfine structure of five lines was observed. Taking into account the anisotropies of the g tensors, change in spectra upon deuterium substitution of the cyclopentadienyl protons, and behavior on annealing, the spectra of radicals I–IV were attributed tentatively as follows: I to a straight molecule-ferricinium ion, II to a protonated ferrocene radical, III to a bent molecule-ferricinium ion, IV to a C_5H_5–Fe–$C_5H_4\cdot$radical. Mechanisms are given for the formation of these radicals as well as for their disappearance on annealing.

I. INTRODUCTION

Ferrocene [bis(cyclopentadienyl) iron (II), $(C_5H_5)_2$-Fe] since its discovery has been the object of numerous studies and most of its chemical and physical properties are well known. The electronic structure of ferrocene, as well as of the other metallocenes, has been discussed in a certain number of papers.[1]

The aim of this work was to determine the nature of the free radicals created in ferrocene by gamma rays of ^{60}Co. These free radicals could be trapped at low temperatures ($t<193$°K) and their g tensors and behavior on annealing led to tentative attributions to certain structures. A preliminary report[2] was given but as the experimental data were insufficient, this work has been pursued.

Irradiation of ferrocene in powder form at 77°K showed the existence of radical I with a cylindrically symmetric g tensor ($g_\perp=2.00$, $g_{||}=2.032$) and a second radical II with a totally asymmetric g tensor ($g_1=2.00$, $g_2=2.098$, $g_3=2.21$). On thermal annealing at temperatures above 143°K, radical I disappears while a third radical, III, appears this one has also a totally asymmetric g tensor with values $g_1=1.999$, $g_2=2.077$, $g_3=2.28$.

Irradiation of single crystals was feasible only in dry-ice acetone baths, for these crystals burst into a powder when plunged into liquid nitrogen. Even keeping the single crystals at 193°K, without irradiation, makes them undergo a transformation with accompanying loss of transparency. Nevertheless, they maintain their singleness long enough to allow simple spectra of Type A to be studied as a function of orientation relative to the magnetic field direction. The signals of these spectra belong to radicals II and III, when recorded in the few hours following the irradiation. These crystals, after overnight standing in dry ice would give spectra of Type B, where the signals of radical III have disappeared and those of another radical, IV, have appeared. This radical, in certain cases, shows a five-line hyperfine structure—in other cases where the crystal has badly deteriorated, an envelope at $g=2.00$.

Ferrocene deuterated to 99.7% D/(D+H) has been prepared and spectra of the gamma-irradiated powder and single crystals were obtained. Spectra of radicals I and III are not modified but those of radical II shows that there is an interaction with a hydrogen or deuterium atom.

II. EXPERIMENTAL METHODS

A. Instrumental

The EPR spectrometer used was a Varian 4502-13 model, with 100 kc/sec. modulation and a 9-in. rotating magnet equipped with a Fieldial. The rotating cavity, V-4533, as well as the V-4531, V-4532 Dual Sample Cavity were employed.

B. Ferrocene

The commercial samples (Kodak, B.D.H., Merck), were purified by repeated sublimation. Most of the single crystals were grown by slow sublimation under vacuum in a closed container, some by slow evaporation of acetone solutions.

The single crystals were checked with a polarizing microscope and the position of the axes relative to the faces of the crystals determined by optical goniometry.

Ferrocene crystals are monoclinic. The space group

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* Research performed in part under the auspices of the U.S. Atomic Energy Commission.

[1] (a) J. D. Dunitz and L. E. Orgel, J. Chem. Phys. **23**, 954 (1955); (b) W. Moffit, J. Am. Chem. Soc. **76**, 3386 (1954); (c) M. Yamazaki, J. Chem. Phys. **24**, 1260 (1956); (d) E. Ruch, Rec. Trav. Chim. **75**, 638 (1956); (e) F. A. Matsen, J. Am. Chem. Soc. **81**, 2023 (1959); (f) A. D. Liehr and C. J. Ballhausen, Acta Chem. Scand. **11**, 207 (1957); (g) D. R. Scott and R. S. Becker, J. Chem. Phys. **35**, 516 (1961); (h) C. J. Ballhausen, *Introduction to Ligand Field Theory* (McGraw-Hill Book Co., 1962), Chap. 9, p. 217.

[2] E. Saito, Brookhaven National Laboratory Rept. 6472 (unpublished).

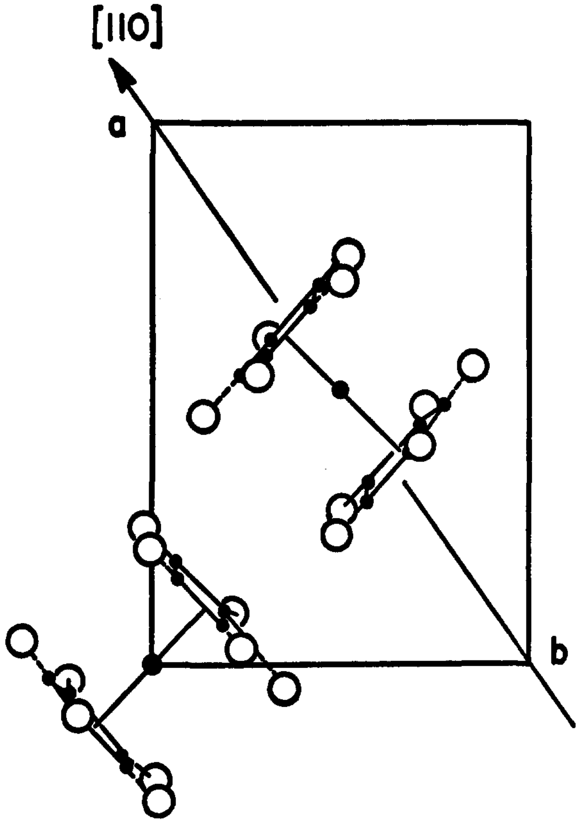

FIG. 1. Projection of the positions of atoms in ferrocene on the (*ab*) plane; ● Fe, ● C, ○ H.

is $P2_1/c$ and the molecular point group symmetry is D_{5d} with the two cyclopentadienyl rings in staggered configuration. The unit cell has the following dimensions: $a=10.56$ Å, $b=7.597$ Å, $c=5.95$ Å, and $\beta=121.02°$.[3] If we consider the principal axis of the ferrocene molecule as that which is perpendicular to the plane of the cyclopentadienyl rings and passing through the two rings and the iron atom, it is at 45° relative to the *a* or *b* axes and lies in the *ab* plane. There are two molecules per unit cell, and the second molecule has its principal axis also in the *ab* plane and perpendicular to that of the other molecule, Fig. 1.

Most single crystals grew with the edges parallel to the [110] axis, others with the edges parallel to the [001] axis. Some were obtained having a large surface parallel to the *ab* plane with the [010] or [100] axes bisecting the angles of the losange.

These single crystals were placed in a silica tube, sealed off under vacuum and irradiated in an acetone dry-ice bath. When the crystals had to be cut so that they could be fitted into the 3-mm-internal-diameter tube, they were checked with the polarizing microscope and those which were too damaged were discarded. The irradiation facilities at the B.N.L. and at the C.E.N.S. were used.

After irradiation, the upper tip of the silica tube was pulled above the dry-ice–acetone bath and the paramagnetic defects of the silica annealed out by heating with a blow torch. The annealed end was then submerged in the bath and the tube was turned over so that the crystal would slide into the annealed part. Care had to be taken in doing this as the crystals become very fragile on irradiation. Many crystals were lost by breakage at this point of the experiment. The silica tube was then transferred to the EPR cavity. The upper part of the tubular Dewar inserted into the cavity had plane windows which permitted the sighting of the single crystal with a telescope. The sample tube was turned till a known face of the crystal paralleled the line of sight, then it was lowered into the cavity carefully without rotation.

When the double cavity was used instead of the rotating cavity, a pointer was attached to the sample tube which was rotated. The second cavity contained the KCl 0.1% pitch standard as a reference for determining the *g* values.

The orientation of the single crystal in the cavity could be determined to 5° but deviations by as much

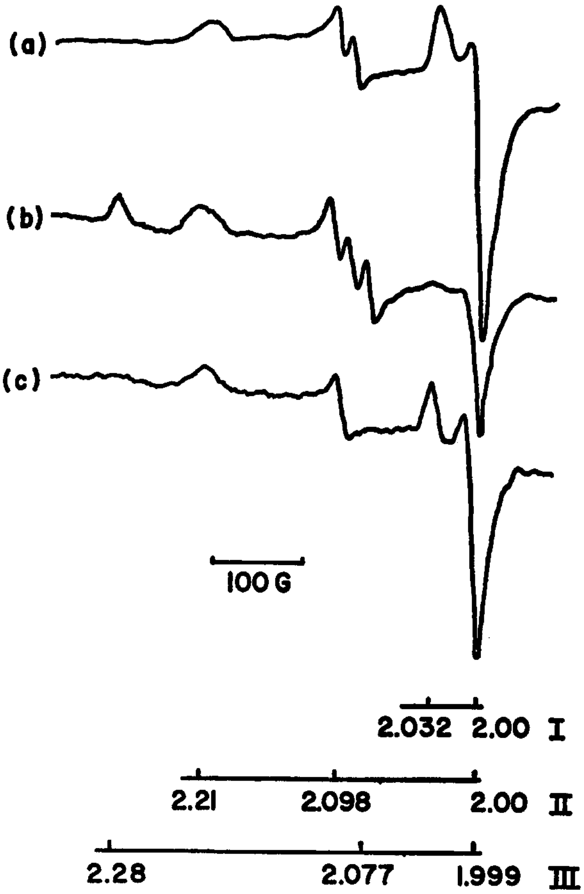

FIG. 2. Spectra for ferrocene powder irradiated at 77°K; (a) before annealing, (b) after 60 min annealing at 148°K, (c) $(C_5D_5)_2Fe$.

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[3] J. D. Dunitz, L. E. Orgel, and A. Rich, Acta Cryst. 9, 373 (1956).

as 10° occurred. These differences could be ascertained *a posteriori* by comparing the experimental values of g and calculated values which gave the best fit for a certain pole of rotation. The poles were 5°–15° off from the nominal axes of rotation.

The low temperature in the tubular Dewar was obtained by a flow of cold nitrogen gas coming from a stock of liquid nitrogen.

Irradiation of the powder was effected at 77°K, and the spectra were obtained at that temperature. The annealing was carried out by transferring the sample to Dewars containing suitable compounds cooled by addition of liquid nitrogen or dry ice. The spectra of the annealed samples were taken always at 77°K.

C. Ferrocene-*d*-10

The method of preparation employed finally was that used by Lippincott and Nelson.[4] $Ca(OD)_2$, is obtained by adding D_2O [99.9% $D/(D+H)$] to CaO which has been previously heated under vacuum to 700°C, in a silica tube. Ferrocene and $Ca(OD)_2$ are placed in a Pyrex tube, sealed off under vacuum, and heated to 320°C for about 20 h. At the end of the exchange, one end of the tube is pulled out of the furnace and this allowed practically all the ferrocene to condense on the cool end. After each exchange, the extent of the deuteration was checked with a mass spectrometer. The exchange was repeated with fresh $Ca(OD)_2$ until the ratio $D/(D+H)=99.7\%$ was obtained.

III. RESULTS

A. Spectra of Powder Irradiated at 77°K

The spectrum obtained after irradiation is given in Fig. 2(a). This is a superposition of two spectra: (1) radical I with a g tensor of axial symmetry: $g_{\perp}=2.00$, $g_{\parallel}=2.032$, and (2) radical II with a totally asymmetric g tensor: $g_1=2.00$, $g_2=2.098$, and $g_3=2.21$.

Annealing gives results which are interesting. If the increase in temperature is rapid, for example, from liquid nitrogen to room temperature in a few seconds, all the signals vanish. A less brutal way of annealing brings the following changes. A modification is preceptible only towards 143°K. Annealing at 148°K, the signal corresponding to radical I starts to decrease while a radical III with a totally asymmetric g tensor appears, $g_1=1.999$, $g_2=2.077$, and $g_3=2.28$. After 1 h annealing the spectrum has the form given in Fig. 2(b). Further annealing at this temperature does not induce any change in the strengths of the signals. We can then increase the annealing temperature to 163°K and we note a further decrease after which the signal heights remain practically constant. For one experiment in which the annealing was performed very gradually from 143°K, with a 10° increase between each step, the signals were still easily recorded at 313°K. One detail we have to take into account in the discussion is that the relative strengths of the peaks in the spectrum does not vary, once the pattern in Fig. 2(b) is attained.

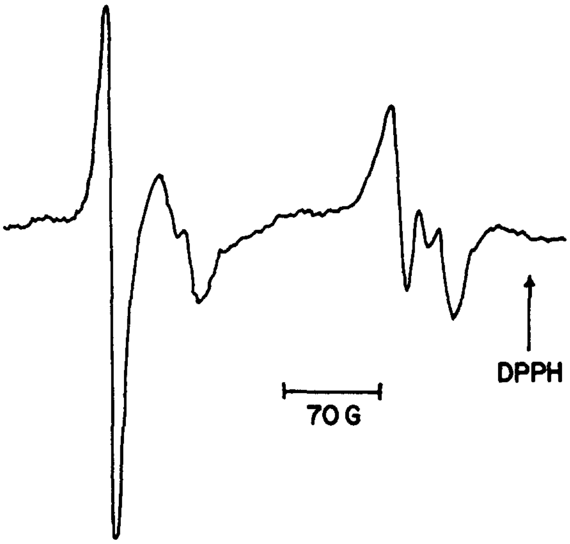

FIG. 3. Spectrum of a single crystal irradiated at 193°K; Type A spectrum.

Figure 2(c) is the powder spectrum of the deuterated ferrocene after irradiation. We see that the spectrum of radical I has not changed, whereas the doublet which belongs to radical II has been replaced by an unresolved single line. The g values, g_1, g_2, g_3 are the same as for the nondeuterated ferrocene. The behavior of the radicals on annealing was also the same as in the case of ordinary ferrocene: radical I disappears, giving rise to radical III with practically identical principal values of g.

B. Spectra of Single Crystals Irradiated at 193°K

Due to the bursting of the ferrocene crystals when plunged into liquid nitrogen, irradiation of single crystals was possible only in dry-ice acetone baths.

Type A spectra obtained just after irradiation showed the presence of four independent signals, two singlets and two doublets. Their relative positions depend on the direction of the external magnetic field relative to the crystalline axes. Figure 3 shows a typical spectrum where the four signals are relatively well separated. There is *no* isotropic free radical visible at $g=2.00$. The linewidth of the singlet is of the order of 10 G at low field and 15 G at high field. The doublet is well resolved at certain angles of the crystal orientation, at others the two lines merge into one broad line. When the signals were weak, the singlets could be detected but the doublets were not always apparent. The graphs [Figs. 4(a) to 4(c)] show the variation of the position of the singlets and doublets as a function of

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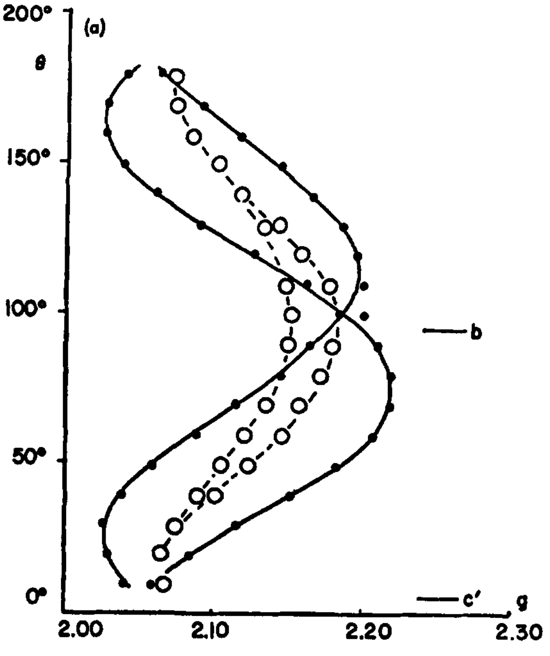
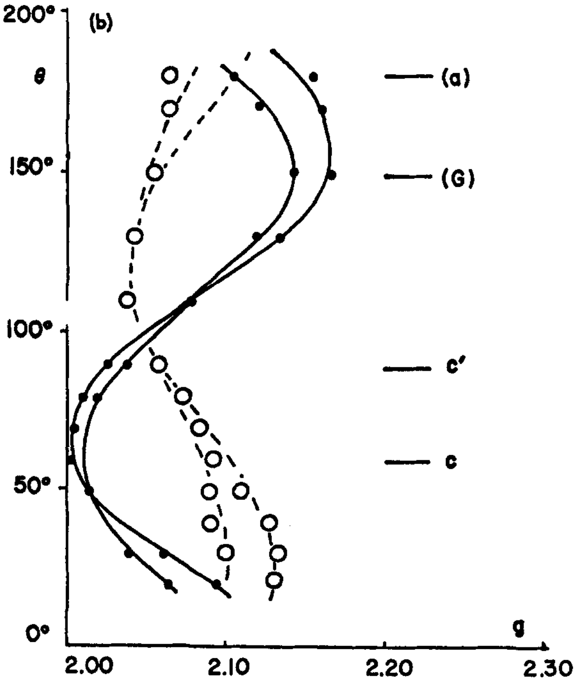
[4] E. R. Lippincott and R. D. Nelson, Spectrochim. Acta **10**, 307 (1958).

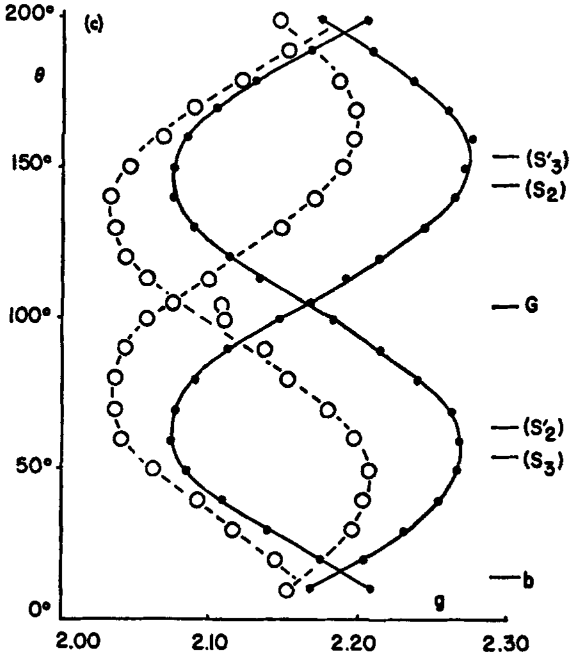
angle in the rotation of the single crystals around axes which are close to [100], [010], and [001]. The experimental values for the singlets are represented by dots and midpoints of the doublets by circles. One sees that the *b* axis is effectively a twofold symmetry axis. Rotation around the *c* axis shows that the (*ac*) plane is a plane of symmetry and that the four ellipsoids of the *g* tensors are oriented symmetrically on both sides of this plane.



(a)



(b)



(c)

FIG. 4. Variation of *g* values as a function of *θ* angle of the magnetic field direction. Singlets (radical III) —●—●—, doublets (radical II) - -○- -○-. Letters: S_1, S_1', D_2, etc correspond to directions indicated on the stereographic projection—Fig. 6. Same letters in parentheses mean "close to." (a) Rotation around *a* axis. (b) Rotation around *b* axis. (c) Rotation around *c* axis.

Figure 5 gives the orientation of the planes of rotation. The plane perpendicular to the *c* axis is at an angle of 31° from the *a* axis and passes through the *b* axis. From the values of *g* in these planes, the *g* tensors have been calculated for the singlets and doublets, using the method given by Schonland.[5]

The analysis of the spectra shows that the rotation around the *b* axis had poles slightly off this axis, those around the *c* axis were the most precise due to the use of relatively long crystals which grew with edges parallel to the *c* axis and which fitted snugly into the silica tubes. In the case of rotation around the *b* axis, the doublet signals were weak and not always apparent on account of the small size of the crystals used. For the values of the maxima and minima of the *g* values in the plane perpendicular to *b* we used an average of values belonging to several experiments. Nevertheless we obtained enough information to calculate the (g^2) tensors, their principal values with their direction cosines. These values are given in Table I. The figures of the principal values of the *g* tensor of a radical belong to

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[5] D. S. Schonland, Proc. Phys. Soc. (London) **73**, 788 (1959); see also, P. W. Atkins and M. C. R. Symons, *The Structure of Inorganic Radicals* (Elsevier Publ. Co., Inc., New York, 1967), p. 265.

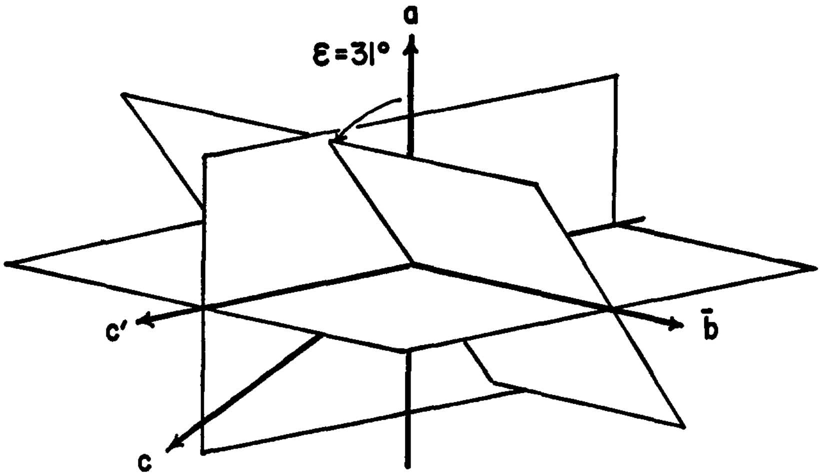

FIG. 5. Position in space of the planes of rotation used in calculating the g tensor.

one of the ellipsoids, the other ellipsoid is obtained by reflection through the (ac) plane.

In the last column of Table I we give the values of g obtained from the powder spectrum. Comparing these values with the principal values of the g tensors we can consider that the singlets of the single crystal belong to radical III and the doublets to radical II.

Figure 6 shows the stereographic projection of the directions of these principal values relative to the crystalline axes. The a and b axes are in the equatorial plane and c is 31° from the zenith (c' in Fig. 5). We see that the lowest principal value (2.00) of the singlet is practically along the c axis and the highest (2.28) in the plane perpendicular to the c axis, at a point 40° from the b axis and about 20° above the (ab) plane. The doublet has its highest principal value (2.21) almost in the (ab) plane but its direction is not parallel to that of the main axis of the ferrocene molecule. The dotted line going through b, G, and $\bar{b}$ is the projection of the plane perpendicular to the c axis. G is the intersection of this plane and the (ac) plane. This direction G is indicated also in Fig. 4(c) and in Fig. 4(b), (G) is a direction close to G, this discrepancy arising from the fact that the axis of rotation was not exactly along b. c' is the direction perpendicular to the (ab) plane. (S_3), (S_2'), (S_2), and (S_3'), indicated in Fig. 4(c), are directions lying on the plane perpendicular to c and close to the directions of the maximal and medium principal values of the g tensor of radical III.

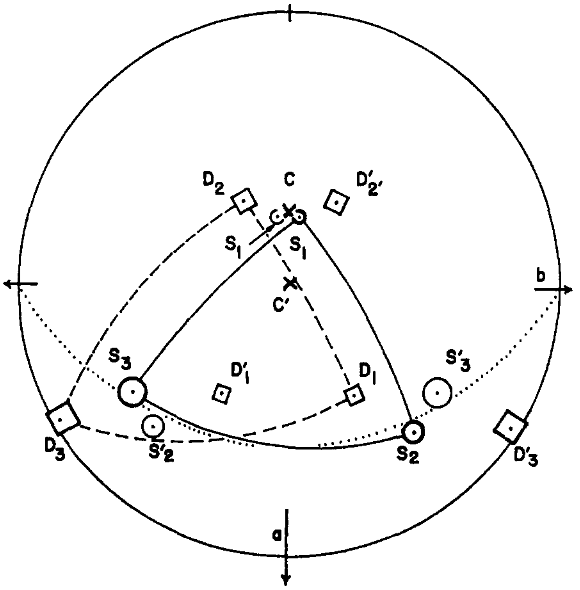

FIG. 6. Stereographic projection of the principal values of g and of the directions of the crystalline axes, where Radical II: $D_1=D_1'=2.008$; $D_2=D_2'=2.097$; $D_3=D_3'=2.207$. Radical III: $S_1=S_1'=2.002$; $S_2=S_2'=2.076$; $S_3=S_3'=2.276$.

Type B spectra, Fig. 7, are obtained after keeping the irradiated single crystals 10–20 h in a dry-ice–acetone bath. In some cases, a mixture of both A and B types of spectra were obtained, which shows the decrease in the signal height of the radical III singlets and the appearance of an organic free radical IV at $g=2.00$. That these singlets belong to radical III is shown by a study of the variation of g as a function of angle, which gave patterns identical with those obtained with pure A type spectra for the same axis of rotation.

In favorable cases—not easily obtained—this organic radical IV showed a hyperfine structure of five lines with intensity ratios 1:4:6:4:1, corresponding to an interaction with four protons. The separation between the lines is 20 G. Slight changes observed in the shape of the five-line spectrum when rotating the magnetic field around the crystal may be due to a weak anisotropy in g as well as a feeble variation in the coupling constant. These changes may also arise from the superposition of a partial powder spectrum of radical II. This is shown by the signal at the left which at certain orientations shows the doublet structure, at others the unresolved broad line. Even when the crystal is badly deteriorated. the microcrystals are not yet completely oriented at random and the radical II spectrum only approaches that of a powder so that the final result is a very distorted signal.

In the case of deuterated ferrocene, we were not

TABLE I. Principal values and direction cosines of the g tensors of radical III and radical II.

g^2 in the c', $\bar{b}$, a-axis[a] system			Principal values	Direction cosines in the c', $\bar{b}$, a-axis system			Powder spectrum
Singlet							Radical III
4.19	0.259	0.292	2.276	0.36	0.77	0.53	$g_3=2.28$
0.259	4.821	0.344	2.076	0.33	−0.64	0.70	$g_2=2.077$
0.292	0.344	4.485	2.002	0.87	-0.07_5	−0.48	$g_1=1.999$
Doublet							Radical II
4.25	0.107	−0.143	2.207	0.029	0.86	0.52	$g_3=2.21$
0.107	4.68	0.307	2.097	0.77	0.31	−0.56	$g_2=2.098$
−0.143	0.307	4.368	2.008	0.64	−0.41	0.65	$g_1=2.00$

[a] c' axis is perpendicular to a and b axes (see Fig. 5).

able to observe the corresponding hyperfine structure, the spectrum at $g=2.00$ was a single distorted derivative curve. Theoretically, if the four deuterium atoms were completely equivalent, we would have observed a nine-line spectrum of intensity ratios 1:4:10:16:19:16:10:4:1, the separation between the extreme lines being about 25 G. An envelope would have a peak-to-peak distance of about 12 G which is in the range of experimental values found: 10–15 G.

The transformation of radical III to radical IV in single crystals of deuterated ferrocene was much slower than for the ordinary ferrocene. After 50 h at 193°K, signals of radical III were still observable, such was not the case with ordinary ferrocene where after 20 h all signals of radical III have disappeared.

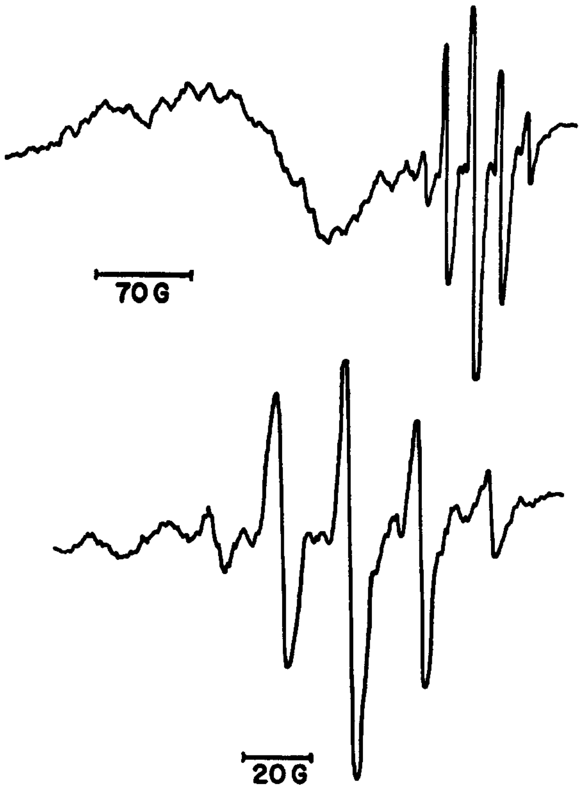

FIG. 7. Spectrum of a single crystal irradiated at 193°K; Type B spectrum with hfs.

IV. DISCUSSION

A. Electronic Structure

Many papers have been published in the literature on the electronic structure of ferrocene and other metal sandwich compounds. Ferrocene has a molecular point group symmetry D_{5d}. The electronic configuration consists of a closed shell of 12 electrons $(a_{1g})^2$, $(e_{1u})^4$, $(a_{2u})^2$, $(e_{1g})^4$, and six electrons $(a_{1g}')^2(e_{2g})^4$. This is diamagnetic with $S=0$. The ferricinium ion will have the $(a_{1g}')^2$, $(e_{2g})^3$ structure and is paramagnetic.

To explain the protonation of metallocenes which has been observed, one can construct three nonbonding hybrids sticking out from the metal atom in a plane between the rings.[6] Protons can add to these orbitals, one in the case of ferrocene, three in the case of $(Cp)_2Ta$ or $(Cp)_2W$. For $(Cp)_2Ta$, the NMR spectrum showed that two hydrogens are equivalent, the third having a different shift. This means that the two rings are not parallel and the compound has a bent structure. The possibility of protonation and the existence of a bent structure will be used in the interpretation of the spectra.

The g factor of the ferricinium ion can be calculated by an expression of the type given by Robertson and McConnell[7]

$$g_\mu=2[1-(\zeta\Lambda_\mu/2S)], \qquad \mu=x, y, z,$$

$$\Lambda_\mu=\sum_{n\neq 0}\sum_i \frac{\langle 0\,|\,l(i)\,|\,n\rangle\langle n\,|\,l(i)\,|\,0\rangle}{E_n-E_0},$$

where ζ is the spin–orbit coupling coefficient, $|\,0\rangle$ is the orbital ground state, $|\,n\rangle$ is the excited orbital state, and S is the total spin, which in the case of the ferricinium ion is $\frac{1}{2}$.

Robertson and McConnell consider the electronic system of the ferricinium ion as one of five electrons or as of one positive hole. In the latter case, the spin–orbit coupling coefficient has a negative value and g becomes greater than 2.00. Their equations predicted the g_x and g_y will be close to 2.00 and $g_z>2.00$.

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[6] C. J. Ballhausen and J. P. Dahl, Acta Chem. Scand. **15**, 1333 (1961).

[7] R. E. Robertson and H. M. McConnell, J. Phys. Chem. **64**, 70 (1960).

German and Diatkina[8] have obtained $g_\perp=0$ and $g_{\|}=6.045$ for the case without the Jahn–Teller effect, and taking this effect into account obtained 1.987 and 2.246, respectively.

Nussbaum and Voigtlander[9] have also calculated g values for different paramagnetic sandwich compounds. For ferrocene, they note that the spectrum primitively attributed to $Fe(Cp)_2\cdot picrate^-$ arose probably from $(FeCl)_4^-$.

B. Interpretation of Spectra

The experimental results presented above of spectra obtained from the powder and from the single crystals show the presence of four radicals. Radicals I and II exist initially at liquid nitrogen temperatures. Annealing transforms radical I into radical III. With single crystals irradiated at 193°K, radicals II and III are obtained initially and at that temperature, radical III gradually disappears leading to the formation of radical IV.

We present here a tentative attribution of the different spectra to the following structures. We give also mechanisms for their formation and for their disappearance.

Irradiation by gamma rays at 77°K knocks out an electron from a ferrocene molecule leading to a *straight molecule–ferricinium ion*. The electron, by dissociative attachment on another molecule, leads to the formation of a hydrogen atom and an anion C_5H_5–Fe–$C_5H_4^-$, which is diamagnetic. The hydrogen atom attaches itself to one of the nonbonding orbitals on the iron atom of a neighbor molecule, leading to a *protonated ferrocene*, which although neutral has an unpaired electron and is paramagnetic, see Fig. 8.

The *straight molecule–ferricinium ion* is of axial symmetry, hence it is reasonable to attribute the spectrum of radical I to this ion. The spectrum of radical II which has a totally asymmetric g tensor can be attributed to the *protonated ferrocene*, this radical in fact having lost its axial symmetry. That the doublet arises from an interaction with the proton has been shown by deuteration of the molecule—the g tensor has not changed but the doublet has been replaced by an unresolved single line.

The transformation of radical I into radical III, which consists of the disappearance of a spectrum of axial symmetry and appearance of a spectrum with a totally asymmetric g tensor, can be accounted for by a tilting of the rings. This tilting gives radical III, the *bent molecule–ferricinium ion*, and the highest value of the g tensor is directed some 20° above the (ab) plane. In the crystal lattice, it seems that this tilting takes place in only one privileged direction due to greater steric hindrance for the other directions. To explain the presence of only radicals II and III when the single crystals are irradiated at 193°K, we may say that the temperature is high enough for the tilting process to occur immediately after the formation of the ferricinium ion.

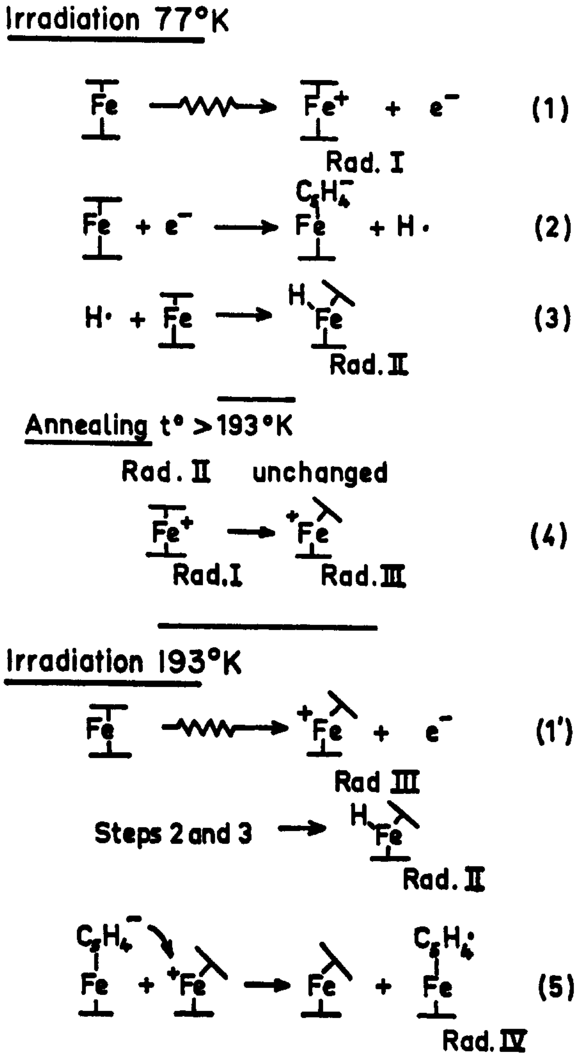

FIG. 8. Mechanisms of radical formation at 77°K and at 193°K.

We have seen that in the course of annealing of the powder, the signals decrease in height but the proportion of radicals II and III does not change, the spectra retaining the same shape even up to 313°K. With single crystals kept overnight at 193°K radical III disappears to give radical IV, which in certain cases appear as a well-resolved five-line hyperfine spectrum and in other cases as a jumbled spectrum or an envelope at $g=2.00$. Clearly we are in the presence of two different mechanisms. The reaction leading from radical III to radical IV is a slow process occurring at a constant temperature. This is to be distinguished from the annealing process where the powder is warmed up by increments 10° or 20° each time the decrease in signal height levels off to a plateau. This behavior will be analyzed in the following two sections.

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[8] E. D. German and M. E. Diatkina, Zh. Strukt. Khim. **6**, 898 (1965).

[9] M. Nussbaum and J. Voigtlander, Z. Naturforsch. **20a**, 1141 (1965).

1. Mechanism of Formation of Radical IV

An electron is transferred from the anion C_5H_5–Fe–$C_5H_4^-$ to the *bent molecule–ferricinium ion*, the radical III, this ion being neutralized, its spectrum disappears and the anion becomes a radical with an unpaired electron on the cyclopentadienyl ring with four protons. The value of 20 G for the coupling constant is relatively high for a radical with a conjugated system. It is nearer to a σ-type radical, although the π-electron system allows an equivalent distribution of the electron spin density on the four protons.

It is interesting to compare this value of the coupling constant with that found for $C_5H_5\cdot$ by Liebling and McConnell.[10] At temperatures above 120°K, the spectrum consists of five lines with a splitting of 6.2 G. At temperatures below 70°K the spectra consist of five or six broad lines with a total spread of 31 G, the same as the high-temperature spectra and with anisotropy. The two types of spectra could be explained and calculated spectra almost identical with the experimental ones obtained, by supposing a rotation of the C_5H_5 rings. A nonrotating $C_5H_5\cdot$ radical with uniform spin cannot produce the spectra obtained.

In the case of the C_5H_5–Fe–$C_5H_4\cdot$ radical, rotation of the ring is not excluded. For ferrocene itself, Mulay *et al.*[11] deduced from PMR absorption that the rings are more or less oscillating. The fact that crystallographic data show the positions of the C atoms in the lattice makes it difficult to say that free rotation exists.

We return now to the other reactions concerning the radicals in the powder.

2. Mechanism of Formation and Disappearance of Radicals II and III

First, it is assumed that the yields of the consecutive Reactions (2) and (3) are the same as long as the conditions of irradiation do not change, and radical II being produced following the formation of radical I, their relative proportions must have a constant value. It seems that from the start of the annealing process, while radical I is converted to radical III, radical II and radical I and/or III are disappearing at practically the same rate. If the rates were different, the spectra would have ended up with radical II or radical III predominanting, but no experiment gave such results and the spectra do not change after the pattern of Fig. 2(b) is obtained, only the over-all strength of the signals decrease.

At low temperatures, the hydrogen atom created by the associative attachment of the electron is captured by a molecule of ferrocene to give the protonated form. On annealing, this protonated ferrocene may disappear by two mechanisms:

(A) the hydrogen attached to the iron may migrate to another protonated molecule and combine with the corresponding hydrogen giving H_2, (only radical II disappears),

(B) this hydrogen may revert to the cycloponta-dienyl anion and the excess electron migrates and neutralizes a nearby ferricinium ion (radicals II and III disappear).

With mechanism (A) the protonated form disappears, independently of the ferricinium ion, so we should expect changes in spectra. We favor mechanism (B) as it explains the simultaneous disappearance, with equal rates, of radicals II and III, in agreement with experiment.

This leads us to the further hypothesis, that in the departure of the hydrogen atom—Reaction (2), Fig. 8,—leaving the anion C_5H_5–Fe–$C_5H_4^-$, fixation of this hydrogen occurs on the Fe of the molecule next to the $C_5H_4^-$ ring. In fact, the arrangement of molecules is such that the Cp rings of the molecule in an (*ab*) plane are partly embedded in between the two rings of the molecules lying in the planes above or below. Edwards, Kingston, and Mason[12] have found that the coefficient of expansion is anisotropic with a maximum value corresponding to the direction of the *c* axis. In the other directions repulsion between the rings is greater, whereas along the *c* axis the rings can shear in and out. If the hydrogen atom remains on the Fe close to the anion ring, one can imagine that recombination predominates over any migration of H· to another protonated form to create the H_2 molecule.

To sum up, the slow chemical change at 193°K transforms radical II to an organic radical IV irreversibly, whereas annealing just reverses the reactions of the formation of radicals II and III. This explains the high stability of ferrocene towards gamma irradiation (in our preliminary experiments, we could not detect signals with the powder irradiated at room temperature). This is also in agreement with the work of Krotszynski,[13] who found low yields of products on electron radiation at 25°C. The yield values he found are $G_{H_2}\sim0.01$, inorganic iron $G\sim0.042$, hydrocarbon products $G\sim0.0036$. The hydrocarbon products are mostly cyclopentadiene and isomeric pentadienes.

For room temperature irradiation, it is reasonable to assume that the chemical changes may be quite rapid and of a different nature than that occurring at low temperatures. The proton created by a rupture of the C–H bond may meet a cyclopentadienyl ring and abstract another hydrogen to give a H_2 molecule. The radical may have enough energy to rearrange or react with other rings and lead to the different organic compounds mentioned by Krotszynski. At these relatively high temperatures, mechanism (A) may contribute partly, yielding some H_2 molecules.

Sutin and Dodson[14] have studied the Szilard–

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Chalmers reaction of ferrocene. The percentage of ^{59}Fe retained is sensitive to the type of radiation used and the subsequent annealing process. The fast neutron dose and the accompanying gamma radiation play an important part in activation, whereas postirradiation with large doses of gamma radiation does not alter the retention. The fragments which led to the different compounds found were free iron atoms, iron monocyclopentadienyl radicals arising from the ($n\gamma$) processes and free cyclopentadienyl radicals and other organic radicals arising from the rupture of the π-C_5H_5 by fast neutrons.

We have seen that in the gamma irradiation of ferrocene, the iron–cyclopentadienyl link is not broken, this, together with the high radiation resistance may explain why pile-irradiated ferrocene led to results which are not sensitive to high post gamma irradiation.

An objection to our interpretation of radicals I and III as belonging to the ferricinium ion, whether straight molecule or bent molecule, is that it has not been possible to observe signals with ferricinium salts in solution or as single crystals. It is possible that relaxation phenomena may broaden out the absorption. Another difference in the case of single crystals of the ferricinium salts is that the lattice is of ionic character with a regular distribution of charges. In gamma-irradiated ferrocene, the charges may exist more or less close to each other, but without any regularity. The fact that the spectra were not observed with ferricinium salts does not rule out the possibility of the existence of the ferricinium ion embedded in a neutral ferrocene matrix. Moreover, we have seen above the values of g calculated for the ferricinium ion by German and Dyatkina[7] taking into account the Jahn–Teller effect. Their values $g_{\perp}=1.987$ and $g_{\parallel}=2.246$ are of the same order of magnitude as the minimum values found for radical III: $g_1=1.999$ and $g_3=2.28$.

V. CONCLUSION

The nature of the free radicals induced in ferrocene by ^{60}Co gamma rays was determined by studying their electron spin resonance spectra. The shapes of these spectra for the powder, for the single crystals, as well as the modifications occuring on annealing or on deuterium substitution, were used to deduce tentatively the attributions to different radicals. Mechanisms for the formation as well as for the disappearance of these radicals have been presented. They may explain in part, the high radiation resistance of ferrocene. It would be interesting to create these individual radicals independently by other means and try to obtain their spectra.

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Hyperfine Spectrum of NaCl by Molecular-Beam Electric Resonance*

J. W. Cederberg
St. Olaf College, Northfield, Minnesota
AND
Carl E. Miller
Mankato State University, Mankato, Minnesota

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The hyperfine spectrum of NaCl has been observed at very low field using the molecular-beam electric resonance method. The Hamiltonian is expressed in a representation in which the combined quadrupole term is diagonal when the quadrupole interaction constants of the two nuclei are equal. The analysis of the spectrum then gives for the constants $X^+\equiv[(eqQ)_{Na}+(eqQ)_{Cl}]/2$, $X^-\equiv[(eqQ)_{Na}-(eqQ)_{Cl}]/2$, $c^+\equiv(c_1+c_2)/2$, c_3, and c_4 the values (in kilohertz) for ^{23}Na^{35}Cl: $X^+=-5658.0\pm0.1$, $X^-=-16\pm50$, $c^+=+0.51\pm0.01$, $c_3=+0.22\pm0.02$, and $c_4=+0.05\pm0.03$ for $v=0$; $X^+=-5716.3\pm0.5$ and $X^-=+116\pm20$ for $v=1$; $X^+=-5772.6\pm0.7$ and $X^-=+235\pm12$ for $v=2$; and $X^+=-5828\pm1$ and $X^-=+340\pm15$ for $v=3$. Lines have also been observed corresponding to ^{23}Na^{35}Cl, $J=2$, and ^{23}Na^{37}Cl, $J=1$.

I. INTRODUCTION

The measurement of the hyperfine constants in the NaCl molecule has long presented special problems not present in most of the other alkali halides. Measured values of the quadrupole interaction constants range from -5.3 to -5.7 mHz for the sodium nucleus and from -5.3 to -5.8 mHz for the chlorine.[1–6] The major

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