PART I

ELECTRON MAGNETIC RESONANCE STUDIES ON IRRADIATED SINGLE CRYSTALS OF SEBACIC ACID

PART II

RATE OF ELECTRON EXCHANGE BETWEEN DIp-ANISYL NITROGEN OXIDE MOLECULES BY ELECTRON PARAMAGNETIC RESONANCE

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I am grateful for the patience and understanding of my wife and my mother.

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ABSTRACT

PART I

The electron magnetic resonance spectrum of freshly x-ray damaged single crystals of sebacic acid shows that two radical species, I and II, are produced, the spectrum of I about twice as intense as that of II. Upon illumination of a damaged crystal with ultraviolet light, radical II is destroyed, leaving I unaffected. Analysis of the magnetic hyperfine spectrum of such a "bleached" crystal identifies I as $HOOC\dot{C}H(CH_2)_7COOH$ and shows that I is oriented within experimental error in the same way in the crystal lattice as the undamaged molecule. The σ proton and π proton hyperfine interactions with the unpaired spin are measured for I and are found to be consistent with those values observed for similar radicals formed in other irradiated dicarboxylic acids. Radical II is not identified but is judged to be structurally similar to I, primarily because of the observed and deduced similarities between the spectra of I and II. A damaged crystal which has been heat treated has a spectrum interpretable in terms of three radicals, I, III, and IV. The evidence is that radical II is the precursor of III and IV. Several models for III and IV are offered, which invoke fractional spin densities to account for the observed small hyperfine splittings. Arguments are advanced that

favor IV being $(\cdot OOC)(CH_2)_8COOH$. Radical III may be $HOOCCHCH{=}CH(CH_2)_6COOH$ or an ionized species as $(O{=}CHCHC\overset{+}{H})(CH_2)_5COOH$.

PART II

The line shape of the EPR spectrum of di-p-anisyl nitrogen oxide (DANO) in $CHCl_3$ was studied over a range of concentrations (0.006-0.2 F) so chosen to show the transition from the hyperfine triplet spectrum (arising from the hyperfine contact interaction of the electron spin with the nitrogen nucleus) to the exchange narrowed single line spectrum as the concentration of free radical increases. The observed change of line shape with concentration agreed well with that predicted by the modified Bloch equations which allow for spin magnetization exchange. The rate of electron exchange between molecules of DANO was calculated to be 7.5×10^9 liter $mole^{-1}$ sec^{-1} at room temperature. The lifetimes of the electron spin state with respect to exchange ranged from 3×10^{-8} sec to 1×10^{-9} sec.

PART I

ELECTRON MAGNETIC RESONANCE STUDIES ON IRRADIATED SINGLE CYRSTALS OF SEBACIC ACID

INTRODUCTION

A number of electron magnetic resonance studies have been made on oriented free radicals present in irradiated single crystals of simple saturated dicarboxylic acids (1-5). One species of free radicals invariably present is derived from the parent molecule by the loss of a hydrogen atom, leaving an unpaired spin localized in a p orbital on a carbon atom adjacent to a carboxyl group.

The electron magnetic resonance hyperfine structure of the central proton of the radical $(HOOC)\mathring{C}H(COOH)$ in irradiated malonic acid is described by a second rank tensor which consists of an isotropic part and an anisotropic part (1). The isotropic part arises through the Fermi contact interaction of the proton and the unpaired spin via the carbon-hydrogen σ bond. The anisotropic part is due to magnetic dipole-dipole interaction between the unpaired spin and the proton. The proton directly bonded to the carbon atom bearing the unpaired spin is called a σ proton.

The radical $(HOOC)\dot{C}HCH_2(COOH)$ in irradiated succinic acid gives a more complicated hyperfine spectrum which arises from the interaction of the unpaired spin with not only the σ proton but also with the methylene or π protons bonded to the adjacent carbon atom (2, 3). This latter type of interaction is due in major part to direct overlap of the p orbital with the π protons and is also described by a second rank tensor. π proton hyperfine splittings are very nearly isotropic but show a marked dependence on the relative orientation of the p orbital and the π proton-carbon bond.

Irradiated adipic acid contains the radical $(HOOC)\dot{C}H(CH_2)_3(COOH)$ and another as yet undetermined free radical (5). Freshly irradiated malonic acid contains another kind of oriented free radical, $\overset{\circ}{C}H_2COOH$ (6, 7).

The present work is a report on the electron magnetic resonance studies on the free radicals present in x-ray damaged single crystals of sebacic acid $(HOOC(CH_2)_8COOH)$ and on the effect of subsequent heat and ultraviolet light treatment on those free radicals.

EXPERIMENTAL

Sebacic acid is monoclinic. The crystal structure has been determined by Robertson and Morrison (9). The unit cell has edges a = 10.10 Å, b = 5.00 Å, c = 15.10 Å, with the monoclinic angle β = 133.8°. Figure 1a gives a convenient picture of the crystal as viewed along the c axis perpendicular to the plane of the figure. The a axis is perpendicular to the b axis and is directed out of the plane of the figure by an angle 43.8°. The space group is P_{2_1}/a ($C_{2_h}^5$). There are two molecules per unit cell, represented by dumbbells A and B. A and B are transformed into one another by rotation about the two fold screw axis b. The molecules are hydrogen bonded end-to-end and form chains parallel to the c axis. In any chain, the methylene carbons lie in one plane, the carboxyl groups in another, the two planes making an angle of 3°. The dumbbells in Figure 1a also represent the edge of the zig-zag methylene carbon chain. For simplicity, the carboxyl group plane is not distinguished. The dotted lines extending from A represent the methylene carbon-hydrogen bonds.

Figure 1b shows the staggered relationship between chains A and B, as viewed along the b axis. It can be seen that there is a close approach of the α and γ carbons in one chain to the carboxyl oxygens in the neighboring chain. The distance between an α carbon and the appropriate hydroxy oxygen in a neighboring chain is 3.3 Å, shorter

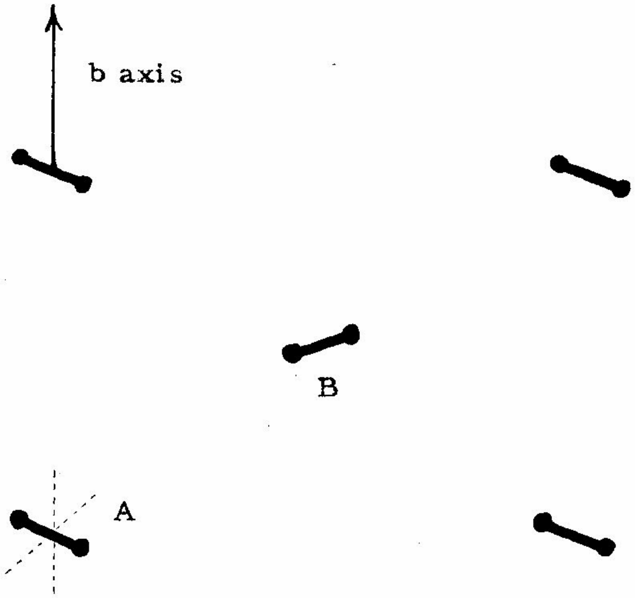


Fig. 1a. Schematic representation of crystal structure as viewed along the c axis.

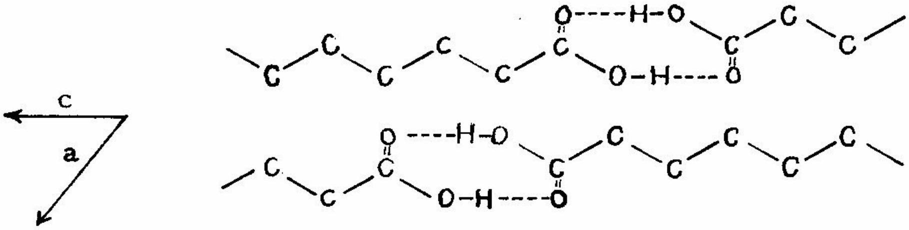


Fig. 1b. Relative orientation of chains A and B as viewed along the b axis.

than in succinic acid and taken as an indication of slight interchain hydrogen bonding. From Figure 1b it is seen that one of two methylene hydrogens on the α and γ carbons in A is directed towards the carboxyl oxygens in B.

The sebacic acid was first purified by treatment of hot alcoholic solutions with activated charcoal, followed by treatment with hot benzene to remove any azelaic acid ($HOOC(CH_2)_7COOH$). The sample was recrystallized from ethyl acetate and then from water. The final stage of purification was passage through a zone refiner of fourteen zones, giving a sample with a melting point of 132.0-132.2°C, comparing well with the most recently reported value of 131.8-132.1°C (8).

Attempts to grow single crystals of reasonable size by the standard techniques of slow evaporation or gradual cooling of saturated solutions proved unproductive. The alternative method of growth from the melt did prove practical.

The sample was packed into a pyrex tube, degassed several times on a vacuum line by alternatively melting, freezing and pumping, and was finally sealed off under vacuum. The sample tube was lowered at a rate of 0.5-1 cm. per day through another tube wound with heating ribbon directly into an oven. The oven was thermostated at a temperature 20°C below the melting point of the sample while the current input to the heating ribbon was adjusted to attain a temperature within the heating tube some 20°C above the melting point of the sample.

Once the entire sample had completed its passage into the oven and had resolidified, the temperature of the oven was lowered to room temperature over a period of twelve hours. The sample cleaved naturally to give single crystals, a common size being about 6x3x1 mm. The crystals were elongated along the c axis, with reasonably well developed faces ((100), (010), and (110)), which were identified with an optical goniometer. The crystals were placed 5 cm. from the tungsten target of an x-ray tube operating at 45 kv. and 30 ma. for periods of time varying from an hour to a few days. Of all the characteristics of the spectra, only the intensity varied with the irradiation time.

For X-band resonance work, a special goniometer head was constructed as shown in Figure 2 for accurate orientation of the crystal with respect to the magnetic field. Section A is essentially a brass rod machined so that the base fits the optical goniometer and the other end permits the insertion of a quartz or sapphire rod to which the crystal may be attached. Section B is anodized aluminum. Section C with polished face c is also aluminum and can be attached to B by screws. Section D of anodized aluminum can be attached to the base of A. The various sides and holes were turned, planed, squared, and centered, as appropriate, to 0.0005".

For operation, section A is inserted in B, section C is attached to B, as in Figure 3, and the entire head is mounted on the optical goniometer. Thus assembled, the symmetry axis of A lies in the

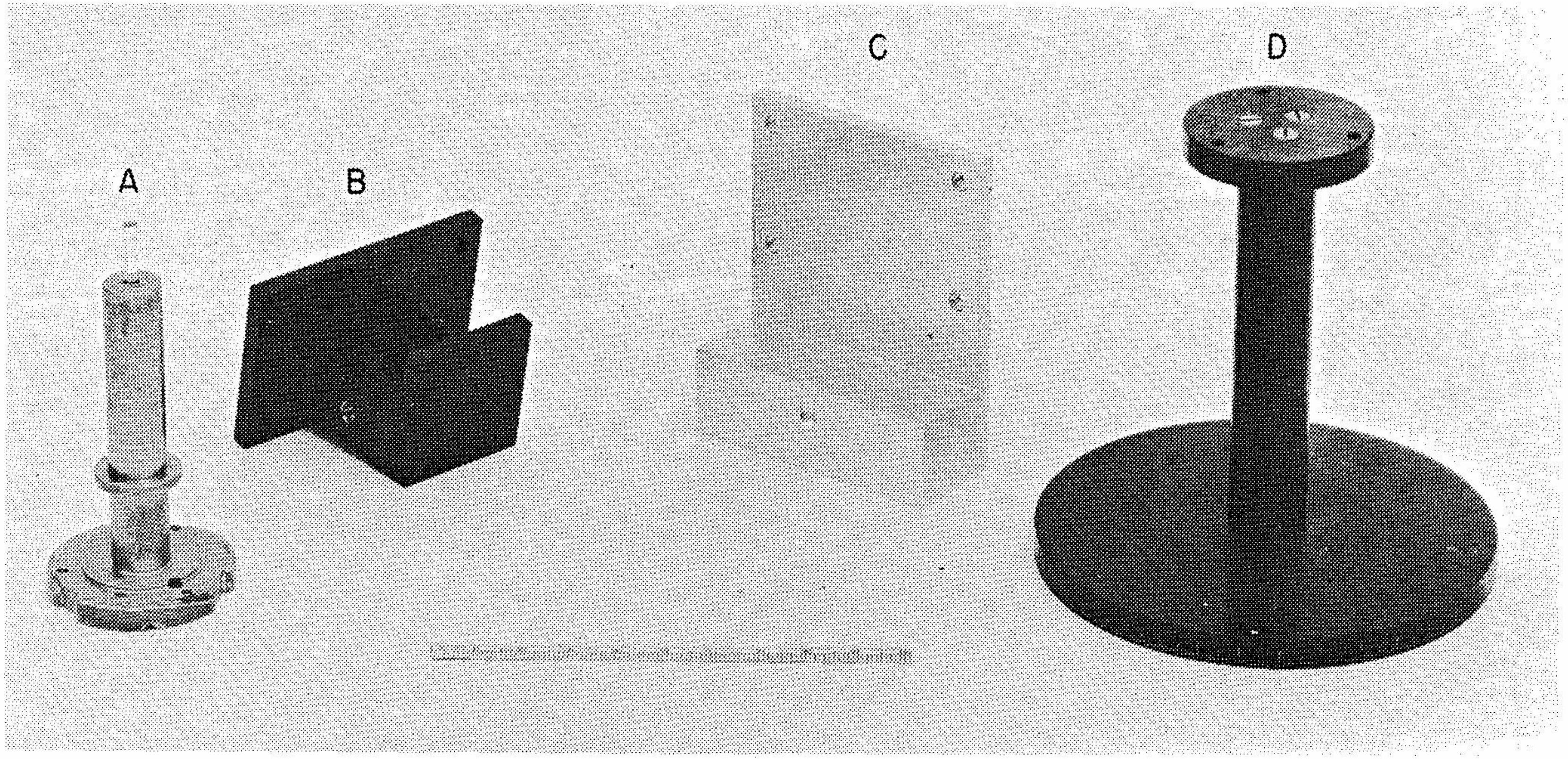


Fig. 1. Exploded View of Goniometer Head

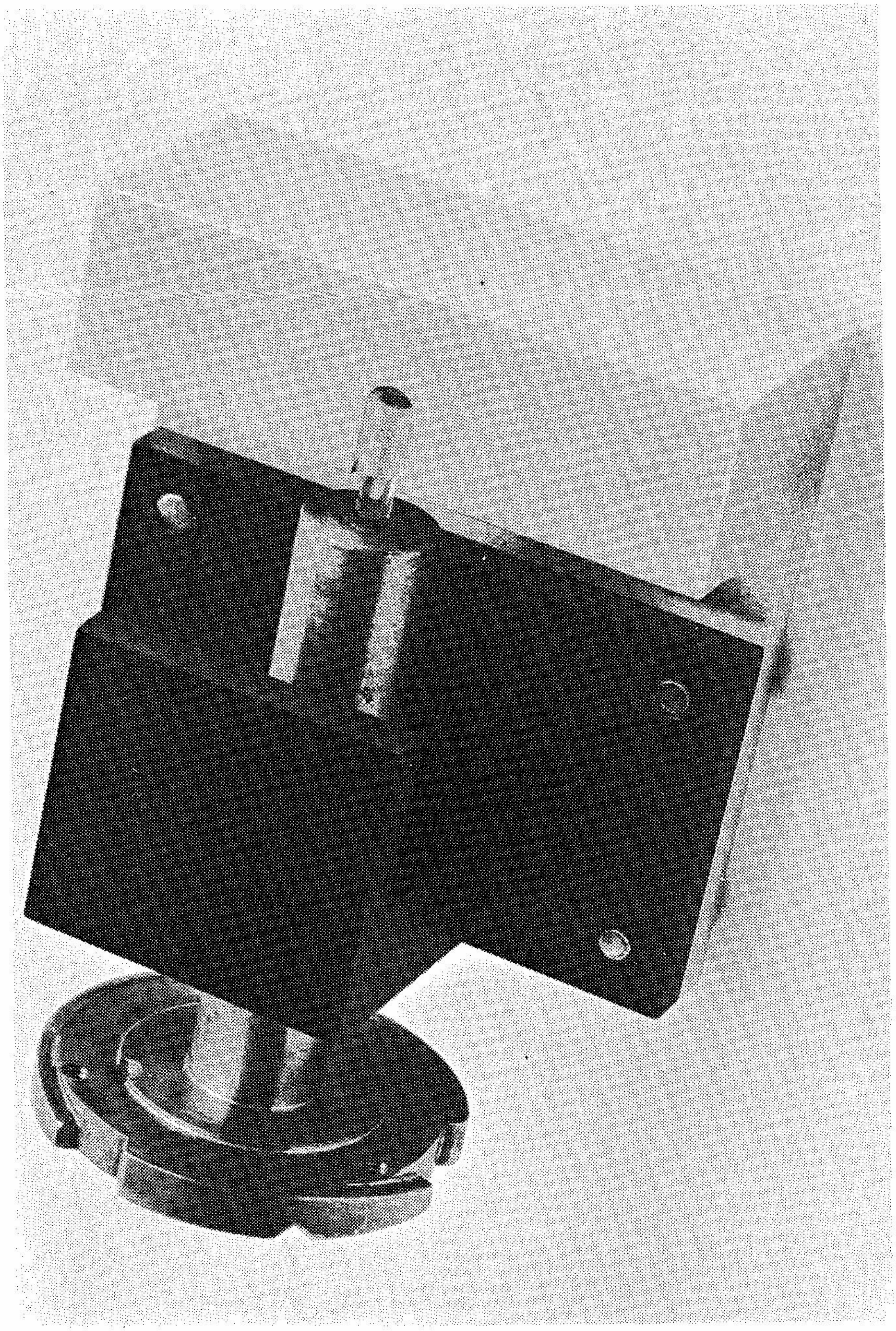


Fig. 2. Goniometer Head Assembled for Use With Goniometer

plane of face c of C, which is also parallel to the two large faces of B.

B and C are rotated about A until polished face c is vertical as determined by a reading of 0° on the optical goniometer. The set screw in B is tightened and then C is removed. The crystal is mounted with wax and is positioned by hand until the desired orientation is attained, i.e., one of the crystalline axes is along the long axis of A and a selected face is vertical. Thus the plane of the selected face is parallel to the plane of the two large faces of B. With a little practice and a crystal with bright, smooth faces, this procedure requires only a few minutes.

The head is removed from the goniometer, section D attached, and inserted in the microwave cavity, which is then positioned in the magnet gap so that one of the large plane faces of B makes positive contact with one of the pole faces of the magnet. Section B is then secured with an appropriate brace. The set screw is loosened and A and D of the goniometer head are ready to be rotated about an axis perpendicular to the magnetic field. The angle of rotation can be easily determined to 20' using a simple pointer system.

Provided that the magnet pole caps are plane and parallel, the orientation of the crystal with respect to the magnetic field is known to within 30'.

Spin resonance spectra were observed at room temperature using conventional X- and K- band spectrometers and a field modulation of 100 kc.

The fact that in the undamaged lattice there were two molecules per unit cell--and that the corresponding radicals are not in general equivalent with respect to their interaction with the applied magnetic field--causes complex spectra at most crystal orientations. If the radicals are related to one another by the space group symmetry operations of the undamaged crystal lattice, then simple spectra should be observed when the applied field $\underset{\sim}{H}_o$ is either perpendicular to or parallel to the b axis. The two types of radicals should give the same spectrum for these orientations. This is observed to be the case in these experiments.

For convenience, a cartesian set of crystal axes, i, j, k, was adopted, where i is parallel to the c axis, j parallel to the b axis, and k, of course, perpendicular to i and j.

As in the cases of irradiated glutaric (4) and adipic acids (5), the magnetic resonance spectrum of freshly x-ray damaged sebacic acid shows the presence of two radicals, I and II. Figures 4 and 5 illustrate such spectra for orientations $\underset{\sim}{H}_o \perp \underset{\sim}{j}$, $\underset{\sim}{H}_o \parallel \underset{\sim}{i}$, and $\underset{\sim}{H}_o \perp \underset{\sim}{j}$, $\underset{\sim}{H}_o \parallel \underset{\sim}{k}$.

Figure 6 shows the spectrum at $\underset{\sim}{H}_o \perp \underset{\sim}{j}$, $\underset{\sim}{H}_o \parallel \underset{\sim}{i}$ of a damaged sebacic acid crystal which was annealed at 88°C for twenty-four hours.

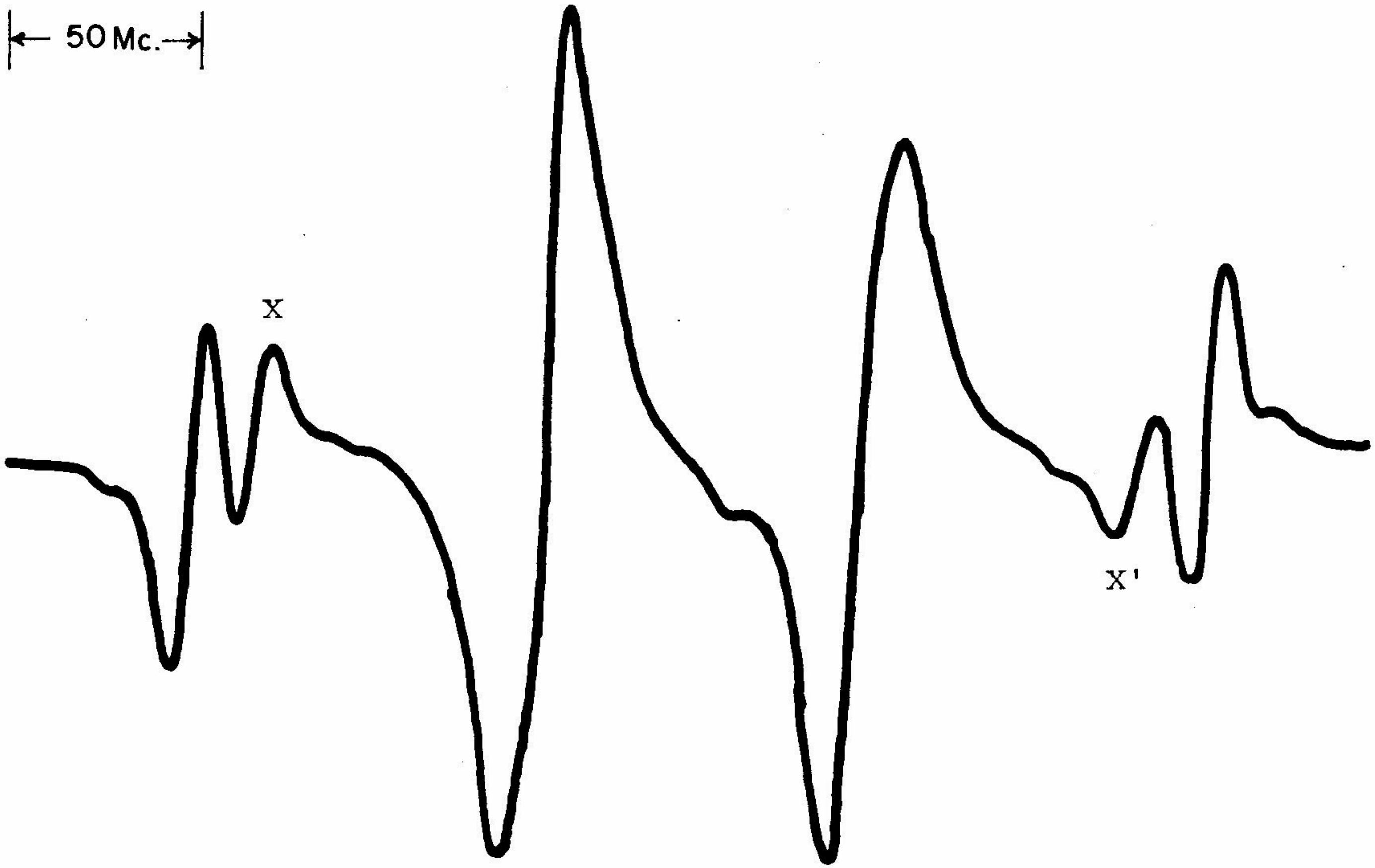


Fig. 4. X-band spectrum of freshly x-ray damaged sebacic acid crystal at $\underset{\sim}{H}_o \perp \underset{\sim}{j}$, $\underset{\sim}{H}_o \parallel \underset{\sim}{i}$ ($\Omega = 90°$).

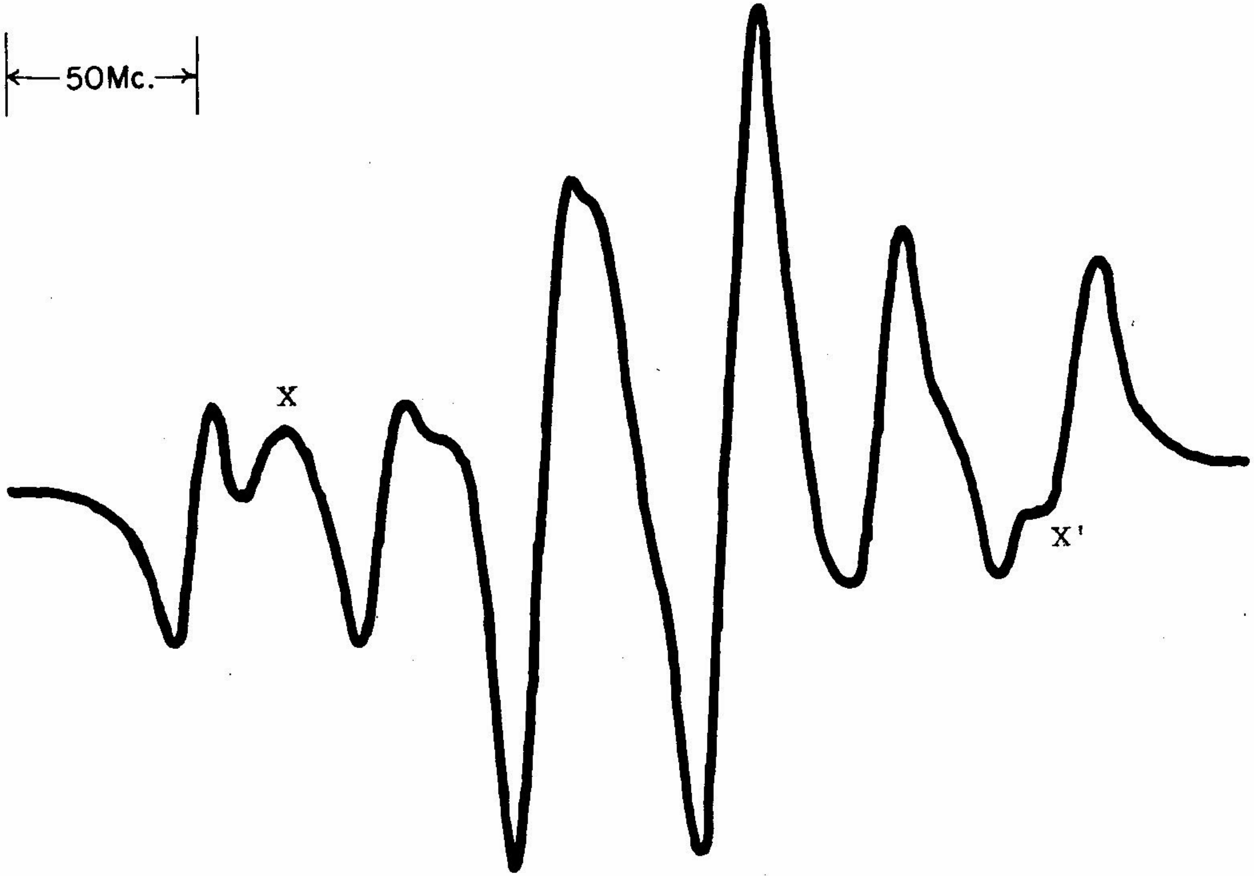


Fig. 5. X-band spectrum of freshly x-ray damaged sebacic acid crystal at $\underset{\sim}{H}_o \perp \underset{\sim}{j}$, $\underset{\sim}{H}_o \parallel \underset{\sim}{k}$ (Ω = 180°).

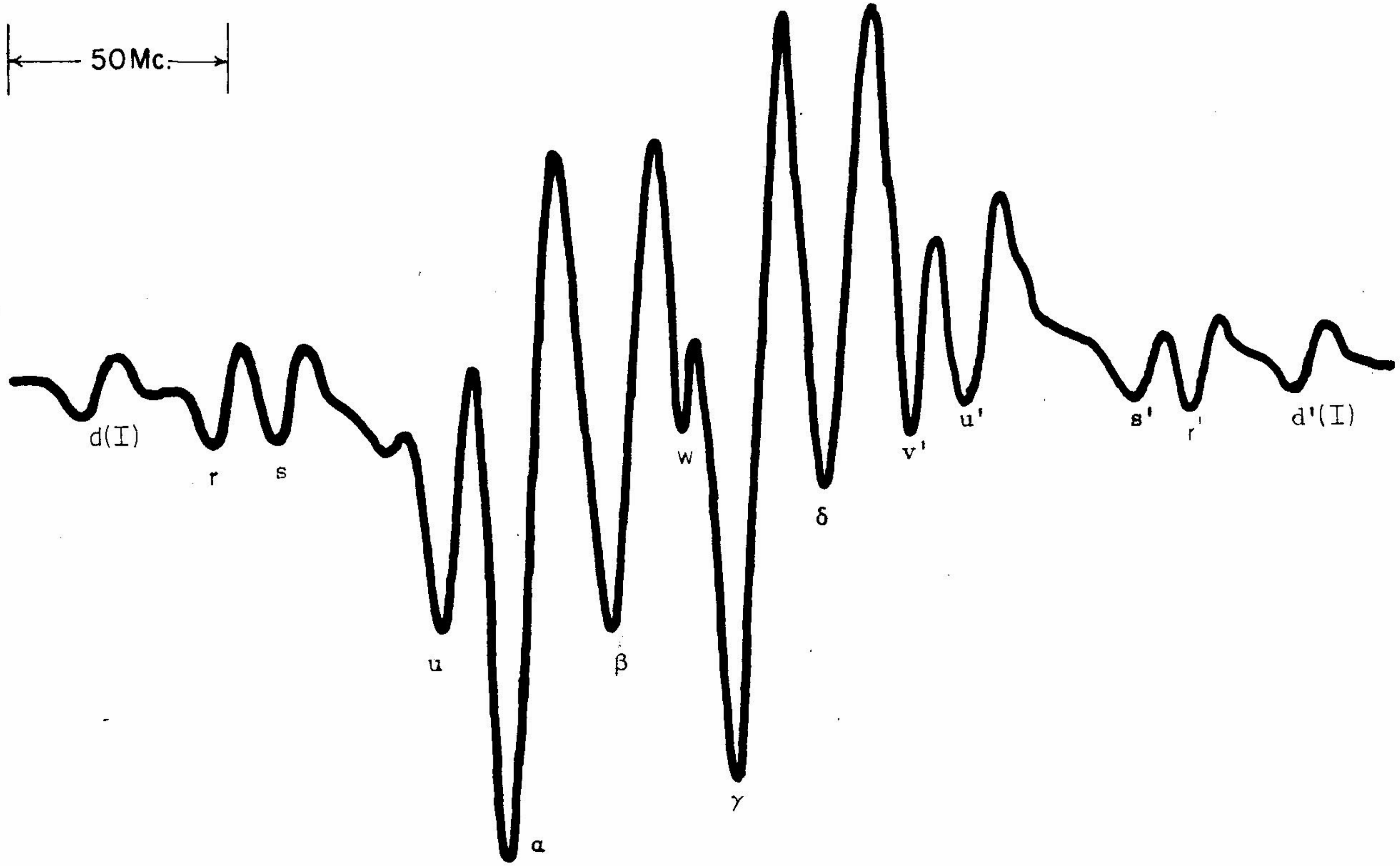


Fig. 6. X-band spectrum of damaged sebacic acid crystal after twenty-four hours at 88°C, $\underset{\sim}{H}_o \perp \underset{\sim}{j}$, $\underset{\sim}{H}_o \parallel \underset{\sim}{i}$.

This spectrum will be interpreted in terms of three radicals, I, III, and IV, as radical II is not present in detectable concentration. A study of spectra recorded periodically during heat treatment showed that radical II seems to change into III preferentially over IV, but that IV is more heat resistant than I or III. Analysis is complicated by the great overlap of the various as well as the variable rates of decay of the radicals. Even longer heat treatment merely decreases the intensity of all spectra until they cannot be resolved from instrumental noise. No success was achieved in obtaining a spectrum of IV uncomplicated by the presence of III and IV.

Higher temperatures increase the decay rates of all radicals while lower temperatures require much longer periods of time. Only the temperature range 80-90°C presents itself as experimentally useful. It should be noted that crystals having undergone long heat treatment (twenty-four hours or more at 88°C) flake and crumble extremely easily under the slightest pretenses.

If a freshly damaged crystal is irradiated with ultra-violet light for several hours, the spectrum of II disappears, the spectrum of I remains, and a very weak spectrum of III and, probably, IV appears. After UV "bleaching" for twelve hours, a very simple spectrum of radical I alone is obtained, as shown in Figure 7 for $\underset{\sim}{H}_o \perp \underset{\sim}{j}$, $\underset{\sim}{H}_o \parallel \underset{\sim}{i}$. The spectrum of a completely bleached crystal is not changed by subsequent heat treatment, except for a gradual loss of intensity. Thus radical I appears to be the necessary precursor of III and IV.

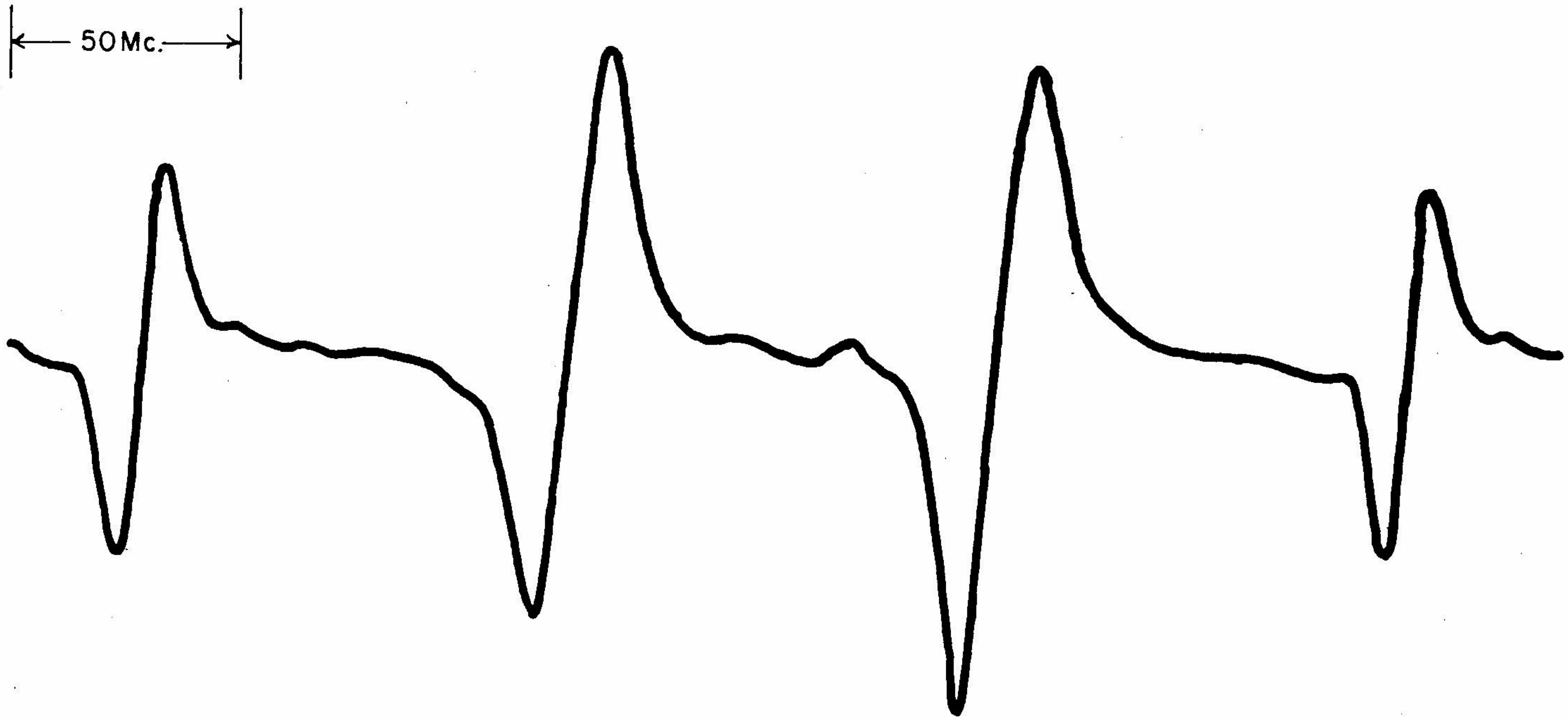
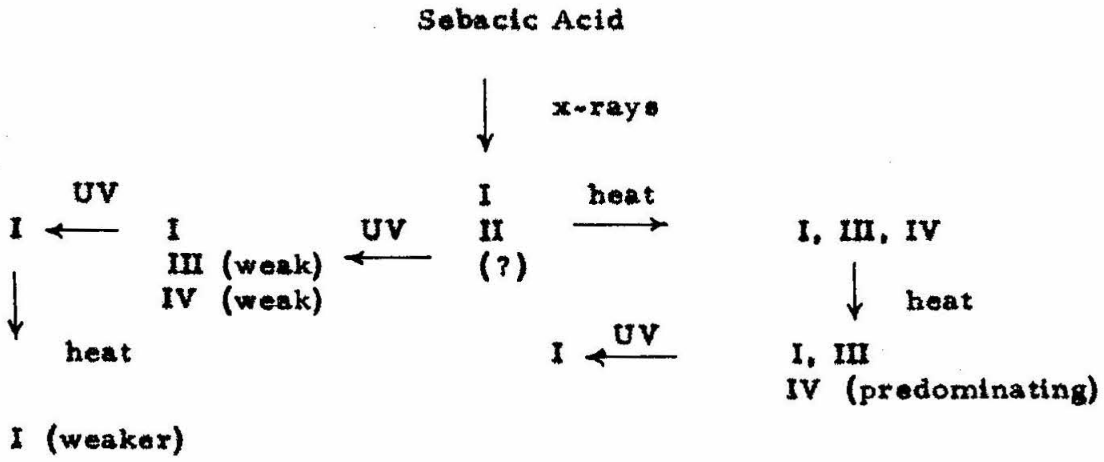


Fig. 7. X-band spectrum of damaged sebacic acid crystal after twelve hours of UV light "bleaching," $\underset{\sim}{H}_o \perp \underset{\sim}{j}$, $\underset{\sim}{H}_o \parallel \underset{\sim}{i}$ ($\Omega = 90°$).

Spectra recorded while a damaged crystal was being bleached in situ indicate that the intensity of the spectrum of I is not appreciably altered by the destruction of II. It appears then that the action of UV light on II is not to change II into I.

The issue is further clouded by the presence of line t and certain other weak lines indicated by double arrows in Figure 6. These latter lines do not have the same center of gravity as those assigned to III. The fact that the relative concentration of IV is less than that of I and III in the early and middle stages of heat treatment suggests the possibility that IV is derived from a radical other than II. It is certain that radicals III and IV are not detectable in freshly damaged crystals. Yet a different precursor of IV might well not be detected in the presence of I and II.

The following flow chart should make it easier to correlate the production of the various radicals by x-ray damage and subsequent heat or UV light treatment.



An AH4 lamp with the outer envelope removed was used for the bleaching experiments. A 4 cm. diameter quartz lens of focal length 15 cm. was used to focus the light on the crystal directly or through a filter solution which restricted the incident radiation to the range 2000-3400 Å. There was no essential difference between results from either procedure.

The crystals undergoing heat treatment were wrapped in aluminum foil or put into evacuated tubes wrapped with foil. Either procedure gave the same results.

A sample of sebacic acid was dissolved in sufficient heavy water to produce about 97% deuteration in the hydroxy proton positions. Crystals of the deuterated acid were grown from the melt, x-ray damaged, heat treated, and bleached. At the appropriate stage of the treatment, similar but somewhat sharper spectra were observed. This result shows that the observed hyperfine structure in the spectra of these radicals is not due to hydroxy proton interactions. The decrease in line widths (no more than 2 Mc.) is most apparent in the spectrum of I and II and in the central portion of the spectrum of the heat treated crystal, indicating that the unpaired spin in I and II does have a slight interaction with the hydroxy proton but that this interaction is not large enough to be resolved from the natural line width. Since the magnetic moment of the deuteron is about one third that of the proton and since the spin of the deuteron is 1, compared to 1/2 for the proton, any substantial interaction of an unpaired spin with a deuteron replacing a proton would be noted by a marked change in the hyperfine structure.

The spectra of freshly damaged deuterated crystals showed that some exchange with the methylene protons had occurred, probably during the time the sample was molten. A weak spectrum with an intensity one-tenth that of the normal spectrum of I and II indicated the presence of a pair of deuterated radicals analogous to I and II.

A procedure of alternately recrystallizing sebacic acid from D_2O and then keeping the dry sample in a molten state for a day or two was initiated in order to increase the extent of deuteration along the methylene chain. As this sequence was repeated, it became increasingly difficult to grow crystals. The highest relative intensity of the spectra of the deuterated and undeuterated radicals obtained was 1:6. This difficulty is probably related to the fact that the purified sebacic acid could be left molten only for a week before it began rapidly to turn dark.

Spectra were taken at X-band and K-band for every 10° of rotation about each crystal axis, i, j, k, for the freshly damaged, heat treated, and bleached crystals.**

The N^{14} splittings of the triplet hyperfine spectrum of peroxylamine disulfonate in aqueous solution were used for calibration purposes (10).

**Unless noted to the contrary, all spectra referred to are taken at X-band.

THE SPIN HAMILTONIAN

For a radical with a single proton, the total spin Hamiltonian may be written

$$\mathcal{H} = |\beta| \underset{\sim}{S} \cdot \underset{\approx}{g} \cdot \underset{\sim}{H}_o - \beta_N g_N I_H \cdot H_o + \mathcal{H}_{HF} \qquad (1)$$

where the first two terms represent the Zeeman coupling of the electronic and nuclear magnetic moments of the unpaired spin and the proton, respectively. $|\beta|$ is the absolute value of the electron Bohr magneton, β_N is the nuclear Bohr magneton, g_N is the nuclear g-factor and $\underset{\approx}{g}$ is the spectroscopic splitting factor dyadic. For most organic radicals, the $\underset{\approx}{g}$ dyadic is nearly isotropic and may be taken equal to $g_o = 2.0023$, the "free spin" g factor, for the purposes of the following derivations. I_H is the component of the nuclear spin angular momentum in the field direction, in units of $\hbar$. Equation 1 may be rewritten

$$\mathcal{H} = h |\nu_e| S_H - h \nu_p I_H + \mathcal{H}_{HF} \qquad (2)$$

where $|\nu_e|$ and ν_p, the electron and nuclear resonance frequencies, are

$$|\nu_e| = h^{-1} g_o |\beta| H_o \qquad (3)$$

$$\nu_p = h^{-1} g_N \beta_N H_o \qquad (4)$$

In the present work, $|\nu_e| = 9250$ Mc. and $\nu_p = 14.1$ Mc. for X-band and $|\nu_e| = 23,700$ Mc. and $\nu_p = 36$ Mc. for K-band.

The third term in 1 and 2 may be written

$$\mathcal{H}_{HF} = \underset{\sim}{S}\cdot\underset{\approx}{S}\cdot\underset{\sim}{I} + \underset{\sim}{V}\cdot(\underset{\sim}{S}\times\underset{\sim}{I}) \qquad (5)$$

$\underset{\sim}{V}$ is a pseudovector fixed in the radical (11). The pseudovector hyperfine interaction occurs when the axes of the diagonalized $\underset{\approx}{g}$ dyadic cannot be made parallel to the axes of the diagonalized (electron-spin)-(nuclear-spin) dipolar interaction. The pseudovector interaction is of the order of Δg times the dipolar interaction, where Δg is a typical anisotropy in $\underset{\approx}{g}$. In the present work, the Δg's are of the order of 10^{-3}. Thus only the first term in equation 5 is important. $\underset{\approx}{S}$ is a symmetric dyadic including the (electron-spin)-(nuclear-spin) Fermi contact and dipolar interactions.

The hyperfine Hamiltonian then may be written

$$\mathcal{H}_{HF} = hAS_zI_z + hBS_xI_x + hCS_yI_y \qquad (6)$$

where x, y, z is a set of cartesian coordinate axes which diagonalize $\underset{\approx}{S}$. For a radical with a σ-proton lying in the nodal plane of a p orbital in which the unpaired spin is localized, the z axis is along the σ C-H bond direction, x is along the symmetry axis of the p orbital, and y perpendicular to x and z.

In radicals with negligible spin orbit interactions, we note that

$$\begin{aligned} A &= A_d + a \\ B &= B_d + a \\ C &= C_d + a \end{aligned} \qquad (7)$$

where a is the isotropic interaction and A_d, B_d, and C_d are the dipolar contributions to A, B, C. Since the trace of the dipolar contribution to $\underset{\approx}{S}$ is zero,

$$a = 1/3\,(A + B + C) \tag{8}$$

Clearly, the hyperfine interactions are determined by the distribution of electron spin angular momentum in the radical. The isotropic coupling constant a is

$$a = h\, g_o\, |\beta|\, g_N\, \beta_N\, \frac{8\pi}{3}\, \rho(\underset{\sim}{r}_N) \tag{9}$$

where $\rho(\underset{\sim}{r})$ is the spin density distribution function which is related to the vector density of electron spin angular momentum at the position $\underset{\sim}{r}$ in a molecule, $\hbar \underset{\sim}{S}\rho(\underset{\sim}{r})$. $\underset{\sim}{r}_N$ is the vector position of the proton.

The principal components of the dipolar interaction are

$$A_d = -h^{-1}\, g_o\, |\beta|\, g_N\, \beta_N \int_{\epsilon} \rho(\underset{\sim}{r})\, \frac{(1 - 3\cos^2\vartheta)}{|\underset{\sim}{r} - \underset{\sim}{r}_N|^3}\, dV \tag{10}$$

$$B_d = -h^{-1}\, g_o\, |\beta|\, g_N\, \beta_N \int_{\epsilon} \rho(\underset{\sim}{r})\, \frac{(1 - 3\sin^2\vartheta\cos^2\phi)}{|\underset{\sim}{r} - \underset{\sim}{r}_N|^3}\, dV \tag{11}$$

$$C_d = -h^{-1}\, g_o\, |\beta|\, g_N\, \beta_N \int_{\epsilon} \rho(\underset{\sim}{r})\, \frac{(1 - 3\sin^2\vartheta\sin^2\phi)}{|\underset{\sim}{r} - \underset{\sim}{r}_N|^3}\, dV \tag{12}$$

where ϑ and ϕ are the polar and azimuthal angles of the vector $\underset{\sim}{r}-\underset{\sim}{r}_N$ in the x, y, z coordinate system (12). The symbol ϵ means that a small region about the nucleus with volume of the order of $(\hbar/mc)^3$ is neglected in the integrations. This omission is unimportant in the calculation of A_d, B_d, and C_d.

It should be noted that experimental and theoretical work show that A, B, C, and a all have negative signs for this type of radical.

When $|\nu_e| >> |A|$, $|B|$, $|C|$, the vector components of S perpendicular to H_o may be neglected. The eigenvalues of the total spin Hamiltonian may be written

$$E = h\,|\nu_e|\,S_H - h\nu\,I_u \tag{13}$$

S_H is one of the eigenvalues ($\pm$ 1/2) of the operator $\underset{\sim}{S}_H$ and I_u is one of the eigenvalues ($\pm$ 1/2) of the operator $\underset{\sim}{I}_u$ for the component of nuclear spin angular momentum in the direction of the unit vector $\underset{\sim}{u}$, which gives the direction of the net field acting at the nucleus. This net field is composed of the applied field $\underset{\sim}{H}_o$ and the hyperfine field from the unpaired spin. ν and $\underset{\sim}{u}$ may be calculated from the equation

$$\nu\,\underset{\sim}{u} = \nu_p\,\underset{\sim}{u}_H - S_H\,[\underset{\sim}{z}\,A\cos\vartheta + \underset{\sim}{x}\,B\sin\vartheta\cos\phi + \underset{\sim}{y}\,C\sin\vartheta\sin\phi] \tag{14}$$

ν is the resonance frequency of the proton in the net field. $\underset{\sim}{x}$, $\underset{\sim}{y}$, $\underset{\sim}{z}$ are unit vectors along the directions of the positive x, y, z axes which diagonalize $\underset{\approx}{S}$. ν and $\underset{\sim}{u}$ depend on the eigenvalue S_H so it is convenient to use a single prime to denote eigenstates for $S_H = +1/2$ and a double prime to denote eigenstates $S_H = -1/2$. Therefore, for $S_H = 1/2$, we have ν' and $\underset{\sim}{u}'$ and a set of eigenenergies E', and for $S_H = -1/2$, ν'' and $\underset{\sim}{u}''$ and a set of eigenenergies E''. A subscript 1 indicates $I_u = +1/2$ and a subscript 2 indicates $I_u = -1/2$.

Thus we have the set of eigenenergies

$$E_1' = 1/2\, h\, |\nu_e| - 1/2\, h\, \nu' \tag{15}$$

$$E_2' = 1/2\, h\, |\nu_e| + 1/2\, h\, \nu' \tag{16}$$

$$E_1' = -1/2\, h\, |\nu_e| - 1/2\, h\, \nu'' \tag{17}$$

$$E_2' = -1/2\, h\, |\nu_e| + 1/2\, h\, \nu'' \tag{18}$$

and the corresponding spin eigenfunctions written below and defined in the standard fashion.

$$\psi_1' = \alpha\,(e)\,\alpha'\,(p) \tag{19}$$

$$\psi_2' = \alpha\,(e)\,\beta'\,(p) \tag{20}$$

$$\psi_1'' = \beta\,(e)\,\alpha''\,(p) \tag{21}$$

$$\psi_2'' = \beta\,(e)\,\beta''\,(p) \tag{22}$$

The possible electron resonance transition frequencies are

$$(E_1' - E_1'')h^{-1} = |\nu_e| - 1/2\,(\nu' - \nu'') \tag{23}$$

$$(E_2' - E_2'')h^{-1} = |\nu_e| + 1/2\,(\nu' - \nu'') \tag{24}$$

$$(E_1' - E_2'')h^{-1} = |\nu_e| - 1/2\,(\nu' + \nu'') \tag{25}$$

$$(E_2' - E_1'')h^{-1} = |\nu_e| + 1/2\,(\nu' + \nu'') \tag{26}$$

In general the resonance spectrum for a radical with a single proton is a symmetrical quartet centered on $|\nu_e|$. The relative intensity of the inner doublet of splitting $(\nu' - \nu'')$ is $\cos^2(\xi/2)$; the relative intensity of the outer doublet $(\nu' + \nu'')$ is $\sin^2(\xi/2)$. ξ is calculated from the equation

$$\underset{\sim}{u}' \cdot \underset{\sim}{u}'' = \cos \xi \qquad (27)$$

For radicals where the unpaired spin has isotropic coupling with π protons as well as anisotropic coupling with σ protons, the π proton hyperfine structure is simply superimposed upon each of the lines of σ proton hyperfine structure.

The generalization of equations 13, 15-21, and 23-26 to include interactions with several anisotropic protons is obvious. We merely calculate the hyperfine structure for each proton and build up the total spectrum in the normal fashion.

McConnell has shown how one may derive the spin density distribution $\rho(\underset{\sim}{r})$ in a π electron radical from a many electron wave function involving several p atomic orbitals by means of an atomic orbital spin density matrix $[\rho_{ij}]$ (12,15). ρ_{ii} represents the spin density residing on atom i, while ρ_{ij} $(i \neq j)$ represents the amount of spin density in the overlap region between atoms i and j. ρ_{ij} is of the order of 0.1- 0.01 or less.

The isotropic hyperfine splitting constant, a_i, for a proton bonded to a carbon atom, i, which would be one of the nuclear centers in a π molecular orbital, is proportional to the diagonal element of a π electron spin density matrix (16)

$$a_i = Q \rho_{ii}^{\pi} \qquad (28)$$

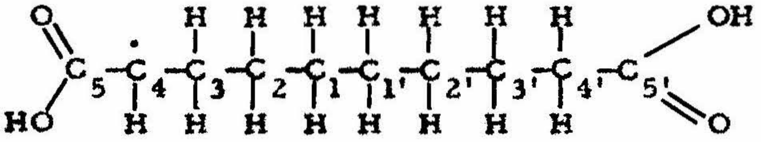
Q appears to have values around -60 Mc. It should also be clear that the magnitudes of the anisotropic coupling of a σ proton and the isotropic coupling of a π proton are also proportional to the spin density on the appropriate carbon.

ANALYSIS OF THE SPECTRA OF I

Representative spectra of radical I are shown in Figures 7 and 9 for $\underset{\sim}{H}_o \perp \underset{\sim}{j}$, $\underset{\sim}{H}_o \parallel \underset{\sim}{i}$ and for $\underset{\sim}{H}_o \perp \underset{\sim}{j}$, $\underset{\sim}{H}_o \parallel k$. These spectra can be interpreted in terms of three coupling constants, two equivalent and nearly isotropic, the other quite anisotropic, varying upon rotation from a value about that for the isotropic couplings to a much lower value.

These results are consistent with the following assertions:

(A) Radical I has the formula



with the unpaired spin, localized in a p orbital on C_4, interacting with a σ proton which lies in the nodal plane of the p orbital and with the two π protons on C_3.

(B) The radicals I are related to one another by the space group symmetry operations of the undamaged crystal lattice.

(C) The C_4-H bond within experimental uncertainty bisects the H-C_3-H angle.

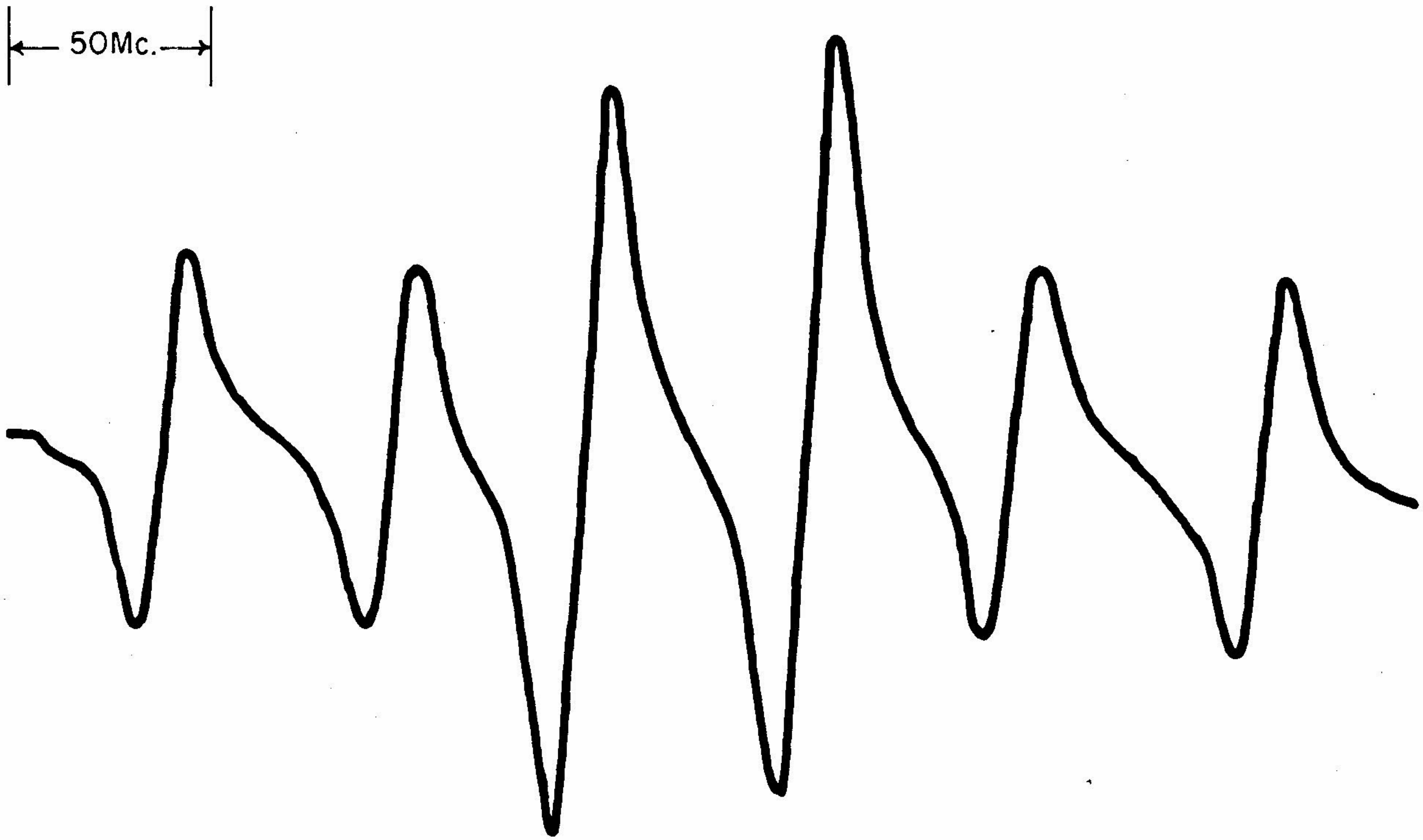


Fig. 9. X-band spectrum of damaged sebacic acid crystal after twelve hours of UV light "bleaching," $H_o \perp j$, $H_o \parallel k$ ($\Omega = 180°$).

(D) The carbon chain in radical I has the same orientation within the crystal as the undamaged molecule.

Table I shows the experimental values for the isotropic and anisotropic coupling constants for the spectrum of radical I for rotation of the crystal about the $\underset{\sim}{j}$ axis perpendicular to the magnetic field. $\Omega = 0°$ for $\underset{\sim}{H}_o \perp -\underset{\sim}{k}$ and $\Omega = 90°$ for $\underset{\sim}{H}_o \parallel \underset{\sim}{i}$. The isotropic values are the same for both π protons or represent an average value for two very nearly equivalent π protons.

In order to calculate σ proton splittings from equations 14, 15, 16, 17, and 18, A, B, C must be known as well as the field direction relative to the diagonalizing axes x, y, z. A set of molecular axes, L, M, N, for the parent molecule may be defined such that L lies in the methylene chain and bisects the carbon-carbon bonds, M bisects the H-C-H angles and N is perpendicular to M and N. Robertson and Morrison make this choice and give $\underset{\sim}{L}$, $\underset{\sim}{M}$, $\underset{\sim}{N}$ as unit vectors in terms of a set of unit vectors along the crystal axes a, b, c, where c′ is perpendicular to the crystalline axes a and b (9).

$$\begin{aligned} \underset{\sim}{L} &= 0.6390\underset{\sim}{a} - 0.1420\underset{\sim}{b} + 0.7560\underset{\sim}{c}' \\ \underset{\sim}{M} &= 0.4493\underset{\sim}{a} + 0.8668\underset{\sim}{b} - 0.2170\underset{\sim}{c}' \\ \underset{\sim}{N} &= 0.6230\underset{\sim}{a} - 0.4780\underset{\sim}{b} - 0.6189\underset{\sim}{c}' \end{aligned} \tag{29}$$

Transforming from the a, b, c′ system into the i, j, k coordinate system, we have

TABLE I

Experimental and Calculated Hyperfine Splittings for Radical I

	Observed Splittings		Calculated σ-CH Proton Splittings
	π	σ	
Angle Ω	$\pm$ 2 Mc	$\pm$ 2 Mc	$\pm$ 2 Mc
0	93	51	52
10	94	55	53
20	95	60	61
30	95	66	65
40	95	73	74
50	95	78	78
60	95	82	83
70	96	85	86
80	95	86	87
90	94	88	88
100	93	85	85
110	93	80	81
120	92	76	76
130	91	70	71
140	91	64	65
150	91	58	56
160	91	53	53
170	92	51	52

$$\begin{aligned} \underset{\sim}{L} &= 0.983\underset{\sim}{i} - 0.142\underset{\sim}{j} + 0.102\underset{\sim}{k} \\ \underset{\sim}{M} &= 0.175\underset{\sim}{i} + 0.867\underset{\sim}{j} - 0.468\underset{\sim}{k} \\ \underset{\sim}{N} &= 0.022\underset{\sim}{i} - 0.478\underset{\sim}{j} - 0.878\underset{\sim}{k} \end{aligned} \tag{30}$$

The essential equivalence of the protons in radical I suggests that the C-H bond and the symmetry axis of the p orbital containing the unpaired spin are along the M and N molecular axes of the originally undamaged molecule, i.e., there is no twist of the carbon-carbon chain in forming radical I. If we assume this for convenience and make the choice

$$\begin{aligned} A &= -27 \text{ Mc.} \\ B &= -56 \text{ Mc.} \\ C &= -88 \text{ Mc.} \end{aligned} \tag{31}$$

we can calculate anisotropic splittings for the σ-proton for any crystal orientation. Table I gives these calculated values for the selected crystal orientations. Surprisingly good agreement with experiment is obtained. It should be noted that at X-band (3300 gauss) and at these particular crystal orientations one doublet of the four lines expected in the hyperfine structure of the σ proton is quite weak. Figure 10 shows the spectrum of radical I at $\underset{\sim}{H}_o \perp \underset{\sim}{j}$, $\Omega = 130°$ at K-band. Here, $\nu_p = 36$ Mc. is large enough compared to $\underset{\approx}{S}$ so that the σ proton hyperfine structure is a distinct quartet, whereas at X-band ($\nu_p = 14.1$ Mc.) only a strong doublet is observed.

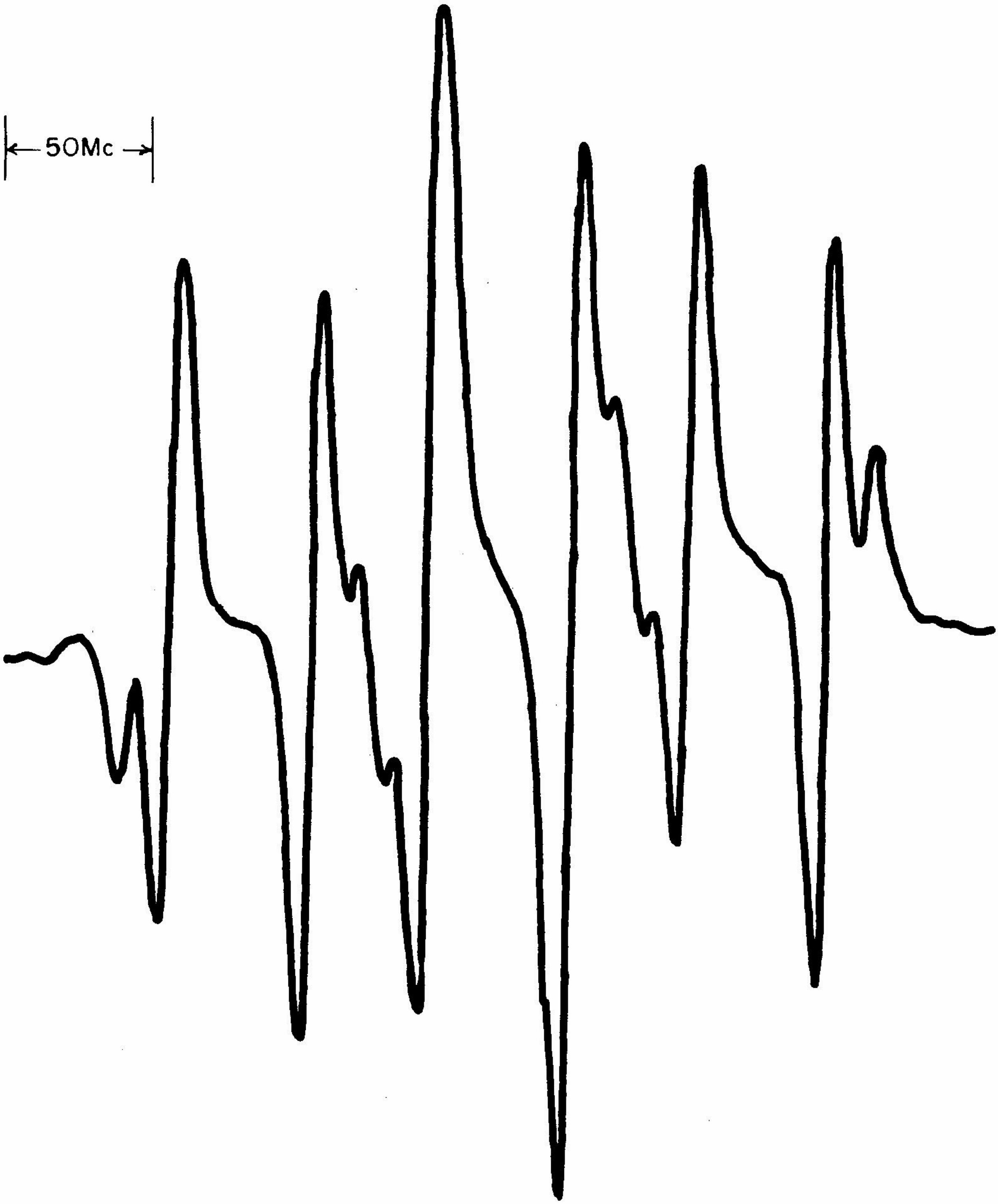


Fig. 10. K-band spectrum of damaged sebacic acid crystal after twelve hours UV light "bleaching," $\underset{\sim}{H}_o \perp \underset{\sim}{j}$, $\Omega = 130°$.

The proton splittings and relative intensities measured from spectra taken at K-band support the assumptions regarding the orientation of the radical and the values for the principal components of the tensor $\underset{\approx}{S}$. These values and that for the isotropic coupling constant, a = -57 Mc., calculated from equation 8, are consistent with those found for similar type radicals (1 - 5). The magnitude of the π -proton splitting constants are also as expected. For example, the analogous values for the σ proton in the radical $(HO_2C)\text{-}\dot{C}HCH_2(CO_2H)$ in irradiated succinic acid are (3)

A = -30 Mc.

B = -59 Mc.

C = -92 Mc.

a = -60 Mc.

The isotropic components of the π proton splittings in this succinic acid radical are 100 Mc. and 80 Mc.

ANALYSIS OF SPECTRA FOR RADICAL II

In Figures 4 and 5, we have noted lines x, x' as the clearest features of the spectrum of radical II. A precise analysis of the spectrum of II, much less the definite identification of the nature of the radical responsible, is precluded by the great degree of overlap of the spectrum of II with the more intense spectrum of I. However, certain characteristics of behavior of the spectrum of II relative to that of I for rotation about the $\underset{\sim}{j}$ axis are suggestive.

It would seem that lines x, x' are the outer lines of the spectrum of II and that, upon rotation of the crystal, they retain their relative positions with respect to the outer lines of I, except for varying degrees of resolution of x, x', depending on the orientation. In fact, the change in the total spread of the spectrum of I upon rotation is very closely paralleled by the change in the total spread of the spectrum of II. It is well to recall that the total spread of a spectrum is just the sum of the absolute values of all the coupling constants involved in the complete spin Hamiltonian. Realizing then that the change in the total spread of the spectrum of I is due essentially to the anisotropic σ proton coupling constant, it seems probable that radical II also contains one σ proton and that the σ protons in I and II enjoy approximately the same relative orientation within the crystal. Moreover, the general masking of the central lines of II by those of I leads one to suspect that the spectrum of II is similar to that of I in the number of lines but has smaller hyperfine splittings.

For the special orientation, $\underset{\sim}{H}_o \perp \underset{\sim}{j}$, $\Omega = 140°$, for a freshly damaged crystal, it is possible to see two extra, partly resolved lines, z' and y', as shown in Figure 11. Reasoning that z', y' belong to II, then the conjugate lines, z, y, would not be expected to be resolved from the spectrum of I because of the slight difference in g factors of the two radicals. The approximate separations of lines z', x', and y', x' are 84 Mc. and 60 Mc. The separations between the analogous lines of I are 91 Mc. and 65 Mc. It should be noted that these latter splittings are precisely the experimental values for the π proton and σ proton coupling constants for radical I. At certain other orientations, line z' alone is partly resolved and the separation between z', x' is always about 84 Mc. At no orientation is there evidence for more than six lines in the spectrum of II.

A tenable conclusion is that radical II like I contains an unpaired spin largely localized in a p orbital, interacting with a σ proton and two nearly equivalent π protons, and that both radicals lie in nearly equivalent positions in the crystal lattice. The smaller hyperfine splittings in the spectrum of II lead to the estimate that the isotropic component, a, of the hyperfine coupling of the σ proton in II is about -52 Mc., compared to a = -57 Mc. for I. The decrease in the hyperfine splittings is probably due to a decrease in the spin density in the p

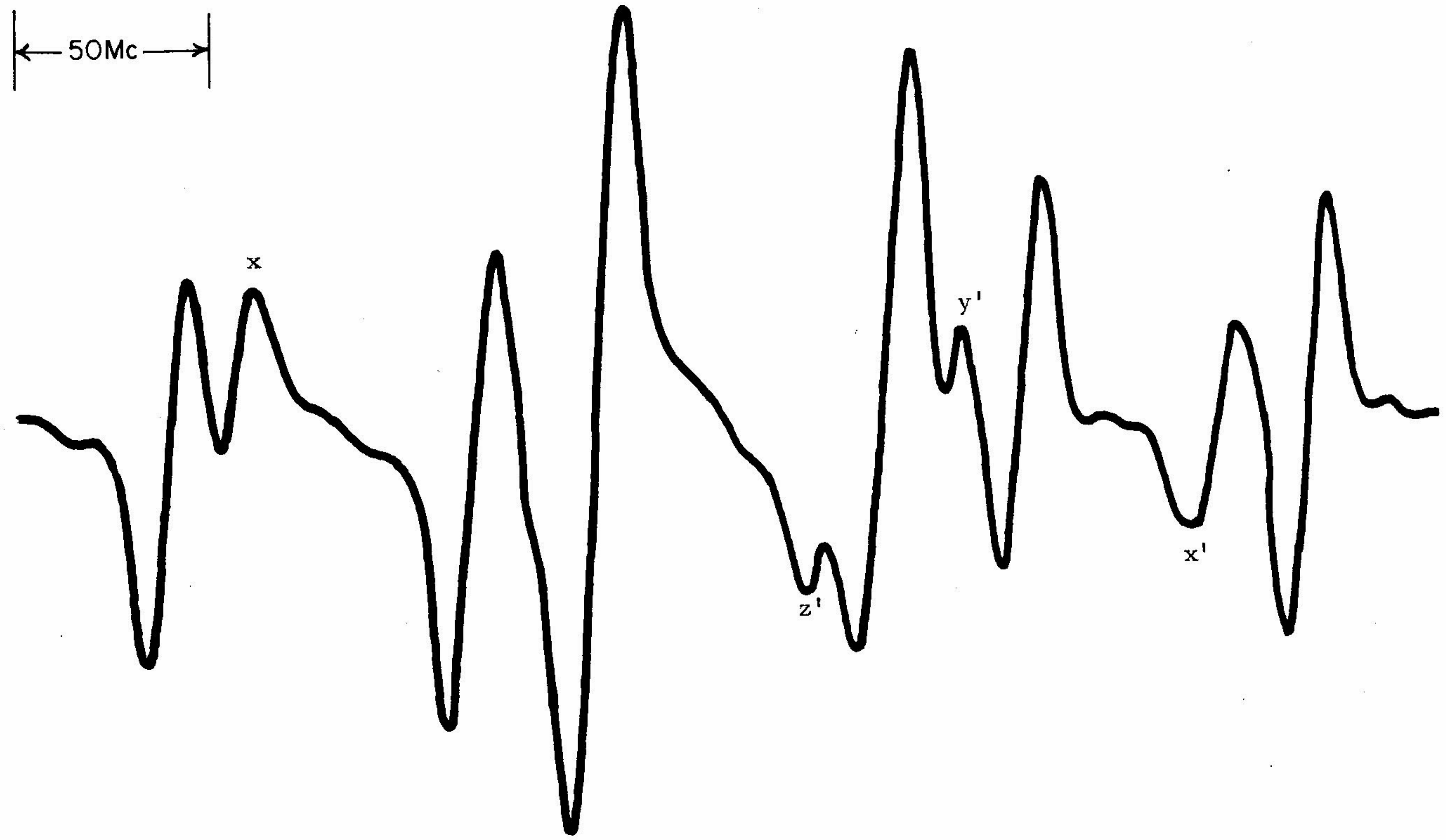


Fig. 11. X-band spectrum of freshly damaged sebacic acid crystal at $\underset{\sim}{H}_o \perp \underset{\sim}{j}$, $\Omega = 130°$.

orbital bearing the unpaired spin in II.

Atherton and Whiffen have irradiated glycolic acid ($HOCH_2COOH$) and a salt of glycolic acid ($HOCH_2COO^-$) and have determined the principle values of $\underset{\approx}{S}$ for the interaction of the unpaired spin with the σ proton in the radicals $HO\dot{C}HCOOH$ and $HO\dot{C}HCOO^-$ (17,18). The values for the acid radical are

A = -30 Mc.

B = -55 Mc.

C = -86 Mc.

a = -57 Mc.

and for the salt radical are

A = -23 Mc.

B = -50 Mc.

C = -80 Mc.

a = -51 Mc.

It would appear that the group COO^- has a greater effect than COOH in decreasing the spin density on the α carbon. Clearly, it is possible that radical II in damaged sebacic acid may be the ionized counterpart of radical I.

An analysis of the electron magnetic resonance spectrum of irradiated glutaric acid led to the proposal for the existence of two conformations of the radical $HOOC\dot{C}H(CH_2)_2COOH$ (4). The spectral resolution was adequate to determine two sets of coupling tensors. For the σ proton in radical A, a = -56 Mc., with isotropic π proton splittings of about 122 Mc. and 47 Mc. For radical B, $a = -51$ Mc. with π proton splittings of about 107 Mc. and 33 Mc. The possibility was advanced that radical B was actually $^{-}OOC\dot{C}H(CH_2)_2COOH$.

It was also observed that the line widths in the spectrum of radical B were greater than in the case of A. Realizing that the total number of spins giving rise to a resonance is proportional to the intensity times the square of the line width (both measured between maximum and minimum of the first derivative resonance curve), the authors were able to estimate that radicals A and B were present in about the same concentration.

We also find that in damaged sebacic acid the spectral line widths for II are greater than for I. In view of our poorer resolution, we estimate only that the concentration of II is between one half of to the same as that of I.

Irradiated adipic acid contains two types of radicals, one similar to radical I of sebacic acid (5). It was suggested that the other radical may be derived from the parent molecule by the loss of a hydrogen from a β carbon. Considering this possibility for radical II, let us assume that C_3 bears the unpaired spin and is bonded to the σ-proton (refer to formula for I). If no appreciable reorientation of the radical occurs, then clearly the unpaired spin interacts with two additional π protons. The spectrum of II would then show additional splitting from these extra π protons and would have a total spread greater than that of I by an amount equal to the sum of the coupling constants for the two extra π protons. The sum would be of the order of 190 Mc.

The magnitude $R(\vartheta)$ of the π proton hyperfine interaction is approximated by the equation

$$R(\vartheta) = B\cos^2(\vartheta) \tag{32}$$

where B seems to have a value varying between 110-130 Mc. (2, 3) and ϑ is the angle of rotation of the C-H π bond relative to the symmetry axis of the p orbital on the adjacent carbon. For a system with two equivalent π protons as in radical I, $\vartheta_1 = \pi/6$, $\vartheta_2 = 5\pi/6$ and $R(\vartheta_1) \sim 90$ Mc. and $R(\vartheta_2) \sim 90$ Mc. If the $\underset{\pi}{H}\text{-C-}\underset{\pi}{H}$ system is rotated until $R(\vartheta_1) = 0$ Mc., then $\vartheta_1 = \pi/2$ and $\vartheta_2 = -\pi/6$, giving $R(\vartheta_2) \sim 90$ Mc. Thus radical II could fit this situation provided that both methylene groups made the appropriate twists, either in the same or opposite sense.

This latter possibility is ruled out by the results obtained on damaged deuterated sebacic acid. The spectra quickly revealed that there were two deuterated radicals, I_d and II_d, analogous to I and II, and that the deuterium had exchanged into the σ proton position. Since it is extremely unlikely that the hydrogens on, say, a β carbon would exchange as rapidly as the more labile hydrogens on a carbon α to the carboxyl group, the deuteration must have occurred on the α carbon. We conclude that the σ proton in both I and II is bonded to the α carbon.

The possibility that radical II is the counterpart of the secondary radical produced by decarboxylation in irradiated malonic acid may be immediately rejected (6, 7). The radical $\cdot CH_2(CH_2)_7$-COOH would show more hyperfine structure and a different anisotropic behavior because of the interaction of the unpaired spin with two σ protons.

The identification of the radicals III and IV should shed more light on the nature of II.

ANALYSIS OF SPECTRA OF RADICAL IV

In Figure 6, radical IV is assigned the lines α, β, γ, δ, which form a quartet with coupling constants, 50 Mc. and 20 Mc. Figure 12, $\underset{\sim}{H}_o \perp \underset{\sim}{j}$, $\Omega = 130°$, the quartet is quite apparent with the same splitting constants. At $\underset{\sim}{H}_o \perp \underset{\sim}{j}$, $\Omega = 180°$ (Figure 13), all radicals now have the same g factors; the lines from I and III obscure resolution of the spectrum of radical IV, causing it to appear as a broadened doublet.

The spectrum of IV is interpretable in terms of two nearly isotropic coupling constants, 50 ± 2 Mc., 20 ± 2 Mc., probably arising from two nonequivalent π protons.

From equation 32, we may make approximate calculations for the two orientations of a H_π-C-H_π system relative to the symmetry axis of the p orbital which give π proton splitting constants with the ration 50/20. One orientation (i) has $\vartheta_1 \simeq 10°$, $\vartheta_2 \simeq 130°$, and the other (ii) has $\vartheta_1 \simeq -52°$, $\vartheta_2 \simeq 68°$. Assuming $B = 125$ Mc., orientation (i) should give splitting constants of 125 Mc., 50 Mc., and (ii) should give 50 Mc., 20 Mc., both sets for a unit spin density.

There are four reasonable candidates for IV,

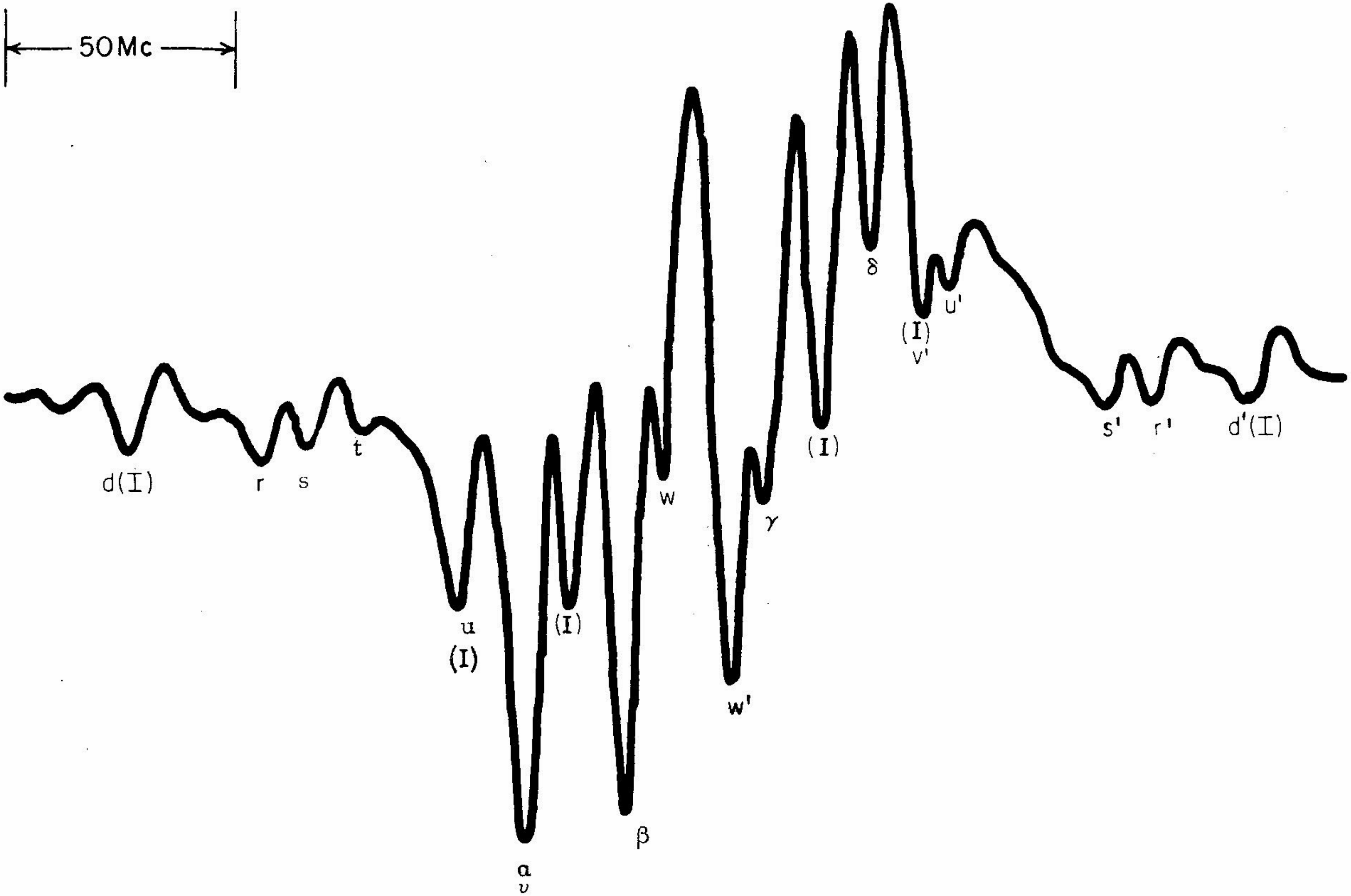


Fig. 12. X-band spectrum of damaged sebacic acid crystal after twenty-four hours at 88°C, $\underset{\sim}{H}_o \mid \underset{\sim}{j}$, $\Omega = 130°$.

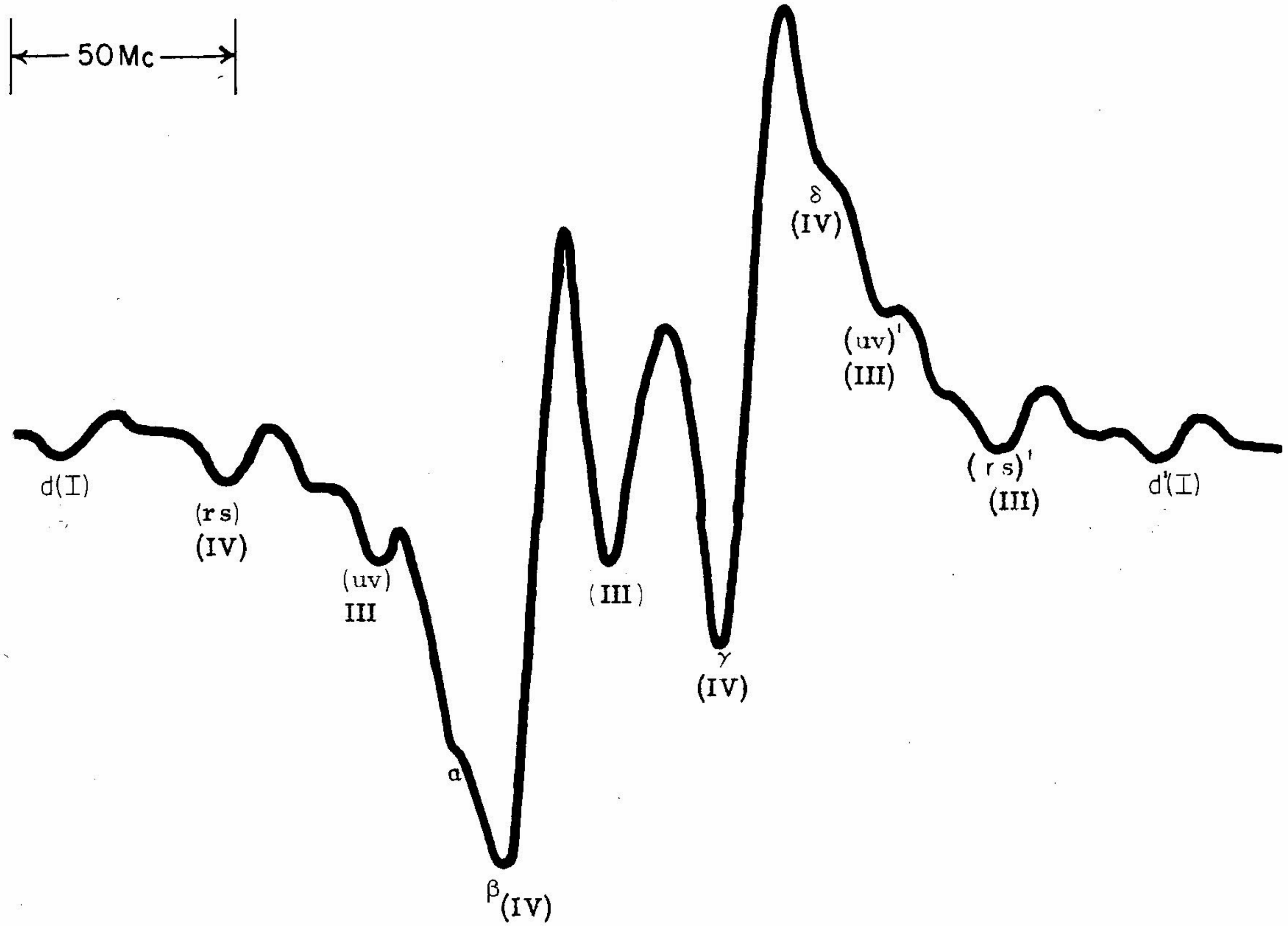
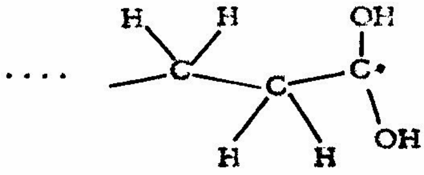
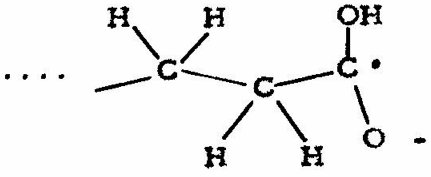


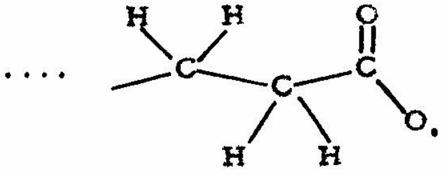
Fig. 13. X-band spectrum of damaged sebacic acid crystal after twenty-four hours at 88°C, $\underset{\sim}{H}_{o} \mid \underset{\sim}{j}$, $\Omega = 180°$.



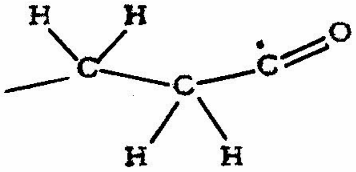
IV_a



IV_b



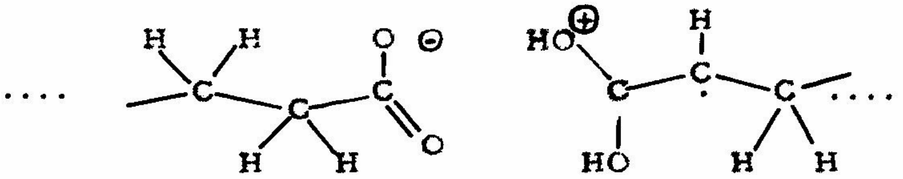
IV_c



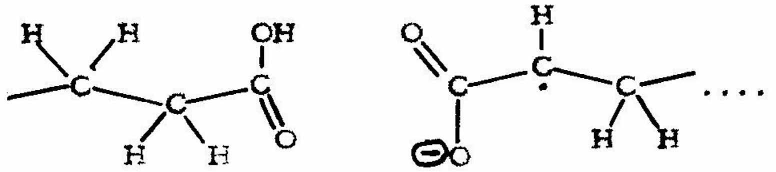
IV_d

Considering IV_a and IV_b, additional splittings from the hydroxy protons are expected. Atherton and Whiffen have determined the hyperfine tensor for the hydroxy proton in the glycolic acid radical, $HO\dot{C}HCO_2H$ (17). There the maximum splitting from the hydroxy proton is 28 Mc. But at no orientation does the spectrum of IV appear to split, nor is there any significant difference in the spectrum of IV in deuterated crystals. We estimate the line widths in the spectrum of IV to be about 10 Mc. It follows that the magnitude of the hyperfine coupling of the hydroxy protons in IV_a or IV_b would have to be substantially lower than in the glycolic acid radical. It seems unlikely that hydrogen bonding to an adjoining molecule could produce this effect.

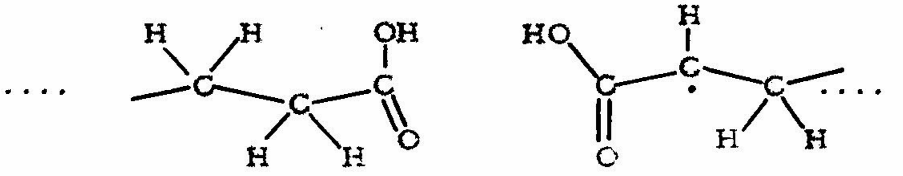
It would be wise to include an additional complication. Having supposed that II is the precursor of IV, we should consider a larger molecular system, to wit, II and the adjoining molecule in the chain. Recalling that Atherton and Whiffen showed that the magnitude of the hyperfine tensor for the σ proton is smaller in $HO\dot{C}HCO_2^-$ than in $HO\dot{C}HCO_2H$, we then postulate a number of possibilities for the structure of II involving irregularities in the hydrogen bonding with the adjoining molecule, for example,



II_a

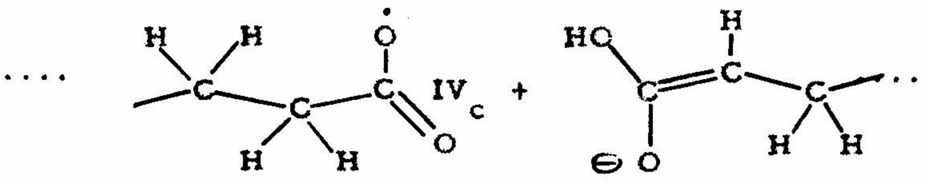


II_b

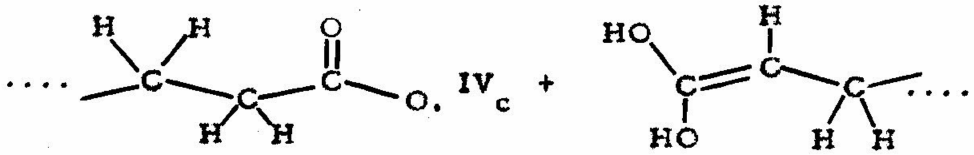


II_c

A simple hydrogen atom transfer for II_b would produce



A net electron transfer for II_a would produce

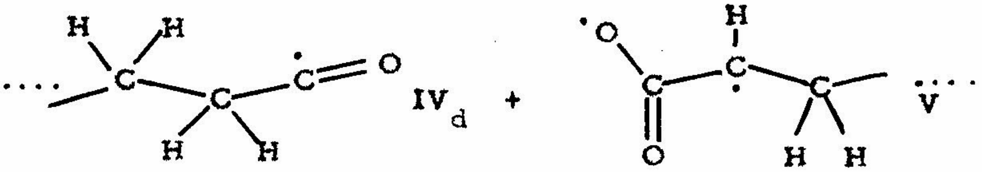


IV_c +

A hydrogen atom transfer for II_c might give rise to IV_c plus

$$H_2O + O{=}C{=}\overset{H}{C}{-}CH_2{-}\ldots$$

or



IV_d +

V

The possible existence of V is an academic question since V could not be responsible for the spectrum of III and since only radicals III and IV in the heat treated crystals give identifiable spectra.

The carboxyl oxygen system in IV_c is analogous to a hydrocarbon allyl conjugated system. Therefore, we might expect some negative spin density on the carboxyl carbon in IV_c, as is present on the center carbon atom in an allyl system (12). A spin density, $\rho = -0.4$, for orientation (i), would give the observed π-proton splittings in the spectrum of IV. It is probable that the unpaired spin in IV_d would be largely localized on the carboxyl carbon, implying orientation (ii). The magnitude of the C^{13} splitting from the carboxyl carbon in the spectrum of IV should give the approximate spin density on that carbon, enabling us to make a choice between the models. In the present work, the signal-to-noise ratio for the spectrum of IV is far too low to determine the splitting constant due to C^{13} present in natural abundance.

ANALYSIS OF SPECTRA FOR RADICAL III

Figure 6 shows the spectrum of a thoroughly heat treated, damaged sebacic acid crystal at $\underset{\sim}{H}_{o} \perp \underset{\sim}{j}, \Omega = 90°$. The lines r, s, r', s', u, u', v' undoubtedly belong to one radical, III. Lines d, d' are from radical I. At this orientation, none of the other lines from I is resolved. Line w seems to belong to III; a line w' would be masked by γ of IV. Line v of III is masked by α of IV. K-band spectra confirm this assignment.

To confirm that there is a pair w, w' in the spectrum of III, let us consider Figure 8, which shows a spectrum at the same orientation of a damaged crystal having undergone somewhat less heat treatment. Here, the spectrum of I, a quartet, is more intense while that of IV is less intense. Lines v, v' of III are masked now by the center lines of I, while w, w' are resolved quite clearly. Lines β, δ of IV are resolved but α, γ are masked by a center line of I and w' of III.

This ten line spectrum of III appears to be formed as a quintet arising from four equivalent protons, each with a coupling constant of 50 Mc.; each line of the quintet is split again into a doublet of 14 Mc. separation.

Figure 14 shows the spectrum of the less thoroughly heat treated crystal at $\underset{\sim}{H}_{o} \perp \underset{\sim}{j}, \Omega = 180°$. The doublets have coalesced and the spectrum of III has contracted. The separations between (rs) and (uv), (rs)' and (uv)' are 30 Mc. The center lines, (uv), and (uv)' appear to

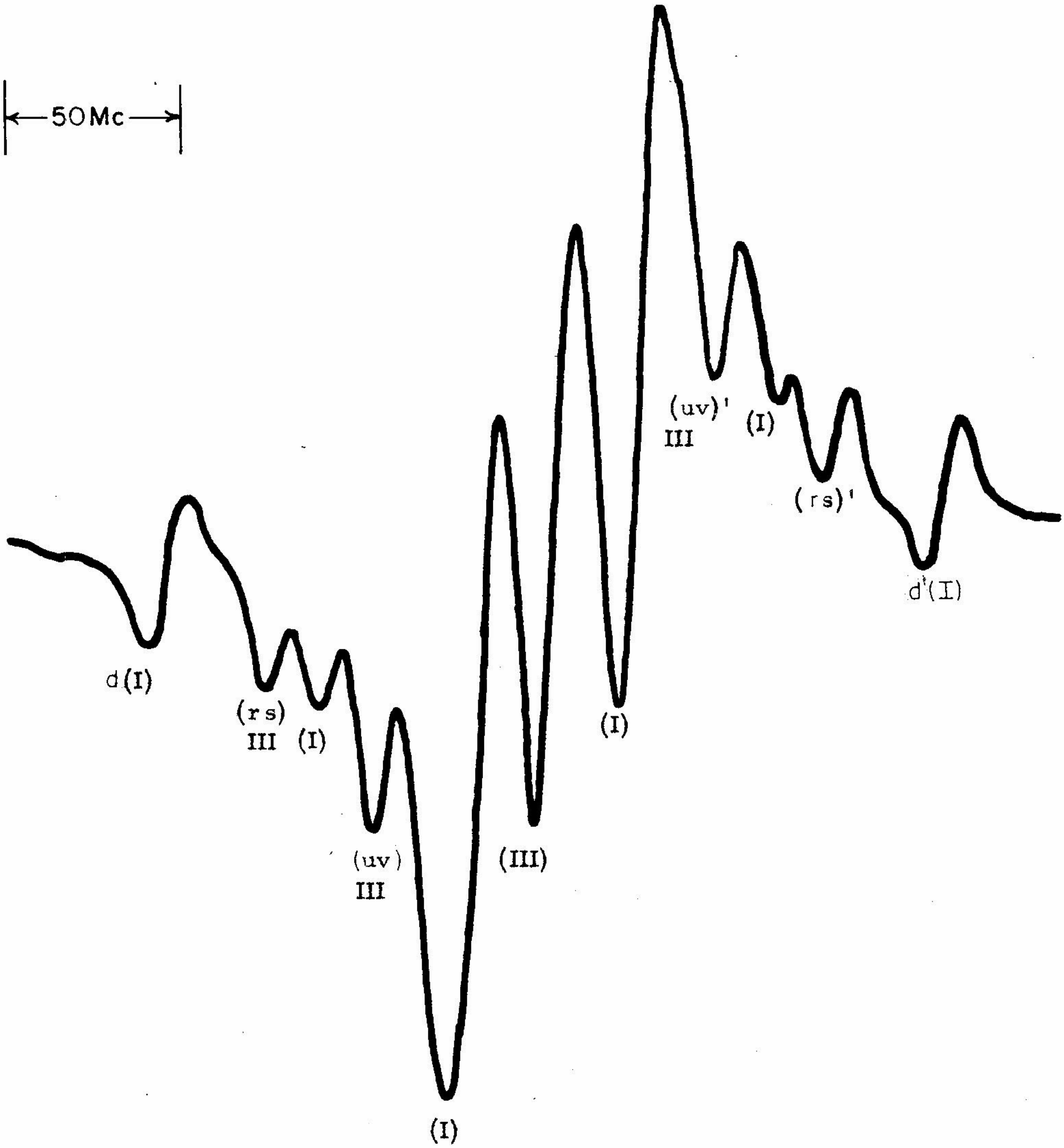


Fig. 14. X-band spectrum of damaged sebacic acid crystal after eighteen hours at 88°C, $\underset{\sim}{H}_o \perp \underset{\sim}{j}$, $\Omega = 180°$.

form a triplet with splittings of 50 Mc. If (rs) and (uv), (rs)' and (uv)' themselves form part of two triplets, the third member of each set would not be resolved from the two innermost lines of I.

At this orientation, the spectrum of III could be formed by a triplet with 50 Mc. splittings, with each line again split into another triplet with 30 Mc. splittings. The outer lines of the central triplet would not be resolved from the superposition of lines from I and IV.

The spectrum of III can be interpreted in terms of two equal nearly isotropic coupling constants of about 50 Mc., two equal anisotropic coupling constants which vary from 50 Mc. to 30 Mc. upon rotation about the j axis, and a third anisotropic coupling constant which varies from 14 Mc. to a value less than the observed line widths.

Postponing consideration of the third and smallest anisotropic splitting, we make the following assertions, subject to the usual limitations imposed by experimental uncertainty:

(A) The two equal large anisotropic splittings are due to two σ -protons interacting with spin densities substantially less than unity.

(B) Both carbon-σ proton bonds are parallel to the M axis of the undamaged molecule.

(C) The symmetry axes of the p orbitals containing the fractional spin densities are parallel to the N axis of the undamaged molecule.

(D) The carbon-σ proton bonds bisect the H_π-C-H_π angle of an adjacent carbon.

(E) The π protons bonded to the adjacent carbon give rise to the isotropic 50 Mc. splittings.

Proceeding as in the analysis of the spectrum of I, we choose the absolute values of the principal components of the hyperfine tensor for each σ proton,

$$|A| = 15 \pm 2 \text{ Mc.}$$

$$|B| = 33 \pm 2 \text{ Mc.}$$

$$|C| = 51 \pm 2 \text{ Mc.}$$

From equation 8, it follows that

$$|a| = 33 \pm 2 \text{ Mc.}$$

Table II shows the calculated and measured σ proton splittings at K-band for various crystal orientations. The good agreement is confirmation for assertions (A)-(C) and for our choice of principal values of the hyperfine tensor for each σ proton.

In view of the magnitude of these hyperfine tensors, K-band spectra are somewhat better for comparison with calculated splittings since the inner pair of the quartet arising from each anisotropic σ-proton is the more intense at all orientations. This is not the case at X-band. For the orientations listed in Table II, the inner doublet is at least ten times as intense as the outer. At X-band, for $\underset{\sim}{H}_0 \perp \underset{\sim}{j}$, $\Omega = 180°$, the outer pair is one and a half times as intense as the inner; yet the separation between an inner line and the adjacent outer line is less than the line width so only a broadened doublet from each proton is observed.

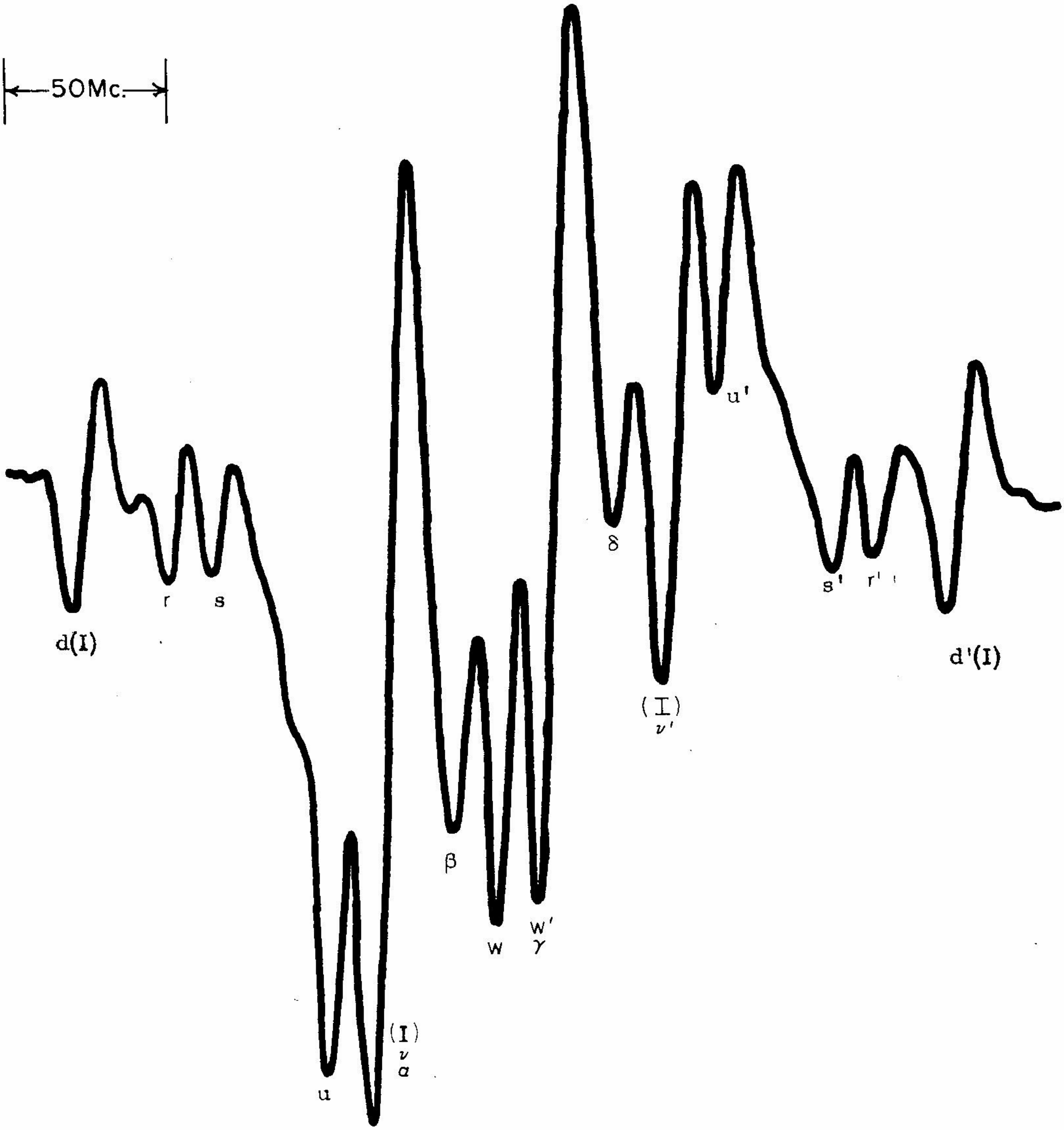


Fig. 8. X-band spectrum of damaged sebacic acid crystal after eighteen hours at 88°C, $\underset{\sim}{H}_o \perp \underset{\sim}{j}$, $\underset{\sim}{H}_o \parallel \underset{\sim}{i}$ ($\Omega = 90°$).

TABLE II

Experimental and Calculated Hyperfine Splittings for Radical III

Angle Ω	Observed σ Splittings ± 2 Mc	Calculated σ Splittings ± 2 Mc
0	30	29
20	30	29
30	31	31
40	34	34
50	38	37
60	40	41
70	44	45
90	50	50
120	47	47
130	44	44
140	39	40
150	35	36
160	32	33

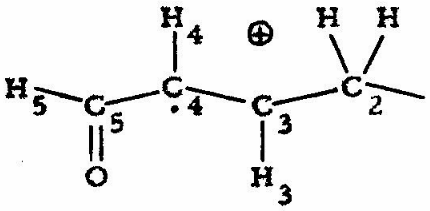
π Splittings = 50 ± 2 Mc for all angles

The use of K-band affords another advantage. The crossing of the inner lines would easily be observed. This occurs when two of the principal values of the hyperfine tensor are opposite in sign. Since the strong inner lines for these two anisotropic proton splittings do not cross, the principal values listed above are of the same sign, as expected for a σ proton.

Moreover, we observe that the ratio of these principal values for the σ protons in III, A:B:C = 1:2.2:3.4, compares well with the corresponding ratio for the σ proton in I, A:B:C = 1:2.1:3.3. This further substantiates assertion (A), which, in turn, requires that the principal values are negative.

The equal, nearly isotropic splittings in the spectrum of III are undoubtedly due to π protons oriented equivalently with respect to the symmetry axis of a p orbital bearing a fractional spin density and located on a carbon once removed. The magnetic equivalence of the protons and the two π protons at $\underset{\sim}{H}_o \perp \underset{\sim}{j}$, $\Omega = 90°$, implies that the carbon chain of III is oriented very similarly to the carbon chain of the undamaged molecule, just as in the case of I.

Let us consider the model



. . . . IIIa

which shall conform to the assertions (A)-(E) made earlier in this analysis. Here, the unpaired spin would be confined to a molecular orbital (M.O.) centered on carbons 4 and 3, whose atomic p orbitals would make the essential contributions to the M.O. Here we are presuming that the carbonyl group in III_a like the carboxyl group in I does not have an appreciable effect in the spin density distribution in III_a. If we assume $\rho_{44} = \rho_{33} = 0.50$, it follows from equation 31 that $Q = -67$ Mc., a reasonable value for σ protons.

It should be apparent that the smallest splitting constant will always be the weak link in any argument proposing any model for III. The fact that the maximum value of the splitting is only 14 Mc. and that the line widths are of the order of 10 Mc. means that an anisotropy of only a few Mc. is necessary to make this doublet unresolvable from the line widths. It is obvious that a σ proton bonded to a carbon bearing a small spin density would be sufficiently anisotropic. We intend to make plausible arguments that the π proton 5 in III could also be responsible for the behavior of the smallest splitting in the spectrum of III.

The following points are of significance:

(A) From equation 32, it follows that π proton 5 must lie very nearly in the nodal plane of the π M.O. in III_a in order that the splitting from proton 5 be small.

(B) The major part of the anistropy of a π proton interaction is considered to be due to dipole-dipole interaction with the unpaired spin two carbons away (2).

(C) In III_a, the diagonalizing axes, z', y', x', for the anisotropic coupling of proton 5 with the unpaired spin on carbon 4 would be as follows:

(1) z' is along the line joining proton 5 to carbon 4

(2) x' is along the symmetry axis of the atomic p orbital on carbon 4

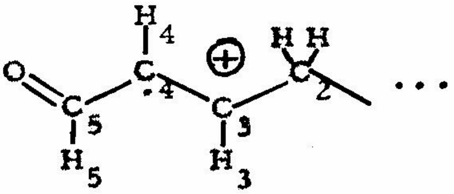
(3) y', of course, is perpendicular to z and x

(D) Whiffen and Pooley have determined the principal values of the anisotropic contribution to the hyperfine tensor of the π protons in the radical $HOO\dot{C}CHCH_2COOH$. Corresponding to z', x', and y', they are about +8 Mc., 0 Mc., -8 Mc. (3).

(E) The isotropic component of π-proton interactions is positive (2-5).

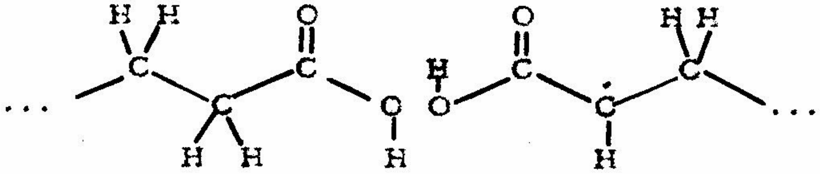
Equations 30 show that the external field at $\underset{\sim}{H}_o \perp \underset{\sim}{j}$, $\Omega = 90°$, is very nearly along the L molecular axis, i.e., very nearly along the diagonalizing axis, z', for proton 5. Since $\rho_{44} = 0.50$, we would expect the maximum anisotropic contribution of some +4 Mc. to the splitting constant of proton 5. This +4 Mc. added to the positive isotropic contribution ensures the maximum splitting from proton 5 at this orientation, exactly what is observed. If the crystal is rotated until $\underset{\sim}{H}_o \perp \underset{\sim}{j}$, $\Omega = 180°$, the external field lies approximately in the x'y' plane, about 30° from the y' axis. Here, the anisotropic contribution would be about -3 Mc.; the total splitting would be some 7 Mc. less than at $\Omega = 90°$, or about +7 Mc., not resolvable from the line widths. In general, the π proton 5 in III_a, oriented as indicated, could very well give rise to the smallest splitting in the spectrum of III. Thus, all the features of the spectrum of III are consistent with the model, III_a.

The model III_a'



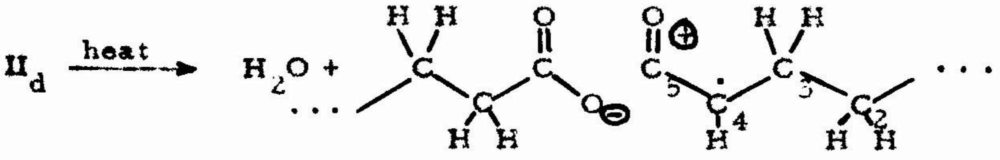
differs from III_a in the orientation of proton 5. We might argue that the appropriate twists around C_5-C_4 and C_3-C_2 occur such that proton 5 and one of the π protons on carbon 2 are magnetically equivalent and that the other π proton on carbon 2 is oriented magnetically similarly to proton 5 in III_a.

Regarding a mechanism for the formation of III_a, let us consider another possible model for II,

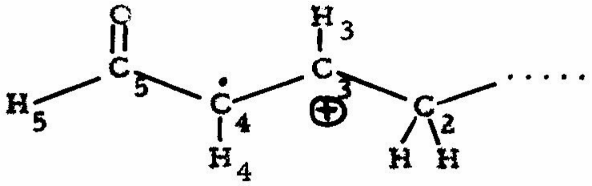


II_d

and postulate a two step reaction. First, the elimination of a molecule of water,



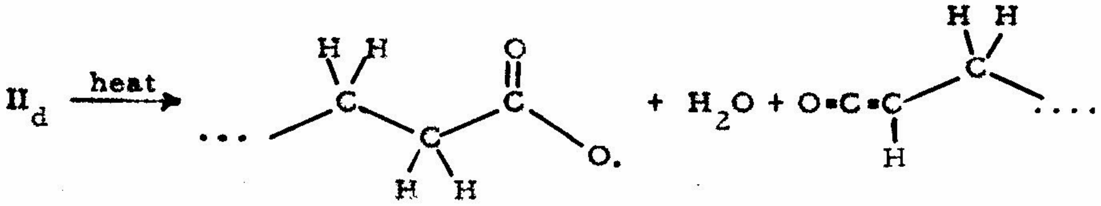
followed by the migration of a hydrogen atom from carbon 3 to carbon 5, to form



III_a

It may be argued that the positive charge makes the hydrogen atoms on carbon 3 more labile, making the migration more plausible.

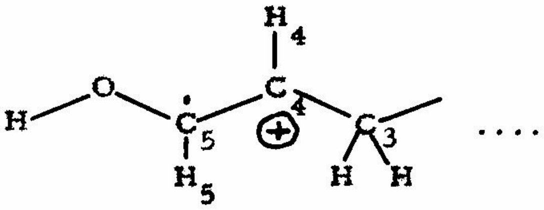
It is interesting to note that the elimination of water from II_d and its adjoining molecule could occur as follows,



IV_c

to form radical IV_c.

Another possible model for III is



III_b

which again shall conform to assertions (A)-(D). The same arguments used to explain the origin of the observed two large anisotropic and the two large isotropic splittings from III_a hold for model III_b. For simplicity, we shall assume that the hydroxy proton in III_b lies in the plane of carbons 5, 4, 3, and, consequently, has an orientation similar to that of the π-proton 5 in III_a. We shall then assume that the diagonalizing axes for the anisotropic hyperfine tensor of the hydroxy proton in III_b are parallel to those used in the discussion of III_a. The principal values of the hyperfine tensor of the hydroxy proton in $HO\dot{C}HCO_2H$ are +28 Mc., +4 Mc., and -7 Mc. (17), referred to a set of diagonalizing axes similar to z', y', x', for III_a and III_b. Then at $\underset{\sim}{H}_o \perp \underset{\sim}{j}$, $\Omega = 90°$, for $\rho_{55} = 0.50$, we would expect a splitting of about +14 Mc. from the hydroxy proton in III_b. As the field is rotated towards the x' y' plane, the hydroxy proton splitting would decrease and become unresolvable from the line widths. Thus, III_b is also a reasonable candidate for radical III, disregarding the shaky assumptions we have made about the orientation of the hydroxy proton.

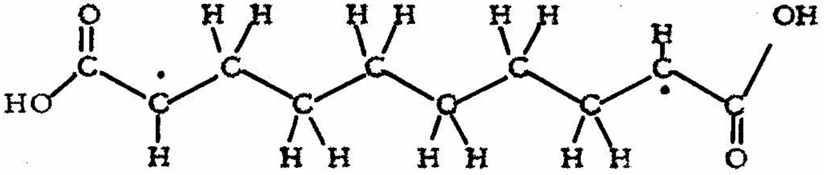
The fact that the spectrum of III is the same in deuterated and undeuterated crystals restricts us to consideration of mechanisms for the production of III_a and III_b such that all the protons giving hyperfine structure are or were originally bonded to the methylene carbons. This necessity was satisfied in the case of III_a but creates considerably more difficulty for III_b, which requires that <u>two</u> methylene hydrogen atoms migrate. Such mechanisms are very complicated and seem necessarily to involve interchain proton or hydrogen migration. It is conceivable that such interchain reactions could occur. The distance, 3.3 Å, between a carboxyl oxygen in one chain and a carbon 4 in the neighboring chain is the closest approach of parallel chains in the undamaged crystal (9). This close approach may indicate a slight amount of hydrogen bonding between parallel chains. The main objection to possible mechanisms for the production of III_b is that they invoke the formation of new radicals, whose unpaired spins would be of the order of 5 Å from the unpaired spin in III. The close approach of unpaired spins would lead to sizeable anisotropic spin-spin interactions, as illustrated in the following simple analysis.

Let us consider the classical dipole-dipole interaction, ΔE, between two electron spins with magnetic moments, $\mu_e = 0.928 \times 10^{-20}$ erg/gauss, in terms of Mc.

$$\Delta E = \frac{\mu_e^2}{r^3} (3\cos^2\theta - 1) = \frac{12900\,(3\cos^2\theta - 1)\mathrm{Mc}}{r^3} \qquad (33)$$

θ is the angle between the direction of the applied magnetic field and the line joining the two electrons considered as point dipoles, a distance r apart. For r = 5 Å, $\Delta E \approx 133\,(3\cos^2\theta - 1)$ Mc., or much larger than any of the splittings noted in the spectra of III. Conceding that we may be dealing with fractional spin densities and that the spin-spin distances could be greater, the suggestion may be made that one of the anisotropic coupling constants for III is actually due to electron spin-electron spin interaction between two radicals. This possibility is refuted almost in general, because along with III we would expect to have present another radical of equal concentration with a spectrum showing a similar anisotropic splitting constant. This is not observed experimentally, unless the two radicals bearing the unpaired spins are precisely magnetically equivalent. Considering this possibility, we infer from the fact that the anisotropic splittings in the spectrum of III are largest when the field is parallel to the molecular chains that the interacting spins would have to lie within the same chain, not in neighboring chains. Equation 33 requires that $\theta = 0°$ or $180°$ for the greatest value of ΔE.

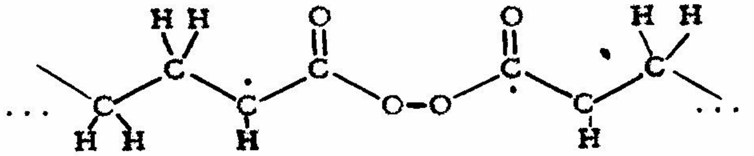
We might suggest that the diradical,



III_c

is a possibility. The separation of the unpaired spins is about 9 Å, with $\Delta E \approx 17 (3 \cos^2 \theta - 1)$ Mc. However, the overlap of the p orbitals is so small that this diradical would behave as two uncoupled mono radicals and give spectra similar to I.

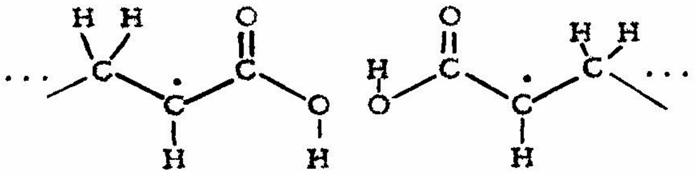
The small values of the coupling constants for III suggest that the two proposed nearby spins may couple so that in effect each electron spin interacts with protons on both radicals. A conceivable structure might be



III$_d$

with the odd electron exchanging via the p orbitals on the linking oxygen atoms, each spin spending equal time at each α carbon. The interaction of each spin with each proton would be reduced to about one-half its normal value. The smallest splitting in the spectrum of III could be laid to a net spin-spin coupling. One objection to this model is that the methylene groups on the β carbons must twist so that only two π-protons could interact with each spin.

If we postulate that radical II must then be like

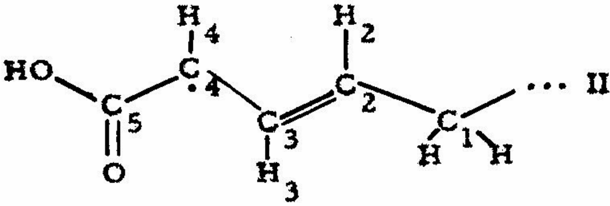


II$_e$

and that heat treatment causes the ejection of a molecule of hydrogen, we must infer from the spectrum of II that the spins in II$_e$ do not exchange and indeed are localized on the respective α carbons. In that case, the interdipole distance is about 7 Å, leading to an interaction, $\Delta E \approx 40\,(3\cos^2\theta - 1)$ Mc., which should be observed in the spectrum of II. Again there is no evidence for this. Moreover, it seems statistically unlikely that there would be such a high concentration of neighboring damage sites. It may be argued that the interaction of the unpaired spins in model II is smaller than calculated and likely to be of the same order of magnitude as postulated in model III. In view of the great overlap of the spectra of I and II, the spectra of II may not be the simple 4 or 6 line pattern suggested. Each line could be split slightly. Recalling Figure 4, we might suppose that the outer lines of I mask lines associated with x and x' of II. Considering this possibility, we might propose that UV light in some way destroys one of the two radicals in the model II. The remaining radical would probably give a spectrum nearly identical to I. Thus the observed constancy of the intensity of the spectra of I under UV bleaching is explained.

Synthesis of sebacic acid with C^{13} ($S = 1/2$) in the α carbon positions is in order. A careful study of the C^{13} splittings in heat-treated crystals should distinguish between III_d and models like III_a. In the latter case, we would expect a doublet from C^{13}, for III_d a triplet.

Another model for III is



··· IIIe

In this allyl type radical, protons 4 and 2 would give the two larger anisotropic splittings, proton 3 the smallest anisotropic splitting, and the protons on the methylene carbon 1 the two isotropic coupling constants. If we assign 4 Mc., 9 Mc., and 15 Mc. as the absolute principal values of the hyperfine tensor for proton 3, we may calculate the isotropic hyperfine splitting for all three σ protons from equation 8,

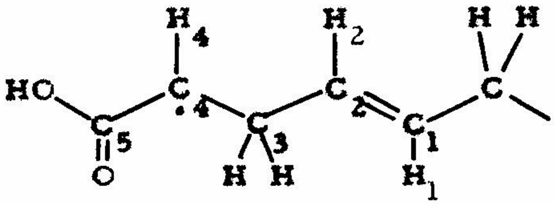
$$|a_4| = |a_2| = 33 \pm 2 \text{ Mc.}; \quad |a_5| = 9 \pm 2 \text{ Mc.}$$

From equation 31, using $|Q| = 57$ Mc., the value found for radical I, we find that

$$|\rho_{44}| = |\rho_{22}| = 0.58; \quad |\rho_{33}| = 0.16$$

In order that $\Sigma\rho_{ii} = 1.0$, it is clear that both ρ_{44} and ρ_{22} must be positive and that ρ_{33} is negative. Theoretical calculations show this assignment of signs to be correct and the values of spin densities to be of the right order of magnitude (12) for an allyl radical. For the self-consistent field treatment, the spin densities are 0.61, 0.61, and -0.19 (12,15). Heller and Cole have irradiated the olefinic compound, glutaconic acid, to produce the radical $(HOOC)\dot{C}H(CH{=}CH)COOH$ (19). The corresponding values for the spin densities are 0.59, 0.59, and -0.19. This excellent agreement with the results for model III is alarming, since we must account for the origin of the double bond in III.

Let us suppose that radical II contains the double bond as in the formula,



.... II_f

Intuitively, it seems likely that some, albeit a small fraction, of the spin density on carbon 4 could leak over into the π-M.O. on carbons 1 and 2. Thus this model for II would give a spectrum similar to that of I but with smaller splittings.

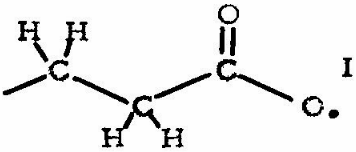
Upon heat treatment, a hydrogen atom migration from carbon 3 to carbon 1 would give rise to III_e. The problem is reduced to the explanation of the double bond in II_f. Either we postulate the occurrence of triple x-ray damage in just the right positions or concede that in spite of the careful attempts at purification the sebacic acid contained an olefinic impurity. The former hypothesis seems unreasonable, the latter unpalatable.

From Figure 4, we see that the intensity of II is about half that of I. It has been found that the radiation damage rate as measured by the production of hydrogen is about the same for the olefin as for the saturated analogue (20). We then expect that the olefin should make up an appreciable percentage of the sample, probably about 25% or more. However, the nuclear magnetic resonance spectrum of an alcoholic solution of purified sebacic showed no trace of olefinic protons. The concentration of a mono-olefin must be below 5%. Infrared spectra of sebacic acid in a KBr pellet showed no trace of an olefin.

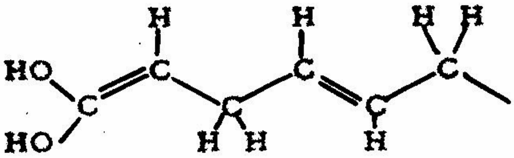
We are led to conclude that if III is an allyl type radical the possible trace of olefin in the sample of sebacic acid must damage considerably more readily than the saturated analogue, in spite of previous experimental knowledge concerning radiation damage rates. It is significant to note that crystals grown from the melt of unpurified sebacic acid when damaged give the same mixed spectra of I and II as the purified sample. Samples of the crude and purified acid were left molten for different periods of time in the crystal growing apparatus. No difference in spectra was observed. It seems unlikely that for all the varying experimental conditions the crystals formed would all have the same concentration of olefin.

We observe, moreover, that the relative intensities of the spectra of I and II remain the same for any period of exposure to x-rays. We estimate that the maximum concentration of radicals that can be obtained by x-ray damage before the crystal disintegrates into powder or slivers is of the order of 0.5%. If the concentration of the impurity is as high as 1%, the impurity is damaging over 50 times faster than the sebacic acid. Thus at high damage levels, there should be a serious depletion of the impurity and a consequent decrease in the rate of formation of II from the impurity. This is not observed.

We might note that the carboxyl oxygen in II_f could accept a hydrogen atom from the adjoining molecule to form

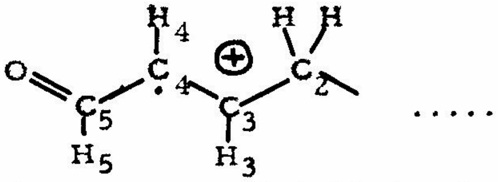


IV$_c$ and

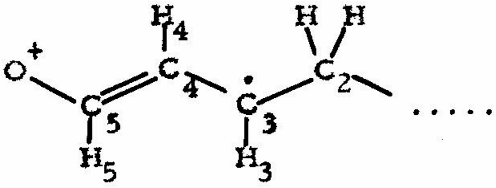


But if we are postulating that the difference between I and II lies in the presence of a double bond in nearly the center of the methylene chain of II and not in hydrogen bonding irregularities, it is difficult to see why I should not give rise to IV$_c$ on heat treatment, unless III and IV have different precursors.

It is interesting to note that III$_a$'



has an allyl type resonance hybrid structure, III$_f$.



which might well give rise to the observed hyperfine splittings. As model III$_f$ implies a greater delocalization of spin, it may be the better representation of the π electronic structure for the nuclear configuration of models III$_a$ and III$_f$.

SUMMARY

The nature of radical I seems firmly established, while the same is far from true for II. Since the experimental evidence suggests strongly that I and II are quite similar in structure, we have supposed that the most likely difference lies in some sort of hydrogen bonding irregularities. The precise nature of these irregularities is not determined. Whether these irregularities are present in the crystal before damage or are produced by the damage was also not determined. We have ignored the possibility that the x-rays produce other damage sites distinct from I and II and their immediate environments and that these damage sites may give rise to III and/or IV. Since the existence of II is necessary for the production of III and IV, we have assumed that II is indeed the precursor of both these radicals.

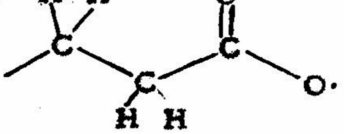
No spectral evidence for decarboxylation is observed in the freshly damaged crystal nor in the heat treated crystal. Most of the models for II imply an incipient formation of water, which could be removed by heat.

Model III_f is rejected because the mechanisms seem too involved and invoke, in general, the formation of nearby radicals. The necessary effects of interaction between spins in neighboring chains are not observed experimentally. Moreover, it seems reasonable that the effect of hydrogen bonding with the adjoining molecule would distort the hydroxy proton from its position as indicated for the structure III_f and cause the anisotropic behavior of such a proton to be distinctly different from the behavior of the smallest splitting in the spectrum of III.

As for model III_d, the diradical, the required high probability of close double damage, the required twist of the methylene groups, the absence in the spectrum of its precursor II_f of electron-spin-electron spin interaction of the magnitude expected, all argue against its credibility.

The allyl type radical, model III_e, agrees very well with the theoretical and experimental data on allyl radicals. Yet this model requires that the probability of triple x-ray damage within one molecule be of the same order of magnitude as that of single x-ray damage. Models III_a' or III_f are consistent with the spectral data. Yet no definite evidence for stable ionised radicals has been found in magnetic resonance studies of irradiated pure organic compounds. We are hesitant to affirm preferences here.

We consider that IV_c



is the more likely model for IV because other models are likely to give spectra showing additional splittings (IV_a and IV_b) or require the production of nearby radicals with the attendant electron spin-electron spin interactions (IV_d).

The question of why sebacic acid is a more complicated system than, say, succinic acid, is unresolved. The fact remains that in x-ray damaged sebacic acid solid state reactions are occurring under the influence of heat and ultraviolet light.

REFERENCES

1. H. M. McConnell, C. Heller, T. Cole, and R. W. Fessenden, J. Am. Chem. Soc., 82, 766 (1960).
2. C. Heller and H. M. McConnell, J. Chem. Phys., 32, 1535 (1960).
3. D. Pooley and D. H. Whiffen, Molecular Physics, 4, 81 (1961).
4. A. Horsfield, J. R. Morton, and D. H. Whiffen, Molecular Physics, 4, 169 (1961).
5. J. R. Morton and A. Horsfield, Molecular Physics, 4, 219 (1961).
6. A. Horsfield, J. R. Morton, and D. H. Whiffen, Molecular Physics, 4, 321 (1961).
7. H. M. McConnell and C. R. Guiliano, J. Chem. Phys., 35, 1910 (1961).
8. D. F. Houston and W. A. Van Sandt, Ind. Eng. Chem. (Anal. Ed.), 18, 538 (1946).
9. J. M. Robertson and J. D. Morrison, J. Chem. Soc., 993 (1949).
10. G. E. Pake, T. Townsend, and S. I. Weissman, Phys. Rev., 85, 682 (1962).
11. H. M. McConnell and R. E. Robertson, J. Chem. Phys., 29, 1361 (1958).
12. H. M. McConnell, J. Chem. Phys., 28, 1188 (1958).

13. H. M. McConnell and J. Strathdee, Molecular Physics, 2, 129 (1959).

14. E. M. Corson, "Perturbation Methods in the Quantum Mechanics of n-Electron Systems," Hafner Publishing Co., 1948, p. 118.

15. H. M. McConnell, J. Chem. Phys., 30, 328 (1959); H. M. McConnell, J. Chem. Phys., 29, 244 (1958).

16. H. M. McConnell and D. B. Chesnut, J. Chem. Phys., 28, 107 (1958); H. M. McConnell, J. Chem. Phys., 24, 764 (1956).

17. N. M. Atherton and D. H. Whiffen, Molecular Physics, 3, 1(1960).

18. N. M. Atherton and D. H. Whiffen, Molecular Physics, 3, 103 (1960).

19. C. Heller and T. Cole (to be published).

20. T. Tolbert and R. Krinke, "Chemical Effects of Ionizing Radiation on Pure Organic Compounds," Radiation Research, 2, 586 (1960).

PART II

RATE OF ELECTRON EXCHANGE BETWEEN DIp-ANISYL NITROGEN OXIDE MOLECULES BY ELECTRON PARAMAGNETIC RESONANCE

INTRODUCTION

Rates of certain fast reversible electron exchange reactions involving chemical species possessing an EPR or NMR spectrum, which arises from transitions between two spin states, have been measured by the change in line shape of the resonance spectrum as the mean lifetime of the spin states is changed. For instance, McConnell (1) used the nuclear resonance of Cu^{63} in Cu^{+}-Cu^{++} HCl solutions to determine the rate of electron exchange between the two oxidation states of copper. Bruce, Norberg, and Weissman (2) have studied proton resonance in mixtures of N,N'-tetramethylparaphenylenediamine and N,N'-tetramethylparaphenylinediamine positive ion to obtain the rate of electron transfer between these two species. Ward and Weissman (3) determined the rate of electron transfer between naphthalene negative ion and naphthalene by observing the EPR spectrum of the negative ion.

In these cases the common feature is the broadening of the resonance by increasing the rate of electron exchange between a paramagnetic reactant and a diamagnetic reactant which decreases the lifetime of the resonant species with respect to suddenly jumping into a different magnetic environment.

Gutowsky, McCall, and Schlicter (GMS) (4) were first to derive from the classical Bloch equations a quantitative relationship between resonance line shapes and rates of certain fast reversible chemical exchange reactions. The GMS method was extended by Gutowsky and Saika (5), McConnell and Berger (6), and Grunwald, Loewenstein, and Meiboom (7) to a number of reaction rate-line shape problems. McConnell (8) has directly generalized the Bloch equations to include the effects of chemical exchange, bypassing the complicated derivations inherent in the GMS method.

The usual procedure for determining electron exchange rates is to choose concentrations such that the electron exchange causes a small increase of the line width over that with negligible exchange. Assuming additivity of line broadening processes, then the increase in line width gives directly the exchange lifetime, from which a rate constant may easily be calculated.

In the present work the purpose is to determine whether the modified Bloch equations describe the transition from the hyperfine triplet (arising from the hyperfine contact with the nitrogen nuclear moment) to the exchange narrowed single line spectrum as the concentration of DANO is increased so that the exchange lifetime could be calculated from the line shape at any intermediate concentration.

THEORY

Consider a rapid reversible electron exchange between any two of the three magnetic environments, A, B, and C (corresponding to the three orientations of the nitrogen nuclear moment in the external stationary magnetic field).

Following the McConnell derivation of the modified Bloch equations for chemical exchange, we have for the rate of change of the magnetization in A

$$\dot{u}_A + \Delta\omega_A v_A = -u_A/\tau_{2A} + u_B/2\tau_B + u_C/2\tau_C \tag{1}$$

$$\dot{v}_A - \Delta\omega_A u_A = -v_A/\tau_{2A} + v_B/2\tau_B + v_C/2\tau_C - \omega_1 M_Z^A \tag{2}$$

$$\dot{M}_Z^A - \Delta\omega_1 v_A = M_o^A/T_{1A} - M_Z^A/\tau_{1A} + M_Z^B/2\tau_B + M_Z^C/2\tau_C \tag{3}$$

with completely analogous sets for the B and C environments. u_A, v_A and M_Z^A represent the components of the electron spin magnetization which are in phase with the effective rotating component of the RF field, out of phase with the rotating RF field, and in the direction of the large stationary field, respectively. M_o^A is equilibrium magnetization of electron spins in A, $\omega_1 = \gamma H$, and

$$\frac{1}{\tau_{1A}} = \frac{1}{T_{1A}} + \frac{1}{\tau_A} \tag{4}$$

$$\frac{1}{\tau} = \frac{1}{T_{2A}} + \frac{1}{\tau_A} \tag{5}$$

In equations 4 and 5 T_{1A} and T_{2A} are the longitudinal and transverse relaxation times of the electron spin in A while τ_A is the first order lifetime of electron spin in A with respect to transfer to B or C. T_{1B}, T_{1C}, T_{2B}, T_{2C}, τ_B, and τ_C are defined similarly.

Equation 1 differs from the usual Bloch equation by the addition of three terms on the right-hand side. $-u_A/\tau_{2A}$ represents rate of transfer of u magnetization out of A; $u_B/2\tau_B$ and $u_C/2\tau_C$ measure the rate at which u magnetization is transferred into A by chemical exchange with B and C. Note the factor two in the $u_B/2\tau_B$ and $u_C/2\tau_C$. (Similar considerations apply for equations 2 and 3 and, of course, for the equations involving the rate of change of magnetization in B and C.) The lifetime of B with respect to transfer into A is exactly twice its lifetime with respect to transfer into A and C. If we assume slow passage then

$$\dot{u}_A = \dot{u}_B = \dot{u}_C = \dot{v}_A = \dot{v}_B = \dot{v}_C = \dot{M}_Z^A = \dot{M}_Z^B = \dot{M}_Z^C = 0 \qquad (6)$$

Since the populations of electron spins in A, B, and C are essentially equal

$$\begin{aligned} &\tau_A = \tau_B = \tau_C = \tau \\ &T_{2A} = T_{2B} = T_{2C} = T_2 \\ &1/\tau_2 = 1/T_2 + 1/\tau \\ &M_o^A = M_o^B = M_o^C = M_o/3 \end{aligned} \qquad (7)$$

Also assuming no RF saturation so that

$$M_Z^A = M_Z^B = M_Z^C = M_o/3 \qquad (8)$$

then the complete set of modified Bloch equations can be solved for the magnetizations in A, B, and C, i.e., G_A, G_B, G_C

$$\left(\frac{1}{\tau_{2A}} - i\Delta\omega_A\right) G_A = \frac{G_B + G_C}{2} - i\omega_1 M_o/3 \qquad (9)$$

$$\left(\frac{1}{\tau_{2B}} - i\Delta\omega_B\right) G_B = \frac{G_A + G_C}{2} - i\omega_1 M_o/3 \qquad (10)$$

$$\left(\frac{1}{\tau_{2C}} - i\Delta\omega_C\right) G_C = \frac{G_A + G_B}{2} - i\omega_1 M_o/3 \qquad (11)$$

Equations 9, 10, and 11 may be combined to form the expression for the total magnetization, $G = G_A + G_B + G_C$

$$G = -\left(\frac{\omega_1 N_c}{3}\right) \frac{(36 + 24\tau^2/T_2) + i(2 + 36\tau/T_2 + 12\tau^2/T_2^2 + 4\tau^2\delta^2 - 12\tau^2(\Delta\omega)^2}{(9/T_2 + 12\tau/T_2^2 + 4\tau^2 + 4\tau\delta^2/T_2^3 + 4\tau^2\delta^2/T_2 - 12(\Delta\omega)^2 - 12\tau^2/T_2(\Delta\omega)^2 + i((-9 - 24\tau/T_2 - 12\tau^2/T_2^2 - 4\tau^2\delta^2)\Delta\omega + 4\tau^2(\Delta\omega)^3)}$$

where $\Delta\omega = \omega - \omega_o$, ω_o = resonant frequency of central peak and δ the hyperfine splitting constant in $\sec^{-1}$.

If we assume that the expression for the rate of electron exchange between A and B and A and C has the simple second order form

$$R_A = k(N)_A(N)_B + k(N)_A(N)_C \tag{12}$$

where R_A is the number of moles of electrons transferred out of A per liter per sec, k the bimolecular rate constant, and $(N)_A$, $(N)_B$, and $(N)_C$, the concentrations in moles per liter of electron spins in the three respective magnetic environments, then it follows that

$$\tau_A = \frac{1}{k(N_B) + k(N_C)} = \frac{1}{2/3\ k(N)} \tag{13}$$

where (N) is total concentration of electron spins.

EXPERIMENTAL

The di-p-anisyl nitrogen oxide (DANO) was prepared exactly according to the prescription of Meyer and Gottleib (9), i.e., nitration of anisol in glacial acetic acid-concentrated sulfuric acid mixtures followed by treatment with perchloric acid to form the DANO perchlorate salt which then was reduced by pyridine to form DANO. The DANO was purified by several crystallizations from 1:1 mixtures of methyl alcohol and water and stored in a dark bottle. The chloroform was spectra grade.

Though crystalline DANO is apparently quite stable, it was desired to check the stability of DANO-chloroform solutions. The percent recovery from a series of nearly saturated DANO solutions allowed to stand for two days in the darkness varied between 95 and 100%. Aliquots were taken daily from a nearly saturated solution and diluted to an appropriate concentration so that the UV spectra could be observed by a Cary Spectrophotometer. Over a period of seven days the intensity of the UV spectrum of the diluted aliquot diminished by about 10%. It was also determined that DANO solution in the concentration range of interest was stable for at least two days under working conditions provided that reasonable precautions were taken to avoid heat and direct exposures to sunlight. It was concluded that concentrations of solutions made by weighing out DANO were reliable to 10% under reasonable conditions.

The SPR spectra of unthermostated DANO samples at room temperatures were obtained using a Varian EPR spectrometer. Since the instrument employs audio frequency field modulation and phase sensitive detection, the derivative of the absorption spectra is displayed on the recorder chart. The EPR spectrum of Mn^{++} in a crystal of $CaCO_3$ was used to calibrate the recorder chart in terms of gauss.

RESULTS AND DISCUSSION

Since the EPR spectrometer displays the derivative of the imaginary component of $G = u + iv$, two methods present themselves for comparing theoretical and experimental line shapes: (1) analytically differentiating v and comparing dv/dH with the experimental results or (2) graphically integrating the experimental derivative curves and comparing with theoretical shapes for v. To avoid the great number of arithmetical operations necessary to evaluate dv/dH, the second method was adopted.

Table 1 shows the comparison of experimental with theoretical results.

Table 1

F	τ (sec)	ΔH_{theo} (gauss)	ΔH_{exp} (gauss)	% discrep from exp.
0.0059	3.3×10^{-8}	8.6	8.6	0
0.0197	0.97×10^{-8}	44.8	46	-3
0.0394	4.9×10^{-9}	31	33	-7
0.0494	3.9×10^{-9}	27.5	27.5	0
0.0694	2.8×10^{-9}	21.8	22.4	-3
0.099	2.0×10^{-9}	18.6	16.0	+18
0.197	0.97×10^{-9}	14.2	13.6	+4.4

The theoretical values for ΔH (width at half maximum intensity) are based on the peak to peak HF separation being 11.4 gauss and T_2 being

2.2×10^{-8} sec. This value of T_2 corresponds to a line width of 5.1 gauss for the case of negligible exchange. Note that the increase in width for the 0.0059 F solution, i.e., 3.5 gauss, gives $\tau = 3.3 \times 10^{-8}$ sec if additivity of line broadening mechanisms is assumed.

Assuming $\tau = 3.3 \times 10^{-8}$ sec for the 0.0059 F solution, the successive values of τ were calculated on the basis of an inverse relationship to concentration (see equation 11) and were substituted into the theoretical expression for v. The width at half maximum intensity was selected as the feature of comparison.

Figures 1 and 2 show representative comparisons of experimental and theoretical line shapes. The common feature is good agreement of line shapes except out in the wings, where the experimental curves fall off more rapidly than the theoretical. This indicates perhaps some gaussian character to the experimental line shapes.

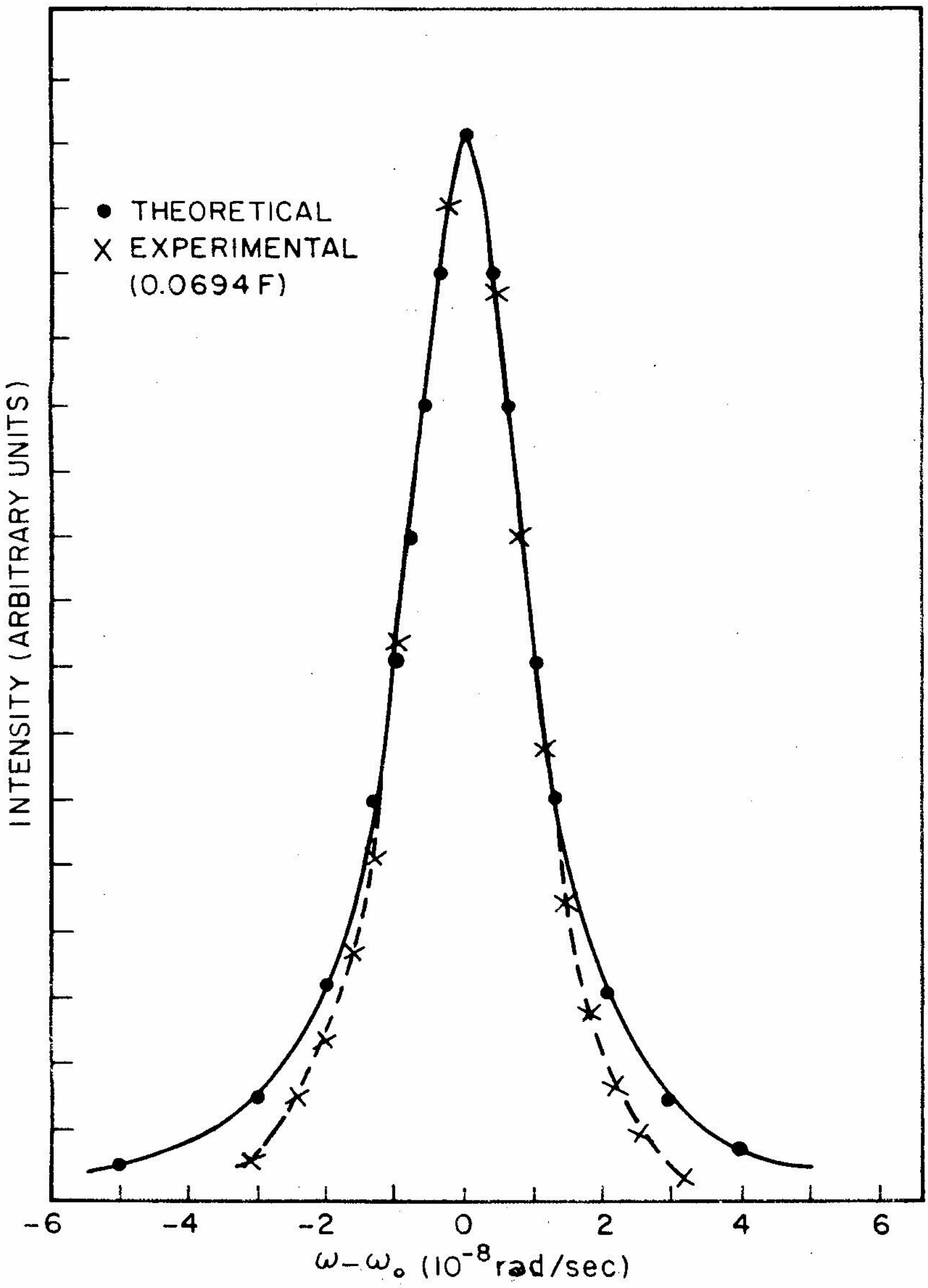
It is clear from equations 7 and 9 that if the HF splitting and T_2 are large enough so that G_B and G_C are small in the region of large G_A then equation 9 may be written

$$\left(\left(\frac{1}{T_2} + \frac{1}{\tau_A}\right) - i\Delta\omega_A\right) G_A = -i\omega_1 M_o/3$$

Solving this equation we find the width at half maximum intensity

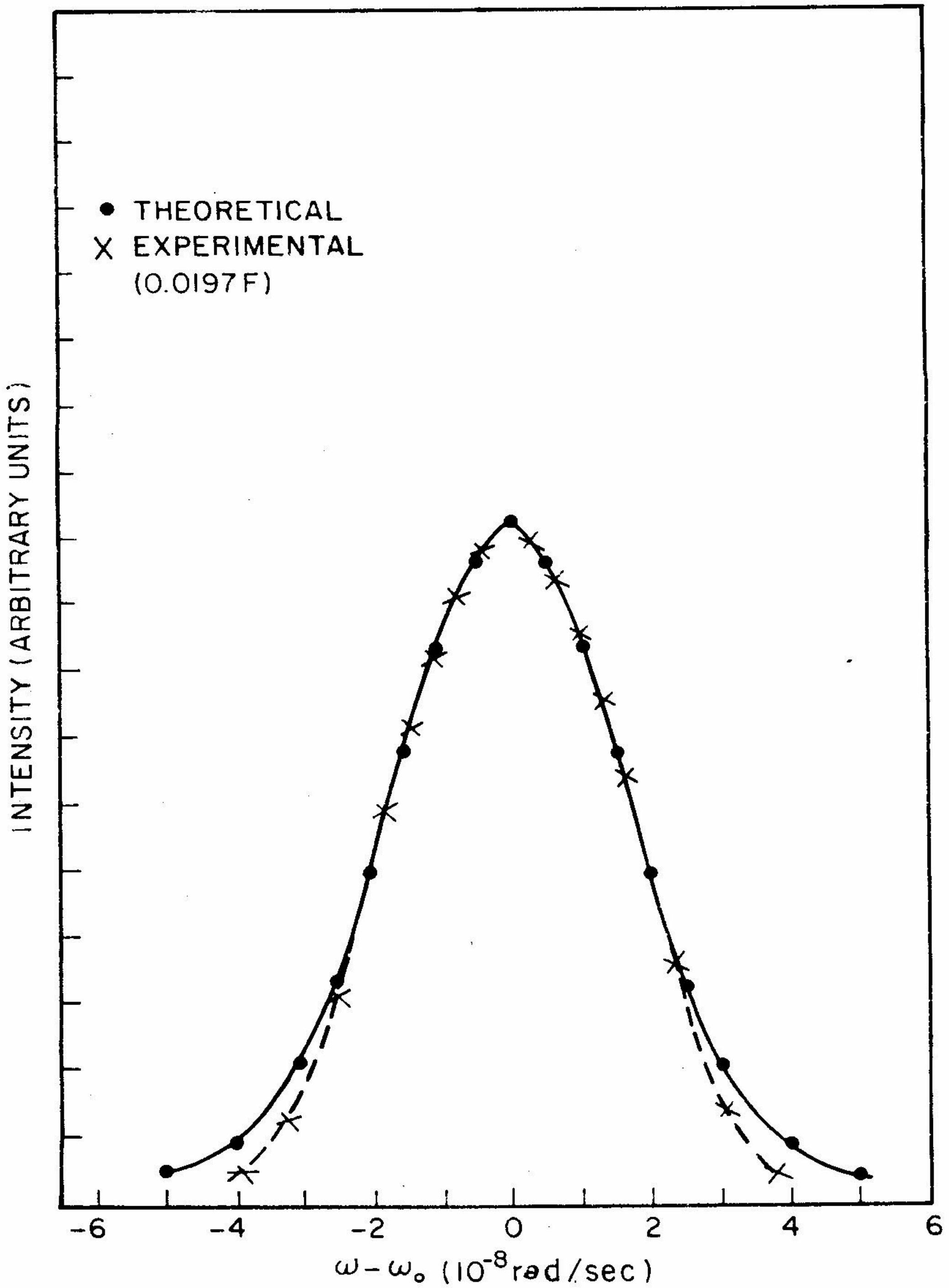
$$\Delta H = \frac{1}{\gamma\pi}\left(\frac{1}{T_2} + \frac{1}{\tau}\right.$$

Then knowing T_2 and ΔH, τ is easily calculated.



COMPARISON OF EXPERIMENTAL AND THEORETICAL LINE SHAPES FOR 0.0694 F DANO

Fig. 1



COMPARISON OF EXPERIMENTAL AND THEORETICAL LINE SHAPES FOR 0.0197 F DANO

Fig. 2

CONCLUSION

The modified Bloch equations were applied to a system of electron spins where exchange of electrons among three magnetic environments may occur. The agreement of the experimental EPR line shape with the theoretical line shape predicted by the modified Bloch equations was found to be good over the region of exchange lifetimes in which the line shape changes most dramatically with lifetime.

Thus from any line shape within in this region it would seem possible to calculate an exchange lifetime, and hence, the rate constant for electron exchange. However, the complexity and length of calculations involved in such a general approach encourages the investigator to take a few small pains to adjust exchange lifetimes to produce a small line broadening which then gives the exchange lifetime directly and simply.

REFERENCES

1. H. M. McConnell and H. E. Weaver, Jr., J. Chem. Phys., 25, 307 (1956).
2. C. R. Bruce, R. E. Norberg and S. I. Weissman, J. Chem. Phys., 24, 473 (1956).
3. R. L. Ward and S. I. Weissman, J. Am. Chem. Soc., 79, 2086 (1957).
4. H. S. Gutowsky, D. W. McCall, C. P. Schlicter, J. Chem. Phys., 21, 279 (1953).
5. H. S. Gutowsky and A. Saika, J. Chem. Phys., 21, 1688 (1953).
6. H. M. McConnell and S. B. Berger, J. Chem. Phys., 27, 230 (1957).
7. E. Grunwald, A. Lowenstein, S. Meiboom, J. Chem. Phys., 27, 630 (1957).
8. H. M. McConnell, J. Chem. Phys., 28, 430 (1958).
9. K. Meyer and H. Gottleib, Ber., 52, 1476 (1919).

PROPOSITIONS

PROPOSITION 1

Alger et al. have studied the electron magnetic resonance spectra of trapped radicals produced in n-propanol at 77°K by radiolysis and compared these spectra to those of radicals in photolyzed n-propanol-H_2O_2 mixtures (1). Identification of radicals was based on modification in the hyperfine structure introduced by deuterium substitution at selected positions in the molecules. Table I displays the isotopic variations on n-propanol.

Table I

$CH_3CH_2CD_2OH$	I
$CH_3CD_2CH_2OH$	II
$CD_3CH_2CH_2OH$	III
$CH_3CH_2CH_2OH$	IV

Systems IV and III, upon x-ray damage, showed quite similar hyperfine spectra of 5 lines symmetrically disposed with equal splittings of about 18 gauss. This result certainly indicates that there is no appreciable spin density on the γ carbons of the radicals derived from IV and III. X-ray damaged $CH_3CD_2CH_2OH$ (II) showed a broadened hyperfine doublet of 18 gauss splitting. This spectrum is undoubtedly due to the radical CH_3CD_2CHOH, the σ proton on the α carbon giving rise to the doublet which is broadened by the unresolvable, much smaller interactions of the unpaired spin with the π deuterons on the β carbon.

The authors argued that the radicals produced in IV and III are $CH_3CH_2\dot{C}HOH$ and $CD_3CH_2\dot{C}HOH$ and that the five line spectra are due to two equivalent protons and a third nonequivalent proton. For these radicals, each β or π proton was assigned a splitting of 18 gauss and the third, σ proton, a splitting of 36 gauss.

Considering the 18 gauss doublet from the σ proton in $CH_3CD_2\dot{C}HOH$ and the fact that σ proton isotropic interactions with unpaired spins in identified radicals run about 23 gauss or less (2), it seems much more reasonable to take one of the β protons as the nonequivalent proton.

It is recognized that

$$R(\vartheta) = B \cos^2\vartheta$$

serves well as an expression for the magnitude of the hyperfine splitting from a π proton (3). B is of the order of 45 gauss while ϑ is so defined that $\vartheta = 0$ corresponds to the "eclipsed" orientation of the π proton C-H bond relative to the π orbital symmetry axis. When $\vartheta = \frac{1}{2}\pi$, the π proton lies in the nodal plane of the π-electron spin distribution.

We suggest that in solid n-propanol rotation about the C_β-C_α bond is restricted to favor an orientation such that the π protons are magnetically nonequivalent as to give rise to hyperfine interactions of

36 and 18 gauss. The hyperfine structure of such π protons alone would be a symmetrically disposed quartet of equally intense lines with equal 18 gauss splittings. We then estimate that the frequency of rotation should be somewhat less than the frequency equivalent of 18 gauss, or about 50 Mc.

Fujimoto and Ingram have noted impairment of internal motion for the radical in isopropanol produced by hydroxy radicals as the temperature is lowered from 110°K to 77°K (4). Though Alger et al. state that the radical produced by radiolysis all disappear at 110°K, it might be profitable to raise the temperature gradually from 77°K to ascertain if the spectrum changes in structure before it disappears.

Irradiation of $CH_3CH_2CD_2OH$ (I) produces a rather poorly resolved, asymmetric quartet (Fig. 1), which the authors suggest is the superposition of a three line spectrum and a six line spectrum. It is clear from the observed spectrum that more than one radical species is present and that very likely one of the radical species contributes a spectrum with an odd number of lines.

If we argue the obvious, postulating the existence of $CH_3CH_2\dot{C}DOH$ and assuming nonequivalence of the π protons as in our picture of the radicals produced in III and IV, we would expect a quartet from the π protons broadened by an unresolvable interaction with the deuteron. This certainly explains the gross features of the observed spectrum for I.

We are tempted to further hypothesize that one of the other radical species present in damaged I is actually the same radical $CH_3CH_2\dot{C}DOH$ which is situated so that the two π protons are equivalent, either by rapid rotation or by localization in magnetically equivalent positions. For this happenstance, the radical would give rise to a triplet spectrum, which could explain the observed asymmetry in Figure 1.

On the other hand, the authors cite evidence that in the case of I the nonequivalence of hydrogen and deuterium makes hydrogen escape from a β or γ position competitive with deuterium escape from the α position. Figure 1 indicates the presence of small lines outside the main group. These small lines might well be the outer lines of a six line spectrum. The authors observe that the six line spectrum could be due to suitable interactions of 3, 4, or 5 hydrogens. Contrary to the statement given, 3 nonequivalent protons give 8 lines, not six. Two equivalent protons and a third nonequivalent proton may give six lines.

The radical $CH_3\dot{C}HCD_2OH$ could give rise to six lines for three equivalent protons (2 π and 1 σ) with splittings of 18 gauss each and a third π proton with a splitting of 36 gauss. Note the striking similarities of this model to those proposed for radicals in III and IV. Irradiation of the compound $CD_3CH_2CD_2OH$ might produce $CD_3\dot{C}HCD_2OH$ which would give a doublet spectrum instead of a sextet. In such a case the observed spectrum of this system should differ significantly from I and confirm the postulated damage at a β carbon.

In summary, we propose

(A) that the radicals produced in III and IV are $CH_3CH_2\dot{C}HOH$ and $CD_3CH_2\dot{C}HOH$ and that the nonequivalent proton giving rise to the 38 gauss hyperfine splitting is a β proton rather than the α proton;

(B) that in these radicals rotation about the $C_\beta - C_\alpha$ bond is restricted, causing the β protons to be nonequivalent;

(C) that careful efforts be made to discover if the impairment of internal motion of these radicals might be reduced at slightly higher temperatures;

(D) that the main species in irradiated $CH_3CH_2CD_2OH$(I) is $CH_3CH_2\dot{C}DOH$ and that the restricted rotation about the $C_\beta - C_\alpha$ bond results in nonequivalent β protons as proposed in (B);

(E) that another species in irradiated (I) is $CH_3\dot{C}HCD_2OH$ and that rotation about the $C_\gamma - C_\beta$ bond is restricted similarly as in the cases already mentioned; and

(F) that irradiation of $CD_3CH_2CD_2OH$ may produce $CD_3\dot{C}HCD_2OH$ and thus confirm the postulated damage at a β carbon.

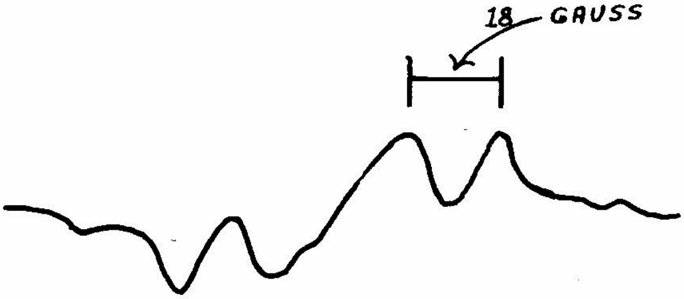


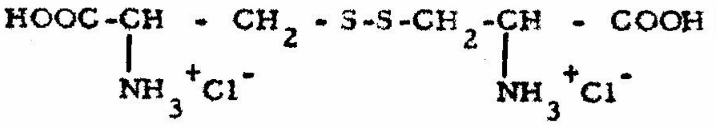
Fig. 1. Experimental spectrum of x-ray irradiated $CH_3CH_2CO_2OH$ (I)

REFERENCES

1. R. S. Alger, T. H. Anderson, L. A. Webb, J. Chem. Phys., 35, 49 (1961).
2. D. J. E. Ingram, Free Radicals, Butterworth Scientific Publications, 1958, p. 170.
3. C. Heller and H. M. McConnell, J. Chem. Phys., 32, 1535 (1960).
4. M. Fujimoto and D. J. E. Ingram, Trans. Faraday Soc., 54, 645 (1951).

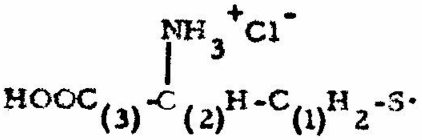
PROPOSITION 2

The electron magnetic resonance of a gamma irradiated single crystal of L-cystine dihydrochloride,



$$\underset{NH_3^+Cl^-}{HOOC\text{-}CH} - CH_2 - S\text{-}S\text{-}CH_2\text{-}\underset{NH_3^+Cl^-}{CH} - COOH \quad (I)$$

has been observed by Kurita and Gordy (1). The resonance pattern was found to be an isotropic doublet with a splitting of 9 gauss. The authors attribute the spectrum to the radical



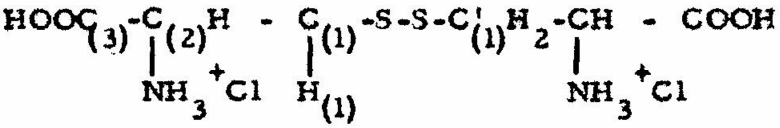
$$HOOC_{(3)}\text{-}\overset{NH_3^+Cl^-}{C_{(2)}}H\text{-}C_{(1)}H_2\text{-}S\cdot \qquad II$$

which is formed by the scission of the sulfur-sulfur bond in I. The anisotropy of the measured g factor indicates that the electron spin is largely localized in the non-bonding 3p orbital of the sulfur atom in II. The authors argue that the corresponding directions of the principal values of the g tensor determine to a good approximation the actual orientation of the 3p orbital as well as the direction of the $C_{(1)}$-S bond. Additional arguments are advanced to show that the actual nuclear configuration is one in which the sulfur has rotated about the $C_{(1)}$-$C_{(2)}$ bond and lies close to the NH_3^+ group. The π protons on $C_{(1)}$ must be so oriented that the unpaired spin on S interacts appreciably with only one proton, i.e., the other proton on $C_{(1)}$ lies very nearly in the nodal plane of the 3p orbital on the sulfur (2).

The rather small π proton hyperfine splitting is consistent with the 3.5 gauss splitting of the triplet observed for the electron magnetic resonance spectrum of the n-butoxy radical, $CH_3CH_2CH_2CH_2\dot{O}$ (3).

Berger has objected to II because scission of the S-S bond in I would produce two radicals I (4). His calculations show that the two unpaired spins located according to Kurita and Gordy should have a coupling of 120 gauss. Moreover, a reasonable amplitude of vibration (0.05 Å) of the C-S bonds should broaden each resonance line enough (6 gauss) to obscure the hyperfine doublet.

Berger proposes instead the model

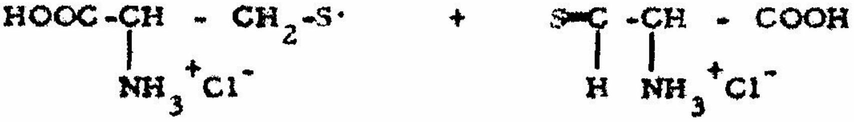


$$\mathrm{HOOC_{(3)}}-\underset{\mathrm{NH_3^+Cl}}{\underset{|}{\mathrm{C_{(2)}}}}\mathrm{H} - \underset{\mathrm{H_{(1)}}}{\underset{|}{\mathrm{C_{(1)}}}}\mathrm{-S-S-C'_{(1)}H_2}-\underset{\mathrm{NH_3^+Cl}}{\underset{|}{\mathrm{CH}}} - \mathrm{COOH} \qquad \mathrm{III}$$

attributing the doublet hyperfine structure to the proton $H_{(1)}$ (4). As the splitting from the σ proton in $\dot{C}H(COOH)_2$ varies from 11 to 33 gauss depending on the orientation (5), it follows that there must be considerable delocalization of the unpaired spin onto the sulfur atoms. Yet we observe no hyperfine interaction from the protons on $C'_{(1)}$. The fact that the electronegativities assigned to C and S are the same (2.5) leads to the expectation that the carbon should retain an appreciable spin density. Thus the doublet splitting should have an appreciable anisotropy.

Gordy's group has engaged in a wide ranging study of the electron magnetic resonance spectra of sulfur containing radicals (6). It has been observed that substitution on S has a marked effect on the spectra of irradiated powdered samples. Yet the resonance spectra of powdered cystine and powdered cysteine ($HOOC-CH(NH_2)CH_2SH$ after irradiation are very similar. It seems most reasonable that the same radical is present in both samples and that this radical must be $HOOCCH(NH_2)CH_2S\cdot$.

We propose that the actual effect of damage on I is the removal of a hydrogen atom together with the S-S bond scission to form the products



$$\mathrm{HOOC-}\underset{\substack{|\\ \mathrm{NH_3^+Cl^-}}}{\mathrm{CH}}\mathrm{-CH_2-S\cdot} \quad + \quad \underset{\substack{|\\ \mathrm{H}}}{\mathrm{S{=}C}}\mathrm{-}\underset{\substack{|\\ \mathrm{NH_3^+Cl^-}}}{\mathrm{CH}}\mathrm{-COOH}$$

Some support for this alternative mode of damage comes from the behavior of cystine systems in basic solutions. It has been shown that cystine can lose a proton by abstraction by a base, followed by scission of S-S bond (7), i.e.,

$$\begin{array}{lcl} \mathrm{RCH_2S-SR' + OH^-} & \longrightarrow & \overset{-}{\mathrm{RCH}}\mathrm{-SR' + H_2O} \\ & & \quad\downarrow \\ & & \mathrm{RCH{=}S + R'S^-} \end{array}$$

If the initial x-ray damage on a cysteine system is the loss of an α-hydrogen atom, followed by the S-S bond scission, it is possible that irradiation at 77°K would produce III alone. Upon standing or warming, III would decompose to give the thiyl radical II. The expected differences in the g factors and anisotropic behavior of the hyperfine spectra of II and III in a single crystal would serve to make such a mechanism easily discernible.

If the π protons in an $RCH_2S^{\cdot}$ radical were equivalent, the isotropic coupling constant for each could easily be as high as $R_o \cos^2 30^{\circ} = 12(3/4) = 9$ gauss. Presuming a unit spin density ($\rho_s = 1$) on S in $RCH_2S^{\cdot}$, a spin density $\rho_s = 0.22$ should give rise to proton splittings of about 2 gauss, instead of the 5.5 gauss observed. The 5.5 gauss value for $R_o = 12$ gauss implies $\rho_s = 0.60$. The latter value for ρ_s seems too high, the former too low.

If S^{33} and C^{13} substitution were made in the appropriate sulfur containing radicals, spectra analyses should give reliable values for the spin densities on the atoms in A. These values in turn would increase our scanty knowledge of R_o for such radicals and also allow for a more dispassionate appraisal of the merits of the intriguing proposal to calculate spin densities from g factors.

In summary, we conclude that Gordy's calculation of spin densities from the magnitude of the g factor of the free radical in irradiated thiodiglycolic acid gives results which are not consistent with hyperfine data obtained for sulfur containing and non sulfur containing free radicals.

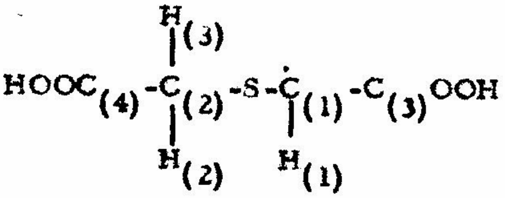
We propose that S^{33} and C^{13} substitution be made in the appropriate sulfur containing radicals. Spectra analyses should give reliable values for spin density distribution.

REFERENCES

1. Y. Kurita and W. Gordy, J. Chem. Phys., 34, 1285 (1961).
2. H. M. McConnell et al., J. Am. Chem. Soc., 82, 766 (1960).
3. M. H. L. Pryce, Proc. Phys. Soc. (London), 463, 25 (1950).
4. Y. Kurita and W. Gordy, J. Chem. Phys., 34, 282 (1961).
5. C. Hellwand and H. M. McConnell, J. Chem. Phys. 32, 1535 (1960).

PROPOSITION 3

The electron magnetic resonance spectrum of a gamma irradiated single crystal of thiodiglycolic acid has been observed by Kurita and Gordy (1). It seems most likely that the radical responsible is



$$HOOC_{(4)}\text{-}\underset{H_{(2)}}{\overset{H_{(3)}}{C}}{}_{(2)}\text{-S-}\underset{H_{(1)}}{\dot{C}}{}_{(1)}\text{-}C_{(3)}OOH$$

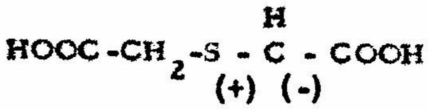
(A)

where $H_{(1)}$, a σ proton, gives rise to the observed anisotropic coupling constant (8-23 gauss) while $H_{(2)}$ and $H_{(3)}$ give rise to the two small, equal, nearly isotropic hyperfine interactions of 5.5 gauss.

The isotropic Fermi component of the hyperfine interaction of $H_{(1)}$ is calculated to be 15 gauss, significantly smaller than the 23 gauss interaction for the σ proton in $\dot{C}H(COOH)_2$ (2). Kurita and Gordy assume a unit spin density on an unsaturated carbon would produce a 25 gauss Fermi interaction with a σ proton and calculate the spin density on $C_{(1)}$ in A to be $15/25 = 0.60$. The spin densities on $H_{(2)}$ and $H_{(3)}$ are calculated to be $5.5/502 = 0.01$.

The small splitting from $H_{(1)}$ implies a delocalization of the unpaired spin onto the S atom. This is supported by the observation of a g factor anisotropy for A some ten times greater than in the case of $\dot{C}H(COOH)_2$ (2). The greater anisotropy is related to the magnitude of the spin orbit coupling for S, which is considerably greater than those for C, N, or O (1). An attempt is to be made to estimate the electron spin density on S in radical A from the anisotropy of the g factor.

To this end, it is argued that



$$\mathrm{HOOC{-}CH_2{-}\underset{(+)}{S}{-}\overset{H}{\underset{(-)}{C}}{-}COOH}$$

II

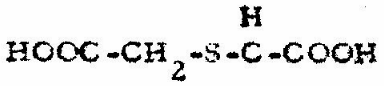
is a contributing structure to A. It is assumed that the unpaired spin in II is localized in a pure p orbital and that the other orbitals on S^+ are equivalent sp^2 hybrids. Four molecular configurations are considered, the obvious ground state configuration and three excited configurations in which the odd electron is assigned to either of the two σ bonds or the non-bonding sp^2 orbital. Pryce's formula for the calculation of the principal values of the g tensor has as parameters the spin orbital coupling constant for S and the various energy differences between the molecular configurations (1, 3). These latter parameters are taken to be those calculated for the radical $RCH_2S\cdot$ in irradiated cystine dihydrochloride (4). In this system, the unpaired spin is assumed to be localized on the S atom. The g tensor is known; the energy parameters are calculated from Pryce's formula. It is argued that the similarity between $RCH_2S\cdot$ and II is sufficient that the energy differences between corresponding molecular configurations are not affected to a first order approximation.

The values calculated for II are

$$g_{x'x'} = 2.0023$$
$$g_{y'y'} = 2.039$$
$$g_{z'z'} = 2.011$$

where x' is along the symmetry axis of the p orbital on S^+, z' is along the symmetry axis of the non-bonding sp^2 orbital of S^+, and y' is perpendicular to x' and z'.

For the other contributing structure, I,



$$HOOC-CH_2-S-\overset{H}{\dot{C}}-COOH$$

$\rho_s = 0$, the principal values of the g factor are expected to be very similar to those observed for $\dot{C}H(COOH)_2$, 2.0026, 2.0033, and 2.0035 (2). Here, the anisotropy is so small that the isotropic value 2.003 is taken as an appropriate reference.

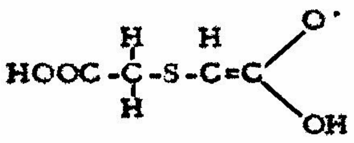
Kurita and Gordy assume that the spin density on the S in the actual structure is proportional to the deviation in g from the values expected for idealized structures I and II, or

$$\rho_s = \frac{(g_{y'y'})_{obs} - (g_{y'y'})_{\rho_s=0}}{(g_{y'y'})_{\rho_s=1} - (g_{y'y'})_{\rho_s=0}} \tag{1}$$

$$\rho_s = 0.22$$

taken to be the most reliable value.

Assuming the spin densities on $C_{(1)}$, S, $H_{(2)}$ and $H_{(3)}$ to have the same sign, a total spin density of 0.22 + 0.60 + 0.02 = 0.84 is now accounted for. The remaining 0.16 is assigned to the carbonyl oxygen, i.e., the structure III.



has a weight of 0.16, or 16%. The electron structure of the radical A is a hybrid of structures I, II, and III, with weights 0.60, 0.22, and 0.16, respectively. It is concluded that this method of calculating spin densities from g factor anisotropies has merit, despite the approximations involved.

Without commenting on the validity of the numerical approximations involved, it seems clear that the ad hoc equation 1 and Pryce's formula must and do give an answer of the right order of magnitude. Yet does a method necessarily have merit when a simple guess would give a similar answer, especially when no estimate of the reliability of the answer based on the method itself is offered or perhaps can be offered? Nor is the calculated value tested against certain obvious criteria.

Kurita and Gordy have assumed that in $\dot{C}H(COOH)_2$ the unpaired spin is localized 100% on the center carbon, i.e., there is no appreciable contribution of a structure analogous to III. Yet for the thiodiglycolic radical, there is invoked a considerable interaction with the carboxyl group. The reason for this assumption seems really to be a desire to explain away the discrepancy in the calculated value for ρ_s.

An accurate crystallographic analysis of the crystal structure might show that the $C_{(1)}$-$C_{(3)}$ separation in A is for some reason appreciably shorter than the corresponding distance in simple hydrocarbon dicarboxylic acids. Then one would expect a greater contribution of III.

We recognize that the magnitude, $R(\vartheta)$, of the interaction of a π proton with an unpaired spin is well described by the relation

$$R(\vartheta) = R_o \cos^2 \vartheta$$

where R_o is a constant and ϑ is defined so that $\vartheta = 0$ corresponds to the eclipsed orientation of the π proton C-H bond relative to the π orbital symmetry axis. When $\vartheta = \pi/2$, the proton lies in the nodal plane of the π electron spin distribution (5).

Kurita and Gordy have put great faith in the identification of the radical in irradiated cystine dihydrochloride as of the type $RCH_2S\cdot$ (4). The hyperfine pattern is an isotropic doublet of 9 gauss splitting which is attributed to the interaction of the unpaired spin on S with only one proton, the other proton lying too near to the nodal plane of the spin distribution to give a resolvable splitting. As the line widths of the doublet seem to be about 3 gauss and since R_o will not be very large, there is more latitude allowed for the π proton orientation in $RCH_2S\cdot$ than is implied by Kurita and Gordy. The authors argue that $R_o = 9$ gauss, $R_1(\vartheta) = 9$ gauss, and $R_2(\vartheta) = 0.2$ gauss. However, from equation 2, we may argue that if $R_1(\vartheta) = 9$ gauss and $R_2(\vartheta) = 0$ gauss, then $R_o = 12$ gauss.

In summary, we propose

(A) that room temperature irradiation of L-cystine dihydrochloride results in the loss of a methylene hydrogen atom and the scission of the S-S bond to give a thiyl radical and a thioaldehyde, and

(B) that low temperature irradiation may result first in the loss of a hydrogen atom and, upon warming, is followed by the S-S bond scission to give the thiyl radical. Such a mechanism should easily be confirmed by analysis of magnetic resonance spectra.

REFERENCES

1. Y. Kurita and W. Gordy, J. Chem. Physics, 34, 282 (1961).
2. C. Heller and H. M. McConnell, J. Chem. Physics, 32, 1535 (1960).
3. L. H. Piette and W. C. Landgraf, ibid., 32, 1106 (1960).
4. S. A. Berger, Propositions, Thesis, 1961, California Institute of Technology.
5. H. M. McConnell et al., J. Am. Chem. Soc., 82, 766 (1960).
6. H. Shields and W. Gordy, J. Phys. Chem., 62, 789 (1958).
7. A. Parker and N. Kharasch, Chem. Rev., 59, 597 (1960).

PROPOSITION 4

M. C. R. Symons has bent considerable effort to relate hyperconjugation in alkyl radicals with the measured hyperfine splittings in the electron magnetic resonance spectra of alkyl radicals in liquid solutions (1, 2).

The theory of hyperconjugation predicts a real delocalization of electrons such that there should be a reduction in the spin density, ρ_c, on the unsaturated carbon, proportional to the degree of hyperconjugation. Theoretical calculations (3) and linear correlations (2) have been applied to the series of radicals, methyl, ethyl, isopropyl, and t-butyl and indicate a considerable decrease in ρ_c with methyl substitution. Yet more accurate results show that ρ_c for this series, as estimated from coupling constants for α protons, is affected but slightly by methyl substitution (4). Symons concludes that hyperconjugation is negligible in these radicals or that some other effect is operative which increases the coupling for α protons upon methyl substitution to counteract the decrease expected from hyperconjugation.

It would seem to be well established that α protons can be used as a measure of ρ_c through the relation

$$a_{\alpha H} = Q_\alpha \rho_c \tag{1}$$

where $a_{\alpha H}$ is the measured hyperfine splitting arising from an α proton directly bonded to a carbon bearing unpaired spin density in a 2p orbital (5). Q_α is a constant which seems to be about -23 gauss. Noting that the isotropic hyperfine splitting for hydrogen atoms is about 502 gauss, it is possible to estimate the analogous constant of proportionality, Q_β, for the hyperfine splitting, $a_{\beta H}$, of β protons, by the equation

$$a_{\beta H} = Q_\beta/(1 + Na_{\beta H}/502) \tag{2}$$

where N is the number of β protons. Values of Q_β calculated from 2 are given in Table I, together with corresponding values for ρ_c, estimated from the relationship

$$\rho_c = 1 - N a_{\beta H}/502 \tag{3}$$

On the other hand, using Q_β calculated from equation 2 and the results for the ethyl radical, $a_{\beta H}$ can be calculated for the remaining radicals. Table I includes these calculations for $a_{\beta H}$ plus values of $a_{\alpha H}$ calculated from 1.

TABLE I

	$a_{\alpha H}$	$a_{\beta H}$	Q_β	ρ_c	$(a_{\alpha H})_{calc.}$	$(a_{\beta H})_{calc.}$
$\cdot CH_3$	-23.0	-	-	1.0	-23	$(Q_\beta = 31.6)$
$Me\dot{C}H_2$	-22.4	26.9	31.6	0.84	-19.3	26.9
$(Me)_2\dot{C}H$	-22.2	24.6	34.8	0.71	-16.3	23.0
$(Me)_3\dot{C}$	-	22.7	38.2	0.595	-	20.2

The internal agreement is not heartening to Symons, who misses an opportunity to resolve this anomaly.

For $\cdot CH_3$, with $a_{\alpha H} = -23$ gauss, we calculate easily that there is associated with each proton a negative spin density of 0.046, or for the three protons a total negative spin density of 0.138. If we assume a general, simple applicability for the conservation of spin, i.e., $\sum_i \rho_{ii} = 1$, summed over all the atoms in the radical, we conclude that the spin density, ρ_c, is 1.138. From equation 1, it follows that $Q_\alpha = -20.2$ gauss.

Using this value for Q_α, we calculate that for $MeCH_2$, $\rho_c = 1.109$. The spin density on each α proton is -0.045, or a total of -0.090 on the α protons. With the calculated value for ρ_c and the measured $a_{\beta H}$, Q_β is found to be 24.2 gauss. The spin density on each β proton is 0.0536. Assuming spin density conservation,

$$1.00 = \rho_c + 2\rho_{\alpha H} + 3\rho_{\beta H} + \rho_{\beta c} \qquad (4)$$

we calculate that $\rho_{\beta c}$, the spin density associated with the methyl carbon, is -0.18.

McLachlan in a valence bond treatment to calculate the expected hyperfine splitting from β protons in an $MeC\cdot$ fragment determined that the methyl carbon should bear a spin density $\rho_{\beta c} = -0.16$ (6).

In a similar manner for $(Me)_2\overset{\circ}{C}H$, we calculate that $\rho_c = 1.10$ and $Q_\beta = 22.4$ gauss. From the analogous equation to 4, it follows that the total spin density associated with the methyl carbons is -0.36, or again -0.18 per methyl carbon.

For $(Me)_3\dot{C}$, we may assume a total $\Sigma \rho_{\beta c} = -0.54$ and calculate that the β protons bear a total spin density of 0.505. Conservation of spin density shows $\rho_c = 0.965$. Q_β is then calculated to be 23.5 gauss. If we presume a proportionality between ρ_c and $\rho_{\beta c}$,

$$\rho_{\beta c} = \mathcal{X} \rho_c \qquad (5)$$

we calculate $\mathcal{X} = -0.164$ from the data on $Me\dot{C}H_2$. For $(Me)_3\dot{C}$,

$$1.00 = 3\mathcal{X}\rho_c + \rho_c + 9\,\rho_{\beta H} \qquad (6)$$

Since $\rho_{\beta H}$ is known, ρ_c is calculated to be 0.974, $\rho_{\beta c} = -0.16$, and $Q_\beta = 24.3$ gauss. Table II summarizes these calculations.

TABLE II

	$a_{\alpha H}$	$a_{\beta H}$	Q_α	ρ_c	Q_β	$\Sigma \rho_{\beta c}$
$\cdot CH_3$	-23.0		-20.2	1.137	-	
$Me\dot{C}H_2$	-22.4	26.9	-20.2	1.109	24.2	-0.18
$(Me)_2\dot{C}H$	-22.2	24.6	-20.2	1.10	22.4	-0.36
$(Me)_3\dot{C}$	-	22.7	-	0.974	24.3	-0.48

We observe rather good internal consistency. It appears that the anomaly shown in Table I is resolved merely by considering negative spin density to be just as real as positive spin density. It is unfortunate that C^{13} splittings are not known, or at least not published, for ethyl, isopropyl, and t-butyl radicals.

REFERENCES

1. M. C. R. Symons, Tetrahedron, 18, 333 (1962).

2. M. C. R. Symons, J. Chem. Soc., 277 (1959).

3. D. B. Chesnut, J. Chem. Physics, 29, 43 (1953).

4. R. W. Fessenden, Quarterly Report of Mellon Institute (April June) (1961).

5. H. M. McConnell et al., J. Am. Chem. Soc., 82, 766 (1960).

6. A. McLachlan, Molecular Physics, 1, 233 (1958).

PROPOSITION 5

Decarbonylation of certain aliphatic aldehydes proceeds by a free radical chain mechanism which can be initiated by di-t-butyl peroxide (1) or by ultraviolet light (2). Addition of small quantities of benzyl mercaptan leads to extensive, rapid decarbonylation of branched aldehydes (3). The peroxide catalyzed decarbonylation is described by equations 1-3.

$$I\cdot + RCHO \longrightarrow IH + R\dot{C}{=}O \tag{1}$$

$$R\dot{C}{=}O \longrightarrow \dot{R} + CO \tag{2}$$

$$R\cdot + RCHO \longrightarrow RH + R\dot{C}{=}O \tag{3}$$

$I\cdot$ is a free radical initiator produced thermally. Addition of R'SH introduces the following relevant reactions,

$$I\cdot + R'SH \longrightarrow IH + R'S\cdot \tag{4}$$

$$R'S + RCHO \longrightarrow R'SH + R\dot{C}{=}O \tag{5}$$

$$R\cdot + R'SH \longrightarrow RH + R'S\cdot \tag{6}$$

Surprisingly, R'SH reacts rapidly with relatively inert hydrocarbon radicals; yet R'S is a more efficient hydrogen atom abstractor than R'.

Cohen et al. have studied the effect of mercaptans and disulfides on the rate of ultraviolet induced decarbonylation of alkyl aldehydes (4). α-ethyl hexanal under UV radiation undergoes rather slow decarbonylation. The addition of a few mole percent of benzyl disulfide ($\phi CH_2SSCH_2\phi$) increases the maximum rate of CO evolution some tenfold. As there is considerable evidence that disulfides are photolyzed to form thiyl radicals (5), it seems reasonable to presume that the increase in the decarbonylation rate of α-ethyl hexanal upon addition of dibenzyl sulfide is due to production of the thiyl radical, which efficiently attacks the aldehyde by the chain reaction 5 and 6.

It was also observed that addition of a few mole percent of benzyl mercaptan (no disulfide) increased the decarbonylation rate some fifty fold. The authors express some doubt then about the relative importance of the photolysis of the disulfide to the initiation of decarbonylation. It is implied that the initial absorption of light is by the aldehyde and that the reaction

$$\mathrm{RCHO(excited)} + \mathrm{R'SH} \longrightarrow \mathrm{R\dot{C}HOH} + \mathrm{R'S\cdot} \qquad (7)$$

makes more efficient use of the incident light energy and furnishes R'S, which propagates a rapid chain reaction. It is known that benzophenone absorbs light and transfers energy to anthracene (6). The excited aldehyde may transfer energy to R'SH rather than react chemically as indicated by equation 7.

A change in viewpoint on this problem may be enlightening. Instead of concentrating on the disulfide and the mercaptan as agents for accelerating decarbonylation rates, we may inquire about the role of the aldehyde as a photosensitizer for the decomposition of the disulfide and the mercaptan.

Walling and Rabinowitz have studied the photolysis of isobutyl disulfide in cumene and have deduced that the solvent is acting as a photosensitizer, transferring absorbed energy to the disulfide (7). The latter dissociates to form thiyl radicals, which, in turn, react with cumene to form the thiol. In order to account for the approach to a steady state mercaptan (thiol) concentration, the authors conclude that the mercaptan is also undergoing photolysis.

It is argued that the quoted molecular extinction coefficient, $\epsilon = 362$ at 2537 Å, for the disulfide is at least an order of magnitude too low to account for the rate of conversion to the mercaptan.

It is observed that the percentage conversion of disulfide to mercaptan approaches 35%, independent of the initial disulfide concentration and the light intensity. As the disulfide molecule presumably gives two thiyl radicals, it would seem that, at steady state conditions, the disulfide and mercaptan concentrations are roughly equal and that both species are making similarly efficient use of the incident light energy. However, Walling and Rabinowitz apparently imply that the mercaptan is undergoing direct photolysis. But since they have argued that direct photolysis of the disulfide is not adquate to explain the rate of conversion of the disulfide, it is difficult to believe that direct photolysis of the mercaptan with a quoted molecular extinction coefficient of 35, a factor of 10 smaller than that for the disulfide, is occurring at the necessary rate. It would seem more reasonable to suppose that the solvent is supplying energy to both the disulfide and the mercaptan.

It is pertinent to suggest that the relative efficiencies of benzyl mercaptan and dibenzyl sulfide in accelerating decarbonylation of aldehydes may be understood in the light of Walling and Rabinowitz type experiments in various solvents. Cohen's results show the mercaptan to be considerably more efficient than the disulfide in promoting decarbonylation while Walling's results suggest that the relative efficiences would be expected to be similar.

We note that Cohen is able to follow the extent of reaction by observing the rate of evolution of CO, in effect, a running analysis. Walling follows the conversion of disulfide by withdrawing samples from the irradiated system and analyzing at a latter time.

We wonder about the chemical reactions the mercaptan and disulfide undergo after receiving energy from the solvent. It seems reasonable that the mercaptan dissociates to form the thiyl radical. A disulfide molecule may dissociate to form two thiyl radicals or perhaps it may lose a hydrogen atom to form $\phi CH_2SS\dot{C}H\phi$, which more slowly dissociates to form $\phi CH_2S\cdot$ and ϕCHS. Such a mechanism would act to slow down the release of thiyl into the system; yet the most likely fate of the thiyl is the formation of the mercaptan. The time lag in analysis for mercaptan is probably sufficient that such a mechanism is not detectable in Walling's work. However, this same mechanism may account for the difference in efficiency of mercaptan and disulfide in Cohen's work.

In Walling's work, a steady state condition is approached and held, implying a rather efficient recycling of the mercaptan, while in Cohen's experiments, the maximum rate of CO evolution may be reached more quickly but obviously tapers off, implying that chain termination reactions are more efficient here.

Electron magnetic resonance studies may well be useful in this problem. Under irradiation at 77°K, $\phi CH_2S\dot{C}H\phi$ may be stable enough to be detected. Upon warming it would dissociate into the thiyl. The differences in hyperfine spectra between the two radicals should be sufficient to follow such a change. However, the thiyl radical may be so reactive that it may not be detectable. It might be well to study the photolysis of the benzyl disulfide in a solvent not noted for its hydrogen donating properties and in this fashion make the detection of the thiyl radical more likely. It may also be possible to detect $R\dot{C}HOH$ if reaction 7 actually occurs and also to detect $R\cdot$ from equation 2. The hyperfine structure in the spectra for these last two radicals would be significantly different.

We conclude that we have considered an area of research which apparently lacks some "intracommunication" but holds promise of fruitful results.

To summarize, we are arguing that the acceleration by disulfide or mercaptan of the ultraviolet light induced decarbonylation of aliphatic aldehydes may be best understood in terms of the solvent aldehyde absorbing incident UV light energy, efficiently transferring it to the disulfide or mercaptan, and the resulting thiyl radicals then attacking the aldehyde.

We propose that the difference in the relative efficiencies of disulfide and mercaptan in accelerating decarbonylation of aliphatic aldehydes may be due to the possibility that the disulfide does not directly decompose to thiyl radicals but rather to an intermediate radical of the form $RCH_2SS\dot{C}HR'$ which in turn decomposes to form $RCH_2S\cdot$ and $R'CHS$. Such a mechanism might be verified by electron magnetic resonance studies on disulfides made to decompose at low temperatures under appropriate conditions.

Electron magnetic resonance studies may also give information about the possibility that the aldehyde having absorbed light energy reacts directly with the disulfide or mercaptan rather than transferring the energy to these substances.

REFERENCES

1. D. Y. Curtin and M. J. Hurwitz, J. Am. Chem. Soc., 74, 5331 (1952).
2. G. K. Rollefson and D. C. Grahame, J. Chem. Phys., 7, 775 (1939).
3. E. F. P. Harris and W. A. Waters, Nature, London, 170, 212 (1952).
4. S. G. Cohen, J. D. Berman, and S. Orman, Tetrahedron Letters, 2, 43 (1962).
5. M. S. Kharasch, W. Nudenberg, and T. H. Meltzer, J. Org. Chem., 18, 1233 (1953).
6. J. B. Farmer et al., J. Chem. Phys., 34, 1058 (1961).
7. C. Walling and R. Rabinowitz, J. Am. Chem. Soc., 81, 1137 (1959).