# Electron Spin Resonance Study of Radical Fragmentation from Positive Primaries in Irradiated Single Crystals of Unsaturated Carboxylic Acids

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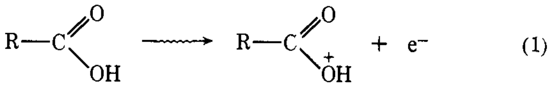
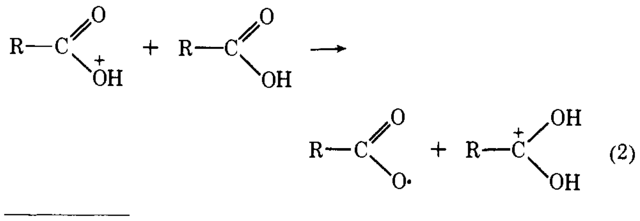
**Abstract:** The fragmentation of the carboxyl radical formed in an irradiated single crystal of potassium hydrogen maleate has been studied by electron spin resonance. Previously we have found that the crystal irradiated at 77°K in the dark gives the symmetrical $\sigma$ radical formed by removal of the acidic proton, where the unpaired electron occupies the antibonding orbital between the two in-plane p orbitals of the two ring oxygen atoms. In the present study, it has been found that this symmetrical radical converts into the asymmetric radical, where the unpaired electron is located in one of the two COO groups when the irradiated crystal is exposed to visible light at 77°K. Furthermore, prolonged exposure to visible light gives rise to the fragmentation of this radical, forming the $CO_2^-$ ion through an intermediate radical which is assumed to be a vinyl-type radical. Since the symmetrical $\sigma$ radical mentioned above is believed to be formed by the ejection of an electron followed by proton transfer to the neighboring molecule, our results indicate the fragmentation path from the positive primaries in irradiated crystals of unsaturated carboxylic acids.

Recent progress in studies on irradiated single crystals of a number of organic compounds has shown that the main primary species induced by ionized radiations are a positive hole produced by the ejection of an electron and a molecular anion produced by the capture of the ejected electron. Other species often stabilized in the crystals are believed to be secondary products originating from such positive and negative primaries. Studies of the fate of these primary species may be important for elucidating the radiation-damage process in the crystals.

Recently we have found that irradiated single crystals of unsaturated carboxylic acids such as maleic acid,[2] potassium hydrogen maleate,[3a] sodium hydrogen maleate,[3b] potassium hydrogen fumarate,[4] and acetylenedicarboxylic acid[5] give carboxyl radicals (RC(=O)O·) formed by removal of the acidic proton, where the unpaired electron occupies the in-plane p orbital of the carboxyl oxygen, resulting in $\sigma$-electron radicals.[2] The carboxyl radicals are assumed to be formed from the positive primaries[6] by transferring the acidic proton to the neighboring molecule.[2,3a]



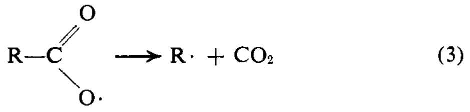
$$\mathrm{R{-}C({=}O)OH} \longrightarrow \mathrm{R{-}C({=}O)\overset{+}{O}H} + e^- \qquad (1)$$



$$\mathrm{R{-}C({=}O)\overset{+}{O}H} + \mathrm{R{-}C({=}O)OH} \longrightarrow \mathrm{R{-}C({=}O)O\cdot} + \mathrm{R{-}\overset{+}{C}(OH)OH} \qquad (2)$$

Recently Box, *et al.*, also found a similar radical in irradiated succinic acid and suggested that it could be formed from the positive primaries.[7]

According to our previous study on irradiated maleic acid,[2] it was found that the carboxyl radical fragments into the vinyl-type radical by a loss of $CO_2$ molecule



$$\mathrm{R{-}C({=}O)O\cdot} \longrightarrow \mathrm{R\cdot} + \mathrm{CO_2} \qquad (3)$$

where R is HOOC—CH=CH. A similar process has been suggested by Schwartz, Hanna, and Bales,[8] and more recently by Moulton and Cernansky[9] in irradiated saturated carboxylic acids, although no experimental evidence was presented.

From these results the radical fragmentation path from the positive primaries became fairly clear. On the other hand, McCalley and Kwiram[10,11] have recently studied the fragmentation path from negative primaries in connection with an assignment of the mysterious "single-line" spectrum often observed in irradiated carboxylic acids.[8] Schwartz, *et al.*,[8] have proposed that the single-line spectrum observed in irradiated succinic acid is attributable to the $CO_2^-$ ion radical because of the similarity of its $g$ tensor elements to the literature values for $CO_2^-$.[12] However, McCalley and Kwiram[11] have argued against this interpretation based on their observation of the $^{13}C$ hyperfine couplings in irradiated malonic acid[10] and have reassigned this

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(2) M. Iwasaki, B. Eda, and K. Toriyama, *J. Amer. Chem. Soc.*, **92**, 3211 (1970).

(3) (a) K. Toriyama and M. Iwasaki, *J. Chem. Phys.*, **55**, 2181 (1971); (b) K. Toriyama, H. Muto, and M. Iwasaki, *ibid.*, **55**, 1885 (1971).

(4) K. Minakata, K. Toriyama, and M. Iwasaki, Abstracts, 13th Symposium on Radiation Chemistry, Tokyo, Japan, 1970, p 95.

(5) H. Muto, K. Toriyama, and M. Iwasaki, in ref 5, p 92.

(6) In ionic salts, the species formed by the ejection of an electron might be thought to have no positive formal charge. However, the term "positive primary" will be used regardless of the formal charge because the charge balance always requires the formation of the "negative primary" as a counterion.

(7) H. C. Box, H. G. Freund, K. T. Lilga, and E. E. Budzinski, *J. Phys. Chem.*, 74, 40 (1970).

(8) R. N. Schwartz, M. W. Hanna, and B. L. Bales, *J. Chem. Phys.*, 51, 4336 (1969).

(9) G. C. Moulton and B. Cernansky, *ibid.*, **53**, 3022 (1970).

(10) R. C. McCalley and A. L. Kwiram, *J. Amer. Chem. Soc.*, **92**, 1441 (1970).

(11) R. C. McCalley and A. L. Kwiram, *J. Chem. Phys.*, **53**, 2541 (1970).

(12) D. W. Ovenall and D. H. Whiffen, *Mol. Phys.*, 4, 135 (1961).

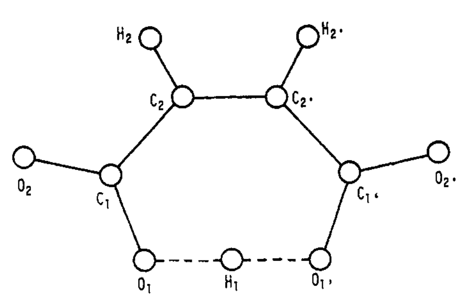
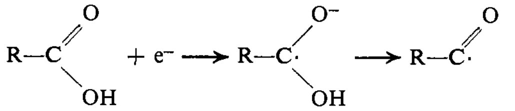


Figure 1. Molecular structure of the hydrogen maleate ion and the atomic numbering system adopted in this paper.

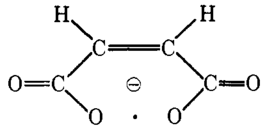
single-line species to the acyl radical formed by C–O bond scission from the negative primary.

 (4)

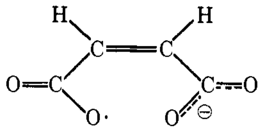
$$\mathrm{R{-}C(=O)OH} + e^- \longrightarrow \mathrm{R{-}\dot{C}(O^-)OH} \longrightarrow \mathrm{R{-}\dot{C}{=}O} \quad (4)$$

It seems that the long history of the controversy about this single-line spectrum has terminated with their conclusive experimental evidence. However, one can still expect to find the $CO_2^-$ ion in irradiated carboxylic acids if ionic salts are used, because radiolysis of the carboxylic acids is known to produce $CO_2$, so decarboxylation of carboxylic acid salts might produce $CO_2^-$ ions. There may exist a significant difference between neutral molecular systems and ionic salt systems.

During the course of our studies on irradiated single crystals of potassium hydrogen maleate, we have found that a single-line spectrum having $g$ tensor elements similar to those of a $CO_2^-$ ion or an acyl radical appears when the crystal is exposed to visible light at 77°K after irradiation at 77°K. The single-line species in our case was found to be formed from the carboxyl radical, and it seems to be attributable to the $CO_2^-$ ion. As previously reported,[3a] potassium hydrogen maleate irradiated at 77°K gives the symmetrical $\sigma$ radical T by removal of the acidic proton, where the unpaired electron occupies the antibonding orbital between the two in-plane p orbitals of the ring oxygen atoms.[13] Since radical T is believed to be formed by the ejection of an electron followed by proton transfer to the neighboring molecule, T is assumed to originate from the positive primary. In the present work, it has been found that radical T converts into the asymmetrical $\sigma$ radical D by exposing the crystal to visible light, where the unpaired electron is located in the in-plane p orbital of one of the two COO groups. Prolonged exposure to visible light led to fragmentation into $CO_2^-$ from radical D.



T



D

Our results indicate that the $CO_2^-$ ion could be formed by fragmentation from positive primaries in accord with a mechanism previously proposed by the authors.[2] The results described in this paper may provide some information for the general scheme of the fragmentation path from positive primaries in irradiated crystals of unsaturated dicarboxylic acids, where a process somewhat different from the case of saturated dicarboxylic acid should be involved.

## Experimental Section

Single crystals of potassium hydrogen maleate and its deuterium compound, in which the acidic proton is replaced by a deuteron, were grown from aqueous and heavy water solutions, respectively, by slow evaporation at room temperature. The single crystals obtained have typical orthorhombic symmetry; the crystallographic axes were identified by taking X-ray diffraction oscillation photographs. The crystal structure was determined by Darlow and Cochran.[14] The crystal belongs to space group *Pbcm*, with cell dimensions $a = 4.578$, $b = 7.791$, $c = 15.953$ Å. The hydrogen maleate ion possesses a mirror plane perpendicular to the C=C bond, due to a symmetrical intramolecular hydrogen bond (see Figure 1).

Single crystals were irradiated at 77°K in the dark by $^{60}$Co $\gamma$ rays or X-rays operated at 40 kV and 40 mA. Subsequent light exposure was made using a 300-W tungsten lamp at a distance of 20 cm through the window attached to the esr sample cavity. The esr spectra were measured at 77°K with a Japan Electron Optics Model JES-3BS spectrometer operated at 9.4 GHz. The spectra were recorded as second-derivative representations with 80-Hz and 100-kHz double modulation. The signal of $Mn^{2+}$ in ZnS or DPPH was used as a marker for the magnetic field and a standard for the intensity measurements. The angular dependence of the spectra was measured at 2–10° intervals by rotating the crystals about the $a$, $b$, and $c$ axes.

## Results

Figure 2a shows the esr spectrum of a single crystal of potassium hydrogen maleate irradiated at 77°K in the dark and annealed at Dry Ice temperature for 5 min, the magnetic field being applied along the $a$ axis with microwave power of 0.85 mW. The sharp three-line spectrum at the center has an intensity ratio of 1:2:1 with the nearly isotropic hyperfine separation of about 5 G. The radical responsible for this spectrum was assigned as radical T, as already described in the previous paper.[3a] Although T[15] is fairly stable at Dry Ice temperature, it was found that exposure to visible light at 77°K gives rise to quick decay, with the appearance of a new signal which is due to D. Figure 2b shows the spectrum measured at 77°K after exposure to visible light for 2 min at 77°K. Signal D exhibits a large positive $g$ shift[16]

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[13] In earlier work on a single crystal of potassium hydrogen maleate irradiated at room temperature [H. C. Heller and T. Cole, *J. Amer. Chem. Soc.*, 84, 4448 (1962); M. Iwasaki and K. Itoh, *Bull. Chem. Soc. Jap.*, 37, 44 (1964)], it was reported that a similar species is formed by the removal of the acidic proton at room temperature. However, in this stable radical the unpaired electron occupies the delocalized $\pi$ orbital. The difference between this radical and T was discussed in ref 3a. The $\pi$-electron radical seems to originate from the negative primary.

[14] S. Darlow and W. Cochran, *Acta Crystallogr.*, 14, 1250 (1961).

[15] Both the radical and its spectrum are represented by the same symbol in this paper.

[16] Although signal D has a similar $g$ tensor to that of the transient single-line species "O" described in ref 3a, D is different from O in hyperfine structure. In addition, the conditions for their appearance and their stability are also different. Since both signals D and O can be observed simultaneously under some conditions, it is evident that they are due to different species. However, we have no exact knowledge about the difference in radical structure between the two.

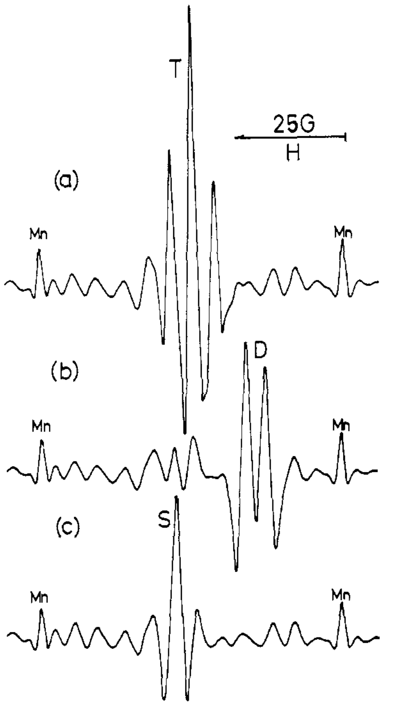


Figure 2. Esr spectra of a single crystal of potassium hydrogen maleate irradiated at 77°K in the dark. The magnetic field is applied along the *a* axis: (a) after annealing at Dry Ice temperature for 5 min, (b) after subsequent exposure to visible light for 2 min at 77°K, (c) after prolonged exposure for 20 min to visible light at 77°K. Mn indicates the signal of $Mn^{2+}$ in ZnS.

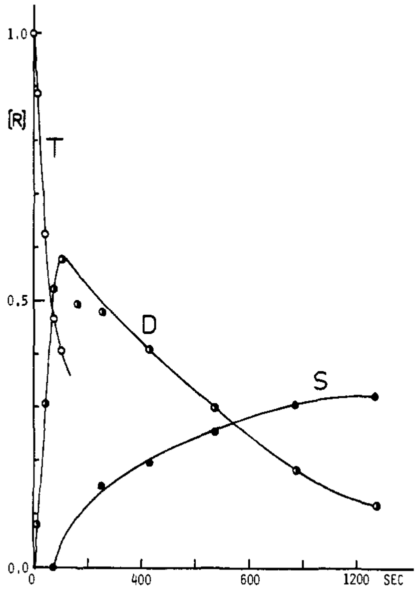


Figure 3. Change of the relative intensities of signals T, D, and S during the visible light exposure. The ordinate is the relative intensity and the abscissa is the exposure time in seconds.

with a two-line hyperfine structure, the separation of which is anisotropic and ranges from 3 to 5 G. This hyperfine structure was not altered by substitution of a deuteron for the acidic proton, indicating the origin to be the vinylene proton.

When visible light exposure is continued, signal D gradually disappears with the appearance of a new single-line spectrum (S) which is attributable to a $CO_2^-$ ion. Figure 2c is the spectrum measured at 77°K after the prolonged exposure to visible light for about 20 min. Signal S exhibits a large negative *g* shift in contrast to the positive shifts of signals T and D.

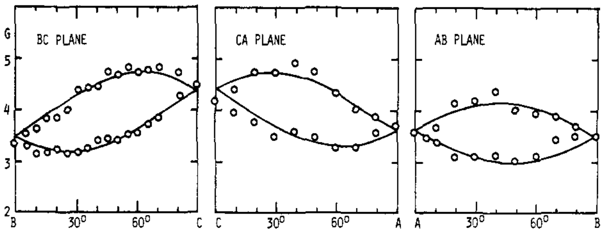


Figure 4. Angular dependence of the hyperfine splittings for the carboxyl radical produced by visible light exposure of an irradiated single crystal of potassium hydrogen maleate.

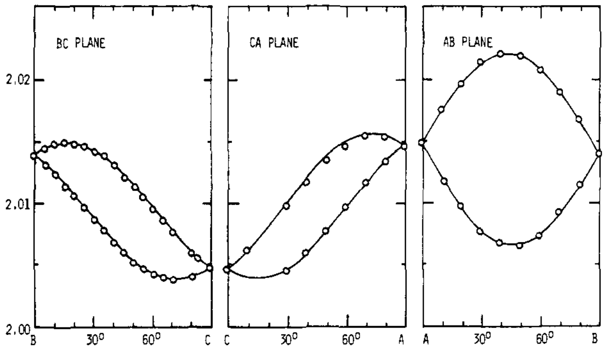


Figure 5. Angular dependence of the *g* values for the carboxyl radical produced by visible light exposure of an irradiated single crystal of potassium hydrogen maleate.

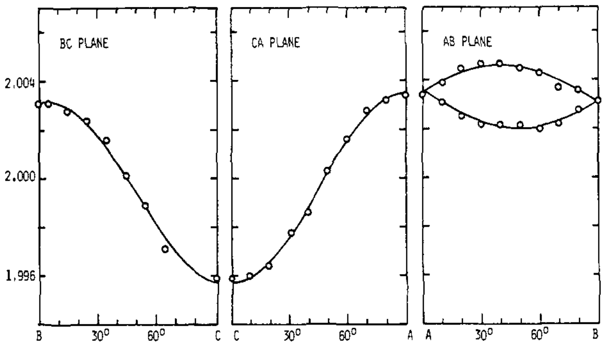


Figure 6. Angular dependence of the *g* values for the $CO_2^-$ ion produced by visible light exposure of an irradiated single crystal of potassium hydrogen maleate.

Figure 3 shows the change of the spectral intensities of T, D, and S during exposure to visible light. Complementary increase of D with decrease of T clearly indicates that radical T converts into D. Quantitative conversion was observed until half of the T converts into D. The intensity of D reaches a maximum within 2 min and then gradually decreases, with complementary increase of S. Although conversion from D to S is not quantitative, the appearance of S starts at the maximum intensity of D and the intensity of S tends to be constant with decay of D so that it is evident that D converts into S. This is also confirmed by the fact that there is no appreciable change in the spectrum other than the signals T, D, and S during the conversion from T to S. In addition, exposure to visible light after thermal bleaching of signal T did not give D and S, indicating that T is the precursor of D and S.

The angular dependence of the hyperfine splittings and *g* values for D is shown in Figures 4 and 5, respectively. Figure 6 shows the angular dependence of the

Table I. Hyperfine and $g$ Tensors for the Carboxyl Radical Produced by Visible Light Exposure of an Irradiated Single Crystal of Potassium Hydrogen Maleate at 77°K

| | Principal values[a] | Direction cosines for *abc* $l$ | $m$ | $n$ | Comparison with X-ray data, deg |
|---|---|---|---|---|---|
| $H_2$ | $A_1$ (+)5.2 | −0.469 | 0.460 | 0.754 | 5.6 with (1) |
| | $A_2$ (+)3.4 | 0.631 | −0.424 | 0.650 | 6.0 with (2) |
| | $A_3$ (+)3.0 | 0.619 | 0.780 | −0.092 | 5.3 with (3) |
| | $A_0$ (+)3.9 | | | | |
| $g$ | $g_1$ 2.0233 | 0.705 | −0.668 | 0.236 | 6.1 with (4) |
| | $g_2$ 2.0066 | 0.692 | 0.721 | −0.027 | 4.9 with (3) |
| | $g_3$ 2.0037 | −0.152 | 0.183 | 0.971 | 6.2 with (5) |
| (1) | Parallel to $O_2 \cdots H_2$ | −0.550 | 0.441 | 0.709 | |
| (2) | Perpendicular to $O_2 \cdots H_2$ in plane | 0.550 | −0.447 | 0.705 | |
| (3) | Perpendicular to the molecular plane | 0.631 | 0.776 | 0.000 | |
| (4) | Parallel to $C_1$—$O_1$ | 0.717 | −0.614 | 0.331 | |
| (5) | Perpendicular to $C_1$—$O_1$ in plane | −0.257 | 0.209 | 0.944 | |

[a] $A$ values in gauss.

Table II $g$ Tensor for the $CO_2^-$ Ion Produced by Visible Light Exposure of an Irradiated Crystal of Potassium Hydrogen Maleate

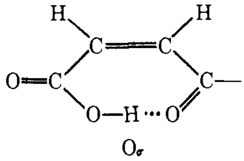
| | Principal values | Direction cosines for *abc* $l$ | $m$ | $n$ | Comparison with X-ray data, deg |
|---|---|---|---|---|---|
| $g$ | $g_1$ 2.0047 | 0.756 | 0.654 | 0.041 | 10.1 with (1) |
| | $g_2$ 2.0021 | 0.655 | −0.751 | −0.083 | 10.8 with (2) |
| | $g_3$ 1.9957 | 0.023 | −0.090 | 0.996 | 5.1 with (3) |
| (1) | Perpendicular to the molecular plane | 0.631 | 0.776 | 0.000 | |
| (2) | Perpendicular to $C_2$=$C_2'$ in plane | 0.776 | −0.631 | 0.000 | |
| (3) | Parallel to $C_2$=$C_2'$ | 0.000 | 0.000 | 1.000 | |

$g$ values for S. It should be mentioned that signal D exhibits site splittings in the *ab*, *bc*, and *ca* planes, while signal S exhibits site splitting only in the *ab* plane. The principal values and directions of the hyperfine and $g$ tensors determined by a first-order perturbation treatment using a least-squares method are listed in Tables I and II.

## Discussion

**Structure of Radical D.** The large positive shift of the maximum principal value of the $g$ tensor suggests that the unpaired electron of radical D is largely localized on the oxygen atoms because of the large spin–orbit coupling constant of the oxygen atom. From comparison with the crystallographic data, it was found that the $g_{max}$ axis is close to the $C_1$–$O_1$ ($C_{1'}$–$O_{1'}$) bond and the $g_{min}$ axis lies in the molecular plane, as shown in Table I. This strongly indicates that the unpaired electron is mainly localized in the in-plane p orbital of the $O_1$ ($O_{1'}$) atom[17] forming the $\sigma$ radical.

In irradiated maleic acid, we have found the carboxyl radical $O_\sigma$,[2] the $g$ tensor of which has similar principal values (2.0261, 2.0061, 2.0035). In this case the $g_{max}$ axis is close to the side C–O bond and the $g_{min}$ axis is in the molecular plane. From this similarity, signal D is assigned to the carboxyl radical formed by removal of the acidic proton, where the unpaired electron is mainly located on one of the two ring oxygen atoms.



$O_\sigma$

This is in contrast to the symmetrical radical T where the $g$ anisotropy is smaller than that of D and the $g_{max}$ axis is perpendicular to $O_1 \cdots O_{1'}$ in the molecular plane. As described in the previous paper,[3a] the reduced $g$ anisotropy in T is interpreted by the interaction of the two ring oxygen atoms, which raises the unpaired electron orbital, $\psi = (p_{O_1} - p_{O_{1'}})/\sqrt{2}$, with respect to the oxygen $p_\pi$ lone-pair orbital, since the admixture of this orbital mainly contributes to the $g$ anisotropy. The large $g_{max}$ value in D indicates that the interaction of the two ring oxygen atoms was reduced, resulting in the lowering of the unpaired electron orbital close to the $p_\pi$ lone-pair orbital. Although the reason is not clear for the localization of the unpaired electron on one of the two COO groups resulting from the reduced interaction between the $O_1$ and $O_{1'}$ atoms, it may be caused by distortion of the molecular framework or by isomerization from the maleic to the fumaric form, as will be discussed later.

The three-line hyperfine structure due to the two equally coupled vinylene protons in T was also reduced to a two-line structure due to coupling with one of the two vinylene protons, consistent with the change of the $g$ tensor. It was found that the $A_{max}$ axis is approximately along the line connecting the $O_2$ and $H_2$ atoms. This may indicate that some of the unpaired spin is on the $O_2$ atom. Thus, the unpaired electron orbital may be expressed by

$$\psi = c_1 p_{O_1} - c_2 p_{O_2}$$

where $p_{O_1}$ and $p_{O_2}$ indicate the in-plane p orbitals of the $O_1$ and $O_2$ atoms, respectively. If $c_1$ is larger than $c_2$, it may be expected that the $A_{max}$ axis will be rather close to $O_2 \cdots H_2$ and that the $g_{max}$ axis will be close to

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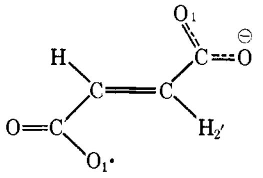
[17] One cannot distinguish the $C_1$–$O_1$ and $C_{1'}$–$O_{1'}$ bonds because of mirror symmetry of this molecule. In the following discussion, only one of them will be represented.

$C_1$—$O_1$. Since it is hard to determine the accurate spin densities on the $O_1$ and $O_2$ atoms from such a small hyperfine anisotropy, $c_1^2/c_2^2$ was tentatively assumed to be 0.7/0.3 for calculating the hyperfine anisotropy. Using the point-dipole approximation, the principal values of the hyperfine tensor[18] were found to be 5.8, 3.2, and 2.7 G, in agreement with the observed tensor (5.2, 3.4, and 3.0 G). The direction of the $A_{max}$ axis also agrees with the observed direction within 26°.

The $g_{max}$ axis was also calculated using the assumption that the mixing of the oxygen $p_\pi$ lone pair orbital, $\psi_{O\pi} = (p_{O_1\pi} - p_{O_2\pi})/\sqrt{2}$, predominantly contributes to the $g$ anisotropy. The calculated direction agrees with the observed direction within 28°. The discrepancy seems to be somewhat larger than the experimental error. However, the accurate orientation and geometry of the radical are not known so that the complete agreement may not be expected.

In the above discussion, however, the same geometry as that of the mother molecule is assumed. There might be some possibility of photoisomerization from the maleic to the fumaric form when radical T converts into D because there is no interaction between the $O_1$ and $O_{1'}$ atoms in the fumaric form. If this is the case, the $H_{2'}$ atom may also give the hyperfine structure



because the distance from the $O_1$ atom is closer than that in the maleic form. Actually, we have observed additional hyperfine coupling with another proton only in the direction of the magnetic field applied along ±30° from the $c$ axis. The rapid decrease of the extra hyperfine separation indicates that the coupling value changes its sign. This means that the isotropic term of this coupling is small and is attributable to the far proton, $H_{2'}$. The maximum coupling, 2.8 G, is also consistent with the anisotropic coupling of this proton. The direction of the maximum coupling was along the $c$ axis. The $O_1 \cdots H_{2'}$ direction in the fumaric form is 30° from the $c$ axis so that the $A'_{max}$ axis is fairly close to the $O_1 \cdots H_{2'}$ direction.

Here, we have to note that the discrepancies between the observed and the expected directions are nearly the same for the three axes *i.e.*, the $A_{max}$ axis for main hyperfine coupling, the $g_{max}$ axis, and the $A'_{max}$ axis for the extra hyperfine coupling. Now, if isomerization from the maleic to the fumaric form takes place, the carboxyl radical in the fumaric form may not preserve the same position as that of the mother molecule in the crystalline lattice because steric interactions with the neighboring molecules increase considerably. It is likely that reorientation of the radical takes place so as to minimize the steric interaction. The reorientation may take place in such a way that the space occupied by the fumaric radical is as close as that of the mother molecule. Since both the forms are planar, the radical may rotate around the normal to the radical plane. If one assumes a rotation of 25–30°, molecular packing quite similar to that of the maleic form is obtained, as shown in Figure 7. If this is the case, the discrepancies between the observed and the expected directions are all removed. All the axes are now in agreement with the expected directions within 3° (see Figure 7). Therefore, it may be suggested that radial D has the fumaric form, although a definite conclusion must await the precise determination of the extra hyperfine coupling by the endor technique.

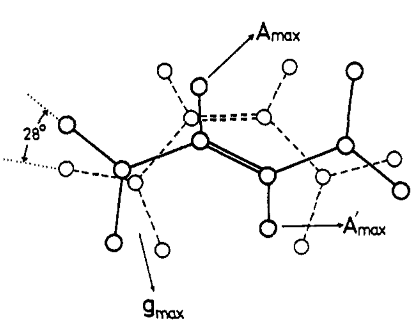


Figure 7. Reorientation of the carboxyl radical of the fumaric form: - - - -, position of the mother molecule; ———, position of the fumaric form.

**Assignment of Signal S.** The $g$ tensor of signal S shows a remarkable negative shift, as shown in Table I. The principal values are very close to the literature values 1.9973, 2.0010, and 2.0046 for the single-line spectrum in succinic acid[8] and 1.9964, 2.0019, and 2.0040 for the acyl radical in malonic acid;[10] and 1.9975, 2.0014, and 2.0032 for the $CO_2^-$ in sodium formate.[12] The acyl radical exhibits small hyperfine structures due to the $\beta$-proton couplings. The hyperfine tensor was reported to be −4, −6, and +2 G. Signal S exhibits no hyperfine structure and the line width was about 3 G in most of the crystal orientations, the maximum width being 5 G. If radical S is the acyl radical produced by removal of the oxygen atom from radical D, the $\beta$-proton coupling may be larger than that in malonic acid because hyperconjugation is expected to be maximum in our radical, where the C–H bond is nearly parallel to the $\sigma$-orbital axis.[10] However, there is no exact knowledge about the origin of the hyperfine coupling of the $\beta$ proton in acyl radicals, so the possibility of assignment to the acyl radical may not be completely denied in a view of the hyperfine couplings.

However, we would like to point out that the principal directions of the $g$ tensor and the site splitting of signal S seem to be inconsistent with the acyl radical. The $g_{int}$ axis in S, which should be the density axis of the unpaired electron orbital, is perpendicular to the C═C bond in the molecular plane.[19] If the acyl radical is the case, the $g_{int}$ axis should make an angle of about 20° with the normal to the C═C bond. The difference of 20° may be small as compared with the experimental error, but one has to observe the site splitting due to the equal probability of the formation

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(18) In obtaining the principal values, the observed isotropic term was added to the calculated anisotropy.

(19) Although the observed direction of the $g_{int}$ axis makes a fairly large angle of 10.8° with the direction perpendicular to the $C_2$—$C_{2'}$ bond in the molecular plane, as shown in Table II, the discrepancy arises mainly from the deviation out of the molecular plane as is indicated by the small value of $n$. The $g_{int}$ axis makes an angle of 94.2° with the direction of the $C_2$═$C_{2'}$ bond.

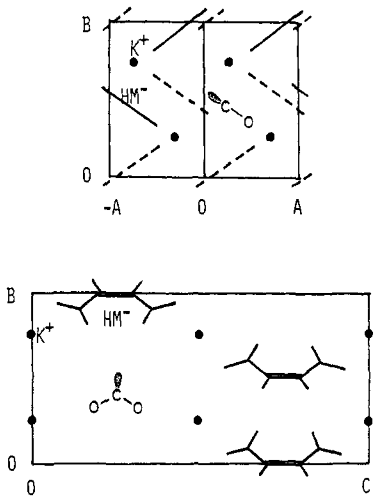

Figure 8. Orientation of the trapped $CO_2^-$ ion in the crystal of potassium hydrogen maleate. One of the hydrogen maleate ions ($HM^-$) is replaced by $CO_2^-$ to show its orientation with respect to the crystallographic axes. The actual position of the $CO_2^-$ ion is not known.

of the acyl radical from the two equivalent COO groups, as was found in the malonic acid crystal.[10] The large difference in the principal values of the $g$ tensor in the molecular plane should make it possible to distinguish the two sites which make an angle of about 40° with each other. In the *ac* and *bc* planes in which our measurements were carried out, the site splitting is expected to be about 8 G, this being sufficiently larger than the line width of 3 G. No site splittings in these planes in our experiments may exclude the possibility of the acyl radical.[20]

On the other hand, if the responsible species is the $CO_2^-$ ion, such a small fragment should not preserve the same orientation as that of the mother molecule and the reorientation may be governed by the crystalline field surrounding the $CO_2^-$ ion. The principal directions indicate that the $CO_2^-$ ion is trapped in such a way that the radical plane is nearly parallel to that of the mother molecule and the symmetry plane of the radical coincides with that of the mother molecule. This seems to be reasonable for the reorientation of $CO_2^-$ in this crystal. Figure 8 shows the relative orientation of the $CO_2^-$ ion to that of the undamaged molecule.

**Radical Fragmentation Path.** In the maleic acid crystal,[2] we have found that the carboxyl radical fragments into a vinyl-type radical and a $CO_2$ molecule when the crystals are exposed to visible light or warmed slightly. Radical D in the present case may also fragment into a vinyl-type radical which is similar to that in maleic acid but is different in the negative formal charge on the COO group. If one assumes the further fragmentation of the negatively charged vinyl-type radical, the following process for $CO_2^-$ formation may be suggested

$$^{-}OOC{-}CH{=}CH{-}COO\cdot \longrightarrow {}^{-}OOC{-}CH{=}\dot{C}H + CO_2 \quad (5)$$

$$^{-}OOC{-}CH{=}\dot{C}H \longrightarrow CO_2^- + CH{\equiv}CH \quad (6)$$

Since the fragmentation of the carboxyl radical takes place thermally in maleic acid, the thermal change of signal D was also examined to find the intermediate vinyl-type radical[21] which is formed in process 5. When the crystal was annealed at Dry Ice temperature for 5 min, signal D completely disappeared without the appearance of signal S. Because of overlap with other signals, it was hard to detect the signal due to the intermediate radical when the low microwave power needed for the detection of the vinyl-type radical was used. The signal due to the vinyl-type radical is known to seriously saturate at 77°K. Although we could not obtain spectral evidence for the existence of the intermediate radical, it was found that signal S came out without causing appreciable change in the remaining spectrum when the crystal was exposed to visible light after signal D completely disappeared. This may suggest indirectly the existence of the intermediate radical, the signal of which was hidden by other spectra because of its saturation.

Since carboxyl radicals are believed to be produced from the positive primaries, the $CO_2^-$ ions are considered to be formed from the fragmentation path of the positive primaries, in contrast to the formation of acyl radicals from the negative primaries. In saturated dicarboxylic acids, both radicals $R\cdot$ and $R\underset{\cdot}{C}{=}O$, originating from the positive and negative primaries, respectively, appear to form the stable radical, $R'\dot{C}HCOOH$, by hydrogen abstraction from the neighboring molecules.[8-10] However, in unsaturated dicarboxylic acids the radical $R\cdot$ (vinyl-type radical) from the positive primaries seems to decompose into small fragments. On the other hand, according to our recent study on an irradiated single crystal of fumaric acid doped succinic acid,[22] the negative primary was found to give the hydrogen addition radical (stable radical) by receiving $H^+$ from the diamagnetic protonated cation $RC^+(OH)_2$ formed in reaction 2.

$$[HOOCCH{=}CHCOOH]^- + H^+ \longrightarrow HOOCCH_2\dot{C}H{-}COOH \quad (7)$$

Although the negative primary could not be identified in the present molecule, the other lines, mentioned above, observed with low microwave power are supposed to be due to the negative primary. When the crystal was warmed to room temperature, the signal due to the stable $\pi$ radical found in the earlier works[13] appeared at the expense of the other lines. Therefore, we speculate that the stable $\pi$ radical in the present system may be formed from the negative primary by dehydrogenation, as in the following reaction.

$$^{-}OOCCH{=}CHCOOH]^- + H^+ \longrightarrow \underset{\pi\ \text{radical}}{^{-}OOCCH{=}CHCOO\cdot} + H_2 \quad (8)$$

Although the reason that dehydrogenation takes place rather than proton addition is not clear, we have also found that an irradiated single crystal of sodium hydrogen maleate trihydrate gives the hydrogen

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[20] If radical D is in the fumaric form and the $C_1$–$O_1$ bond accidentally directs along the normal to the $C_2$–$C_2'$ bond due to reorientation, the acyl radical formed by the scission of the $C_1$–$O_1$ bond is expected to give a one-site spectra. Therefore, the possibility of the acyl radical cannot be definitely excluded.

[21] The vinyl-type radical, $HOOCCH{=}\dot{C}H$, described in ref 3a, is different from this intermediate radical, $^{-}OOCCH{=}\dot{C}H$, having no acidic proton. The former is supposed to be formed directly from the positive primary by loss of a $CO_2$ molecule, while the latter is formed from the carboxyl radical which lost an acidic proton.

[22] M. Iwasaki, H. Muto, and K. Toriyama, *J. Chem. Phys.*, **55**, 1894 (1971).

addition radical at room temperature.[3b] The crystalline field effect on the radical reaction in the crystal may be suggested.

In conclusion, there is a similarity in the decarboxylation process of saturated and unsaturated dicarboxylic acids, where R· is formed from the positive primary *via* the carboxyl radical. There is, however, a significant difference in the following reaction of R produced. Furthermore, the fate of the negative primary is entirely different.

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# Studies of the Effects of Ion Pair Formation on the Electron Paramagnetic Resonance Parameters of Radical Anions[1]

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**Abstract:** A detailed analysis of the effect of ion pair formation on epr parameters such as proton, $^{13}$C, and $^{14}$N hyperfine splittings and $g$ factors was made for several radical anions. The analysis was made by using McLachlan MO's combined with the McClelland approximation. The systems studied were anthracene, fluorenone, anthraquinone, and 2,2′-dipyridyl anions. Using $-e^2/\epsilon r$ as an interaction, it was found that a relatively large $\epsilon$ is necessary in order to explain the observed changes in the epr parameters. In general, qualitatively satisfactory agreement was obtained between the observed changes and the ones predicted using the assumed structures. The observed perturbations and the results of calculations are discussed in terms of the possible ion pair structures. The results of the $g$-factor analysis are found to be in excellent agreement with those obtained from carbonyl $^{13}$C splittings.

The hyperfine splittings and $g$ factors of epr spectra of radical ions are known to be sensitive to environmental perturbations such as ion pair formation or solvation. In principle, such perturbational effects should provide information concerning the structures of ion pairs and the interactions between ions in ion pair systems, if appropriate analysis of such effects can be made. For example, changes in the hyperfine splittings should strongly depend on the position of the cation with respect to the anion. Information on ion pair structures should be obtainable from such data. The magnitude of the perturbation should reflect the strength of the interactions between cation and anion. In spite of the large amount of work carried out on epr spectra of radical ions in ion pair systems, we still have very little knowledge about the actual structures of ion pairs in solution and the strength of the interaction between ions in ion pairs. Although studies of perturbational effects in ion pairs have been made previously by several authors,[2-4] it appears that no comprehensive and detailed analysis in connection with the ion pair structure have been made. Accordingly, we have chosen representative examples of different types of radical ions and investigated perturbational effects on the epr parameters upon ion pair formation. The types of systems and our choice of the representative molecules are: (1) aromatic hydrocarbon, anthracene; (2) ketyls, fluorenone; (3) semiquinones, anthraquinone; and (4) nitrogen heterocyclics, 2,2′-dipyridyl.

Analysis of the data was made by applying McLachlan's MO treatment[5] with the use of the McConnell relationship for proton splittings,[6] the Fraenkel–Karplus[7] formula for $^{13}$C splittings, and Stone's theory of $g$ factors.[8] Naturally our analysis suffers from any shortcomings inherent in a simple $\pi$-electron MO treatment such as McLachlan's. Nevertheless, a great amount of work accumulated in the last decade shows that McLachlan's calculation of spin densities can provide reasonably good agreement with the experimental values if appropriate choices of parameters are made. At present, even more sophisticated unrestricted Hartree–Fock calculations can only give the same order of agreement with the experimental values as the McLachlan method does.[9] Therefore, we have employed McLachlan's method together with the McClelland treatment of the ion pair effect[10] in order to analyze the effect of ion pair formation on the epr parameters. Recently Goldberg and Bolton reported the calculation of potential energies and alkali metal splittings in several alkali metal aromatics.[11] Their calculations also used the McClelland procedure in order to take into account the ion pair effect.

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