*The Electron Spin Resonance of an Irradiated Single Crystal of Potassium Hydrogen Maleate**

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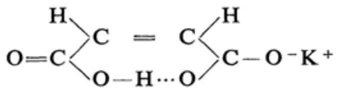
Although the electron spin resonance (ESR) of many irradiated single crystals of organic molecules has been reported on in the past five years, few attempts have been made to examine molecules containing conjugate systems. It has been found by I. Miyagawa** that the ESR spectra of several dicarboxylic acids, such as formic acid, fumaric acid, and maleic acid, were very weak, while very much stronger spectra were obtained from saturated carboxylic acids. The common characteristics of these dicarboxylic acids are that all molecules in a crystal are linked by intermolecular hydrogen bonds and that each molecule has a conjugate system. The odd electrons or holes produced in a crystal by irradiation may easily migrate throughout the entire crystal through the conjugate systems and the intermolecular hydrogen bonds, accompanied by the recombination and disappearance of the odd electrons or holes. In this respect, potassium hydrogen maleate (KHM) is an especially interesting case. In this molecule the intermolecular hydrogen bonds are broken by the substitution with potassium as:



Unlike maleic acid, this molecule gave strong and sharp spectra, supporting the interpretation of the phenomenon mentioned above. This paper will deal with the identification of the radical produced in a single crystal of this interesting molecule.

Experimental Procedure

Single crystals of potassium hydrogen maleate and its deuterium-exchanged compound (KOOCCH=CHCOOD) were grown from aqueous and heavy water solutions respectively by the slow cooling method. The purity of the deuterium-exchanged compound was tested by means of its infrared spectra. The single crystals obtained were typical orthorhombic crystals, the crystal axes of which were identified by taking vibration photographs of the X-ray diffraction. The crystal structure of KHM has been completely analyzed by Darlow and Cochran,1) giving the orthorhombic space group Pbcm, with four molecules per unit cell and cell dimensions of $a=4.578$ Å, $b=7.791$ Å and $c=15.953$ Å. The results of the ESR will be compared with their crystal analysis in a later paragraph of this paper.

The single crystals were irradiated at room temperature with an X-ray source operating at 30 kV. and 15 mamp. The ESR of irradiated single crystals was measured mainly at 24 kMc./sec. for various orientations of the crystal in the magnetic field at room temperature. As a reference for the spectroscopic splitting factor, the sharp resonance of DPPH was used. The separations of the hyperfine structures were measured by a proton resonance with a side-band technique.

Experimental Results

The ESR spectra first observed at 9 kMc./sec. showed a marked second order effect,2) making the spectra somewhat complicated, but the

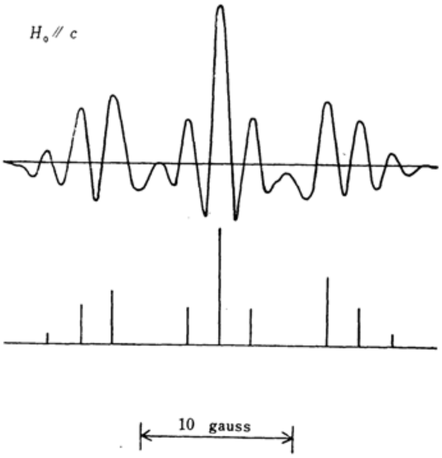


Fig. 1. Electron spin resonance curves at 9 kMc./sec. of an X-irradiated single crystal of potassium hydrogen maleate with the static magnetic field parallel to the c-axis. The vertical lines indicate the theoretical positions and intensities.

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** Private communication.

1) S. F. Darlow and W. Cochran, *Acta Cryst.*, **14**, 1250 (1961).

2) I. Miyagawa and W. Gordy, *J. Chem. Phys.*, **32**, 255 (1960).

one observed at 24 kMc./sec. showed practically no second order effect, making the spectra simple enough to interpret very easily and accurately. Therefore, the measurements for various orientations of the crystal were mainly carried out at 24 kMc./sec. Figure 1 depicts the ESR spectrum measured at 9 kMc./sec. for the orientation of the crystal in the magnetic field parallel to the crystal c-axis. The hyperfine structure of the spectrum was interpreted on the basis of the theory of the second-order effect[2], giving a good agreement with observed results. The vertical lines under the absorption lines indicate the theoretical spectral positions and their intensities.

The spectra observed at 24 kMc./sec. for orientations of the crystal in the magnetic field parallel to the three crystallographic axes consist of three lines, the relative intensities of which are 1 : 2 : 1. If the crystal is rotated around the a- or b-axis, fixing the magnetic field in the (bc) or (ca) plane of the crystal respectively, the triplet is resolved into a quartet consisting of the pair of doublets expected for two non-equivalent protons with a spin of 1/2 (see Figs. 2 and 3). This suggests that, for these orientations, the unit cell contains only one radical having two chemically-equivalent protons, and that the two protons

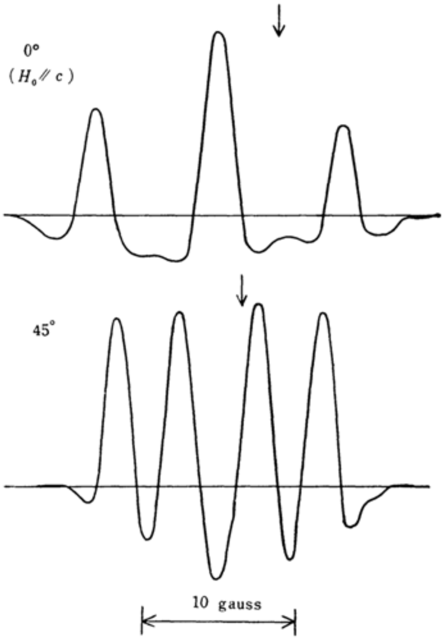


Fig. 3. Electron spin resonance curves at 24 kMc./sec. of an X-irradiated single crystal of potassium hydrogen maleate with the static magnetic field in the (ca) plane. Angles are measured from the c-axis.

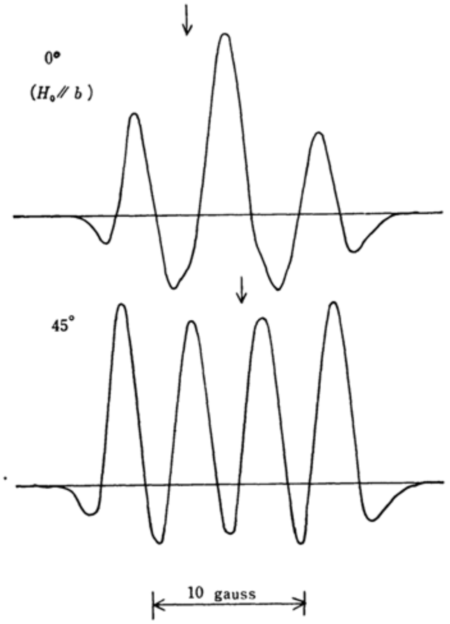


Fig. 2. Electron spin resonance curves at 24 kMc./sec. of an X-irradiated single crystal of potassium hydrogen maleate with the static magnetic field in the (bc) plane. Angles are measured from the b-axis. Arrows show the position for the DPPH resonance.

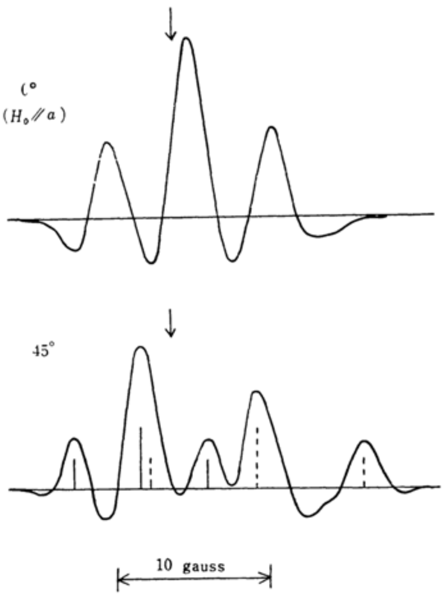


Fig. 4. Electron spin resonance curves at 24 kMc./sec. of an X-irradiated single crystal of potassium hydrogen maleate with the static magnetic field in the (ab) plane. Angles are measured from the a-axis.

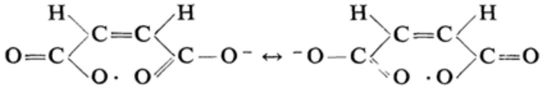
are not magnetically equivalent for the field along the intermediate directions of the crystal axes. However, if the crystal is rotated around the c-axis, fixing the magnetic field in the (ab) plane of the crystal, the single triplet is resolved into a pair of triplets, the *g*-factors of which are different from each other (see Fig. 4). This means that, for this orientation of the crystal, there are two magnetically non-equivalent radicals. In this case, the triplets were not resolved into a quartet as in the case of the rotation around the a- or b-axis. Therefore, two coupling protons in a radical are magnetically equivalent for any orientation produced by the rotation around the c-axis.

From the interpretation of the observed spectra, it is concluded that there are four coupling protons in a unit cell. The principal values and the direction cosines of the hyperfine tensors for these protons determined from the angular dependence of the coupling constants are tabulated in Table I. The principal values and the direction cosines of the *g*-tensors were determined from the angular dependence of the center of the hyperfine patterns and are also listed in Table I.

The ESR of an irradiated single crystal of potassium deuterium maleate (KDM) was also measured in order to get some additional information about the structure of the free radical. The observed spectra, however, was not any different in the coupling values from the one for KHM. The line widths for both compounds were very narrow and in both the distance between maximum slopes was 1—2 gauss. Although slightly sharper lines were observed for KDM, it was shown by a comparison of the spectra for rotations around the a-, b-, and c-axes that the largest difference between the line widths of the two compounds was only 0.5 gauss.

Analysis of the Results and Discussion

These features of the observed spectra suggest that the radical is produced by the removal of OH hydrogen, and that the coupling protons are two vinylene protons which can be chemically equivalent because of the following resonance:



Two vinylene protons are always equivalent for the orientations of the crystal in the magnetic field in the (ab) plane, so the (ab) plane should be perpendicluar to the C=C bond. Furthermore, it is expected from the experimental results that the two kinds of molecules in a unit cell are oriented in such a way that the (ca) or (bc) plane of the crystal makes an equal angle to the two planes of molecules corresponding to the two magnetically-non-equivalent radicals.

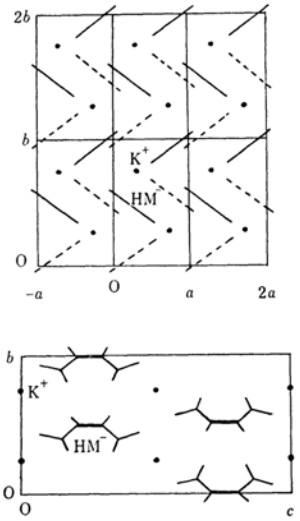


Fig. 5. Projection of the structure of potassium hydrogen maleate to the c- and a-axes.

Shown in Fig. 5 is the arrangement of the four molecules in the unit cell as determined by Darlow and Cochran.[1] It may be seen that the orientations of the molecules expected from the observed ESR spectra are entirely consistent with the crystallographic results. The direction cosines of the C–H bond and the directions perpendicular to it can be calculated from the crystallographic data and compared with those of the principal axes of the hyperfine tensor. As Tables I and II indicate, the direction for the smallest element approximately coincides with the C–H bond direction, while that for the largest coincides with the direction perpendicular to the C–H bond in the molecular plane. This finding indicates that the origin of the hyperfine structure is two vinylene protons, and that the structure of the free radical produced is not very much deformed from the parent molecule as far as the vinylene portion of the molecule is concerned.

The results listed in Table I indicate that the smallest principal element of the *g*-tensor has its axis perpendicular to the molecular plane and that the other two pincipal elements are approximately equal and are directed in the molecular plane. This means that the spin density is in a p-orbital of the carbon,

TABLE I. VALUES OF THE PROTON HYPERFINE AND *g*-FACTOR TENSORS IN X-IRRADIATED POTASSIUM HYDROGEN MALEATE

Tensor	Principal values gauss obs.	theo.	Direction cosines* with respect to the a-, b- and c-axes			Directions with respect to the molecule
Proton	(−)2.1_1	−2.5	∓0.649	±0.560	⊏0.515	∥ C_2-H_2**
H_2	(−)7.0_1	−6.8	‡0.669	±0.743	0.000	⊥molecular plane
	(−)10.1_3	−9.9	±0.360	⊏0.370	⊏0.857	⊥C_2-H_2 in molecular plane
Proton	(−)2.1_1	−2.5	∓0.649	‡0.560	‡0.515	∥ $C_2'-H_2'$
H_2'	(−)7.0_1	−6.8	‡0.669	±0.743	0.000	⊥molecular plane
	(−)10.1_3	−9.9	∓0.360	‡0.370	⊏0.857	⊥$C_2'-H_2'$ in molecular plane
g	2.0024		‡0.629	±0.778	0.000	⊥molecular plane
	2.0040		∓0.778	‡0.629	0.000	⊥C=C in molecular plane
	2.0045		0.000	0.000	‡1.000	∥ C=C

* The uncertainties in the coupling constants, the *g*-factor, and the directions of the couplng constants are estimated to be 0.3 gauss, 0.0006, and 2°, respectively.

** Determined by X-ray diffraction data.1)

TABLE II. DIRECTION COSINES OF THE C–H BOND AND ITS PERPENDICULAR IN THE MOLECULAR PLANE OBTAINED FROM THE X-RAY DATA

Direction	Direction cosines with respect to the a-, b-, and c-axes			Angle made with the principal axes of the hyperfine tensor
∥ C_2-H_2	∓0.715	±0.548	⊏0.435	6°
⊥C_2-H_2 in plane	±0.339	⊏0.272	⊏0.901	6°
∥ $C_2'-H_2'$	∓0.715	‡0.548	‡0.435	6°
⊥$C_2'-H_2'$ in plane	∓0.339	‡0.272	⊏0.901	6°

which has its direction perpendicular to the molecular plane.

The nuclear hyperfine interaction constant, *A*, of the ·C—H fragment consists of an isotropic Fermi term, A_f, and an anisotropic dipole-dipole interaction term, $A\mu$. The isotropic term, A_f, is determined from the three principal elements by $(A_1+A_2+A_3)/3$ to be 6.4 gauss for the present free radical. With this value, the spin density on the vinylene carbon atom is found to be 0.26, employing 25 gauss as the A_f value for unit spin density. The anisotropic hyperfine interaction for π-eletron free radicals has been estimated by McConnell and Strathdee,3) who gave the principal elements the values of 15.4, −1.7, and −13.6 gauss along the C–H bond, along the density axis of the p-orbital, and perpendicular to those two respectively. For the present radical these principal values should be reduced by 74% to 3.9, −0.4, and −3.5 gauss respectively. Since A_f is known to be negative in sign,4) adding the observed isotropic component, $A_f=-6.4$ gauss, to the theoretical anisotropic components yields −2.5 gauss for the total coupling constant along the C–H bond, −6.8 gauss along the p-orbital, and −9.9 gauss perpendicular to the C–H bond in the molecular plane. These values are in very good agreement with the observed principal elements of the hyperfine tensor shown in Table I. Figure 6 indicates the directions of the principal axes, A_1, and A_3; A_2, which is not indicated, is perpendicular to the molecular plane.

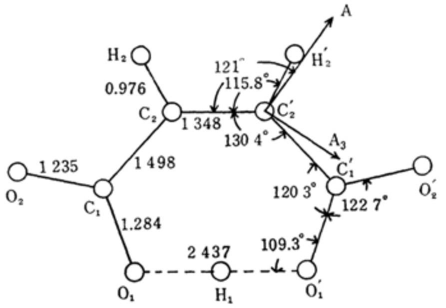


Fig. 6. The molecular structure of the hydrogen maleate ion and the directions of the proton coupling tensor.

The observed narrow line widths and their small change upon deuterium substitution

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3) H. M. McConnell and J. Strathdee, *Mol. Phys.*, **2**, 129 (1959)

4) H M. McConnell and D. E. Chesnut, *J. Chem. Phys.*, **28**, 108 (1958); H. M. McConnell, C Heller, T. Cole and R. W. Fessenden, *J. Am. Chem. Soc.*, **82**, 766 (1960).

suggest that no nuclear spin except two vinylene protons exists in the present radical. The difference of line width in both compounds when the OH proton exists in the produced radical was estimated on the basis of the following assumptions: (1) the radical has the same geometrical structure as that of the parent molecule;[1] (2) the spin density in the vinylene carbon atom is +0.26; (3) the remaining spin density, +0.48, is equally assigned to the most distant side oxygen atoms from the OH protons; (4) each spin density is located on the nucleus as a point spin density; (5) the Fermi term of the OH proton-coupling constant is assumed to be −0.1 gauss, which gives the smallest possible total coupling constant; (6) the contributions from the neighboring molecules to the line width are disregarded. As nothing is known about the quantities in assumptions 3 and 5, they are assumed to give the lowest possible value for differences in line widths as far as these quantities are concerned. Thus, the principal elements of the coupling constant for the OH proton were estimated to be +1.5, −1.5, and −0.3 gauss for the direction perpendicular to the C=C bond in the molecular plane, for that perpendicular to the molecular plane, and for that parallel to the C=C bond respectively. When the OH proton is substituted with deuteron, the line widths are expected to be reduced at least by 1.0, 1.0, and 0.2 gauss for the principal directions. A comparison of these calculated values with the observed ones excludes the possibility that the radical which gives the observed absorption has an OH hydrogen atom as does the parent molecule.

It is interesting to note that the discrepancy between the observed direction of the C–H bond in the radical and the calculated direction from the X-ray crystallographic data of the parent molecule may be responsible for the loss of the bridge hydrogen bond. Darlow[5] pointed out that this intramolecular hydrogen bond produces strain in the bond angles of this molecule. The C=C–C angle in unstrained molecules[5] is about 121.5±1.0°, while the same angle in the present molecule[1] is 130.4 ±0.2°, the strain angle being 8.9±1.0°. Therefore, if the strain is removed by the loss of the bridge hydrogen, the C=C–C angle will be closed by about 8.9°, accompanied by a change in the C=C–H angle which will amount to about a half of this strain, that is, to 4.5°. Thus, the C=C–H angle will change from 115.8° (X-ray value) to 120.3° in the unstrained radical. The observed C=C–H angle in the radical, 121°, is in good agreement with the expected value, 120.3°.

It is of interest that simple LCAO calculation shows that the unpaired electron must be a π-electron for the proposed radical produced by the removal of the OH hydrogen during irradiation. It is assumed in the calculations that the Coulomb integral to the ring oxygen is smaller than the side oxygen for the following reasons. (1) According to the X-ray data, the side C–O distance is shorter than the ring C–O in the parent molecule (see Fig. 6). (2) In the radical produced upon the removal of the OH hydrogen, the ring O···O distance becomes so short that the β_{OO} can not be ignored. Instead of including β_{OO}, the contribution from the β_{OO} may be replaced by taking the smaller value of the Coulomb integral for the ring oxygen. With $\alpha_O(\text{ring}) = \alpha_C + 1.8\beta_C$, $\beta_{CO}(\text{ring}) = 0.85\beta_C$, $\alpha_O(\text{sid}) = \alpha_C + 1.2\beta_C$, and $\beta_{CO}(\text{side}) = 0.95\beta_C$, the energy level of the highest-filled π-orbital was found to be higher than that of a pπ lone-pair electron on an oxygen atom by $0.71|\beta_C|$, where α_C is the Coulomb integral and β_C is the resonance integral of a pπ electron in a C=C bond. The unpaired electron which should be formed on the oxygen atom by the removal of the OH hydrogen atom is equivalent to one of the σ lone-pair electrons. The energy level of the latter electron is equal to that of a pπ lone-pair electron on the same atom for a simple LCAO approximation. Thus, to minimize the energy of the radical, an electron in the highest-filled orbital is relocated at the half-filled σ lone-pair orbital, the remaining π electron becoming an unpaired electron. The spin density on the vinylene carbon atom was found to be +0.28, which is in very good agreement with the +0.26 estimated from the proton-coupling constant.

After finishing our work, we found that Heller and Cole[6] had obtained a similar results. However, our results may be more accurate than those of (HC), since their results were derived mainly from measurements at 9 kMc./sec. These two independent measurements are in very good agreement with each other. The discrepancies between the principal values in Table I and those given by (HC) are within 0.2 gauss and 2.5° for the values and directions of the principal elements of the proton-coupling constant respectively, and within 0.0012 and 1° for those of the *g*-factor respectively.

The authors are greatly indebted to Professor Ichiro Miyagawa of Duke University for his

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[5] S. P. Darlow, *Acta Cryst.*, **14**, 1257 (1961).

[6] H. C. Heller and T. Cole, *J. Am. Chem. Soc.*, **84**, 4448 (1962).

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