−63 cal. deg.$^{-1}$ mole^{-1}. This entropy loss is considerably in excess of the value for a simple −1 ion, such as Br$^-$ for example, and seems large even if all the rotational entropy (28 cal. deg.$^{-1}$ mole^{-1}) were lost. Thus, it seems probable that the GaBr$_4^-$ ion has an abnormally large order-ing effect on the solvent due either to its large size or to a retention of a certain amount of ionic charge by the component atoms. In the latter case, the ion should not be considered simply as a large −1 ion, but as one having over short distances, a greater effective charge.

Electron Magnetic Resonance of X-Irradiated Potassium Hydrogen Maleate

By H. C. Heller and T. Cole

X-Irradiation of a single crystal of potassium hydrogen maleate HOOCCH=CHCOOK has been found to produce a free radical in which the unpaired electron interacts with only two protons. The electron magnetic resonance of this radical, shown to be ·OOCCH=CHCOO$^-$, indicates that it is oriented in the host crystal in the same way as the parent hydrogen maleate ion. The principal values of the proton hyperfine tensors of the radical are: −19.0, −28.4, and −6.0 Mc. These rather small principal values and their directions indicate that the unpaired electron in the radical is in a $p\pi$ orbital de-localized over the whole radical, including the carboxyl groups. The directions of the principal values are in agreement with the cis-structure of the parent molecule. The utilization of e.m.r. spectra in differentiating between cis- and trans-structures of radicals is briefly discussed.

Introduction

Several free radicals produced by high-energy radiation in dicarboxylic acids have been studied by means of electron magnetic resonance (e.m.r.).[1-6] The unpaired electron in these radicals was shown to be in a $p\pi$-orbital localized on one of the carbon atoms[7] forming the backbone of the radical. Recently, an allyl-type radical, i.e., HOOC—CH=CH—·CH—COOH was found[8] to be formed in X-irradiated glutaconic acid. The odd electron in this radical was found to be in a delocalized $p\pi$-orbital, the delocalization extending only over the radical's three central carbons. We here report the e.m.r. study of a radical produced in X-irradiated potas-sium hydrogen maleate KOOCCH=CHCOOH, in which there is considerable unpaired spin delocal-ization onto the π-orbitals of the carboxyl groups.

Experimental

Potassium hydrogen maleate (KHM) was prepared by neutralizing maleic acid with an appropriate amount of potassium carbonate. Single crystals were grown by the slow evaporation of saturated aqueous solutions. KOOC-CH=CHCOOD was obtained by exchange of KHM with D$_2$O, and several crystals of the deuterated acid salt were grown from D$_2$O solutions.

The KHM crystal is reported to be orthorhombic[9,10] and contains four molecules per unit cell. The HM$^-$ ion in the crystal is planar,[9,10] with carboxyl proton H$_1$ forming an intramolecular hydrogen bond between the carboxyl groups (Fig. 1 upper). There is a plane of symmetry perpendicu-lar to the ion and passing through H$_1$ and the midpoint of the double bond.

KHM crystals were X-irradiated at room temperature with a tungsten target tube operating at 50 kv. and 50 ma. Irradiation time was one hour.

(1) H. M. McConnell, C. Heller, T. Cole and R. W. Fessenden, J. Am. Chem. Soc., 82, 766 (1960).

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E.m.r. spectra were observed at room temperature with a spectrometer of conventional design employing 100 kc. field modulation and operating at X-band frequency (∼9750 Mc.). Spectra were taken every 10° during rotation of the magnetic field about the a, b, and c axes. Initial orienta-tions of the crystals were made by means of an optical goniom-eter. An n.m.r. servo system was used to continuously monitor and control the magnetic field. A K-band spectrom-eter (∼24,000 Mc.) was used to observe spectra for certain orientations of the crystal (see Results and Analysis section). The spectroscopic splitting factor G was obtained in a manner described previously.[6]

Results and Analysis

Simple e.m.r. spectra are obtained with the ex-ternal magnetic field along the a, b, and c-axes, and also for rotations about the a and b-axes. The molecules in the unit cell are magnetically equivalent for these directions. These simple spectra consist of either four main lines with an integrated intensity ratio of approximately 1:1:1:1 (Fig. 2C) or three lines with a ratio of 1:2:1 (Figs. 2A, 2B, and 2D). "Forbidden" transitions[1] are also evident, especially with the field along the c-axis (Fig. 2B). Calculations (details of which are given elsewhere[1]) show that the probability of these transitions should be almost zero for spectra ob-tained at higher fields. The simple spectrum at Fig. 2D, obtained at K-band frequencies (∼24,000 Mc.), is in agreement with these calculations (compare Fig. 2B and 2D). E.m.r. spectra for rotations about other axes, e.g., the c-axis, are more complex. A crystal in which the carboxyl proton was replaced by a deuteron via exchange with D$_2$O gave similar spectra, but with narrower and sharper lines. The main spectra, therefore, do not arise from hyperfine (h.f.) coupling to the carboxyl proton.

All the e.m.r. spectra show that the unpaired electron in the free radical, formed by the X-ir-radiation, is coupled to two protons. The total magnetic interaction may be described by the spin Hamiltonian, where β_n and β are the nuclear and

$$\mathcal{H} = -\beta S \cdot g \cdot B_0 + \Sigma_i g_n \beta_n I_i \cdot B_0 + S \cdot \Sigma_i A_i \cdot I_i \quad (1)$$

electronic Bohr magnetons, respectively, g is the electronic spectroscopic splitting tensor, g_n is the nuclear spectroscopic splitting factor, B$_0$ is the
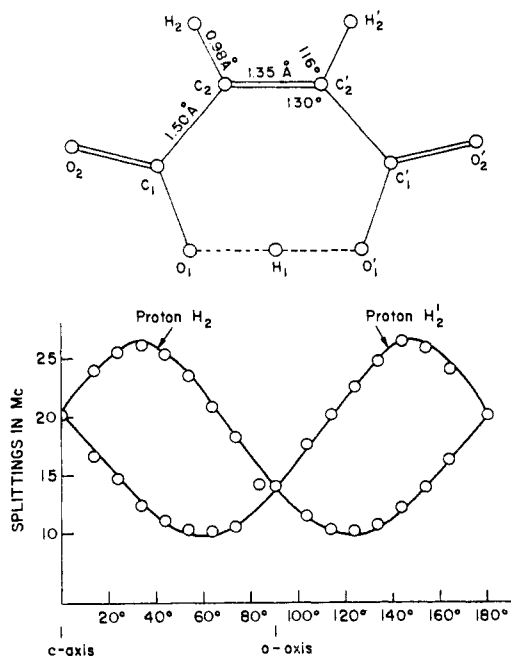
Fig. 1.—Upper: structure of the hydrogen maleate ion (more details are given in ref. 9, 10). Lower: calculated (solid line) and observed (open circles) proton hyperfine splittings during the rotation of the external magnetic field about the b-axis of an X-irradiated crystal of potassium hydrogen maleate.
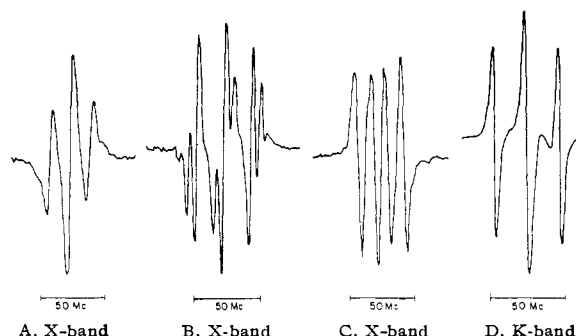

Fig. 2.—A, X-band e.m.r. spectrum of an X-irradiated KHM crystal taken with the external magnetic field parallel to the b-axis. B, X-band e.m.r. spectrum taken with the external field parallel to the c-axis. C, X-band e.m.r. spectrum taken with the external field parallel to direction (0, 0.87, 0.50). D, K-band e.m.r. spectrum taken with the external field parallel to the c-axis.

external magnetic induction, I_i and S are the nuclear and electronic spin operators (index i indicates one of the two protons) and A_i is the hfs tensor for proton i. Values determined for the elements of the hf coupling tensors A_i, due to protons H_2 and H_2', and the g-factor tensor are given in Table I.

TABLE I

PRINCIPAL VALUES OF THE PROTON HYPERFINE- AND g-FACTOR TENSORS IN RADICAL IN X-IRRADIATED KH MALE-ATE

Tensor	Principal values, Mc.	Direction cosines[a] with respect to a, b, and c
Proton H_2	$(-)\ 19.0 \pm 0.5$	$(\mp 0.64, \pm 0.77, 0)$
	$(-)\ 28.4 \pm\ \ .5$	$(\pm 0.38, \mp 0.32, \mp 0.87)$
	$(-)\ \ 6.0 \pm\ \ .5$	$(\mp 0.67, \pm 0.55, \mp 0.50)$
Proton H_2'	$(-)\ 19.0 \pm\ \ .5$	$(\mp 0.64, \pm 0.77, 0)$
	$(-)\ 28.4 \pm\ \ .5$	$(\mp 0.38, \mp 0.32, \mp 0.87)$
	$(-)\ \ 6.0 \pm\ \ .5$	$(\mp 0.67, \pm 0.55, \mp 0.50)$
g	$(-)\ \ 2.0032$	$(\mp 0.64, \pm 0.77, 0)$
	$(-)\ \ 2.0052$	$(\mp 0.77, \mp 0.64, 0)$
	$(-)\ \ 2.0051$	$(0, 0, \mp 1.00)$

[a] Uncertainty in angles is estimated to be $\pm 2°$.

Discussion

The Structure of the Radical.—A $p\pi$ radical is one in which the unpaired electron is present in a single localized $2p\pi$ orbital (e.g., $\cdot CH(COOH)_2$ in irradiated malonic acid[1]) or in a delocalized $p\pi$ orbital (e.g. the allyl-type radical HOOC–$\cdot$CH–CH=CHCOOH) in irradiated glutaconic acid.[8] In such radicals, it has been shown both theoretically[11] and experimentally[1,3,8] that the direction of

the minimum value of the g-tensor is perpendicular to the plane of the radical. In the present radical, the direction of the minimum principal value of the g-tensor and the intermediate value of the hf tensors are found to be perpendicular to the HM$^-$ plane, as given by Darlow and Cochran.[9] In addition, the direction of the minimum value of the hf tensor for each proton is very nearly along the C–H bond (actually $\sim 4°$ away from the C–H bond and toward the carboxyl group), as is the case for several other $p\pi$ radicals.[1,3] These facts and the rather small splittings observed[12] indicate that the present radical is a $p\pi$ radical.[2]

The identical hyperfine tensors in Table I and the fact that the directions of their minimum values are practically along the respective C–H bonds indicate that the two protons interacting with the unpaired electron are H_2 and H_2'. This is also borne out by the experimental results with deuteriated KHM (see above).

The principal values of each proton hyperfine tensor in Table I have the same relative signs (all positive or all negative). This is demonstrated by the excellent agreement between the experimental and calculated results in Fig. 1 (lower). In this figure the circles represent the experimentally determined splittings for protons H_2 and H_2' during a rotation of the external magnetic field about the b-axis of the crystal (i.e., $B_0 \perp b$). The solid curve was calculated[1] from the tensors in Table I, with all principal values having the same relative sign. Similar good agreement between experimental and calculated results obtains for rotation of B_0 about the a- and c-axes. The absolute signs of the hyperfine tensors are taken to be negative, in agreement with theoretical considerations[13] and other experimental verifications.[1]

The unpaired spin density ρ_{C_2} on carbon atom C_2 (or C_2') may be estimated by means of the re-

lationship[13] $a_2 = Q\rho_{C_2}$, where a_2 is the isotropic hf component of H_2, *i.e.*, $a_2 = 1/3$ trace of the principal values of the experimental tensor $= (-)1/3$ $(19.0 + 28.4 + 6.0) = (-)17.8$ and $Q = -63$ Mc. One obtains $\rho_{C_2} = \rho_{C_2'} = +0.28$. The choice of a positive spin density for both C_2 and C_2' is supported by the following considerations: (a) H_2 and H_2' have identical hf tensors. The HM^- ion is known to possess a mirror plane perpendicular to the plane of the ion and passing through H_1 and the midpoint of the double bond. The e.m.r. results suggest that a similar symmetry element exists in the present radical. Hence, the spin densities on C_2 and C_2' should be of the same sign. Since the total spin density on the radical must equal $+1.0$, C_2 and C_2' should have positive spin densities.[14] (b) The principal values of the hf tensors and their directions may be estimated for a proton, say H_2, by assuming that H_2 is coupled to the spin density on C_2 both isotropically and anisotropically,[1] and only anisotropically (since H_2 is coplanar with the carbon backbone of the molecule[2]) with the spin densities on adjacent carbon atoms, *i.e.*, C_2' and C_1. The coupling to C_2 may be readily obtained from results of $\dot{C}H(COOH)_2$ in malonic acid.[1] The couplings to spin densities on C_2' and C_1 may be calculated from the work of McConnell and Strathdee.[15] The calculated (details are given elsewhere[8]) hyperfine tensors for H_2 agree well with the experimentally determined tensor only when ρ_{C_2} and $\rho_{C_2'}$ are both positive. For example, choosing $\rho_{C_2} = \rho_{C_2'} = +0.28$, and $\rho_{C_1} = +0.07$ (*i.e.*, assuming that one-third of the remaining spin density is concentrated on C_1) yields these principal values: -20.1, -27.1 and -6.3 Mc. On the other hand, $\rho_{C_2} = +0.28$, $\rho_{C_2} = -0.28$, and $\rho_{C_1} = +0.07$ yields: -16.3, -28.0, -9.3 Mc., while $\rho_{C_2} = +0.28$, $\rho_{C_2'} = -0.28$, and $\rho_{C_1} = -0.07$ yield: -15.5, -27.6, and -10.5 Mc. These calculations, of course, are only approximate since the exact spin density on C_1 is not known. Such calculations (for $\rho_{C_2'} = +0.28$) also indicate that the direction of the minimum value of the hyperfine tensor for each proton lies in the plane of the radical, $3-9°$ away from the $C-H$ bond direction and toward the carboxyl groups, in agreement with experimental results.
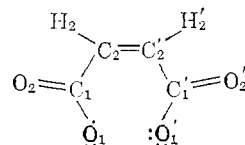
A spin density of $+0.22$ is therefore left for each carboxyl group. It is difficult at this time to estimate the distribution of this density on the various atoms in the carboxyl group. A detailed study of the unpaired spin density distribution on the carboxyl group would require the substitution of C^{13} and/or O^{17} (*i.e.*, isotopes possessing spin) in the group. The presence of considerable spin density on the carboxyl groups is also supported by the g-values observed in the present radical, which are somewhat larger than in other radicals in dicarboxylic acids. This increase in g-value would arise from spin–orbit coupling of the unpaired spin at the oxygen atoms ($\lambda \sim 152$ cm.$^{-1}$ for O while $\lambda \sim 28$ cm.$^{-1}$ for C).[16]

The above related facts strongly suggest that the free radical under study is formed by the removal of a hydrogen atom from the carboxyl groups by the irradiation. The removed hydrogen atom may react with another hydrogen atom to give H_2. The resulting radical would have a pair of elec-

trons in the p_x orbital (taken to be perpendicular to the radical's plane) of one oxygen, say O_1'. The unshared electron at oxygen O_1 is then located in a $p\pi$ orbital, formed by the overlap of atomic p_x orbitals, and extending over atoms $O_1-C_1-O_2-C_2-C_2'-C_1'-O_2'$. Such strong overlap is possible because of the planarity of the molecule. Similar "resonance" structures may be formed by successively placing the paired electrons at O_1, O_2, and O_2'. A weak overlap may also occur between the p_x orbitals on O_1 and O_1'.[17,18]

The present $p\pi$ radical is stabilized by the extensive delocalization of its unpaired electron. No such delocalization can take place in the σ-radical.[12] Hence, its formation is less probable.

On the cis-Configuration of the Radical.—In conclusion, we note that the marked anisotropy in the coupling of a σ- or α-proton,[2] *i.e.*, a proton directly attached to a carbon atom with spin density on it, provides a sensitive way of distinguishing between *cis*- and *trans*-isomers of a radical. It has been found both experimentally[1-3] and theoretically[1,15] that, for a unit positive spin density in a single $p\pi$ orbital of a carbon atom of a $>C'-H$ species, the direction of the minimum principal value (~ 30 Mc.) of the proton hyperfine tensor is along the $C-H$ bond. The direction of the maximum principal value (~ 90 Mc.) is orthogonal to the $C-H$ direction and in the nodal plane of the $p\pi$ orbital. Any small angle change within this nodal plane, therefore, will be accompanied by an experimentally detectable change in the hyperfine splittings.

It was shown in the previous section and elsewhere[8] that the delocalization of the unpaired spin density over several carbon atoms changes somewhat the values and directions of the principal values of the hyperfine tensor. However, for carbon atoms with substantial positive spin densities in this delocalized net, the direction of the minimum value is still, to a good first approximation, along the $C-H$ bond. Thus, in the radical created in irradiated KHM, the direction of the 6 Mc. value is only $4°$ away from the $C-H$ direction as

(14) It is very unlikely that the oxygen atoms in the radical possess extremely large positive spin densities, thereby causing the carbon atoms to have negative spin densities.

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

(16) D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).

(17) The absence of additional e.m.r. lines due to a carboxyl proton and/or free K atoms seems to eliminate possibility that the radical under investigation is $HOOCCH=CHCOO^-$ produced by the removal of an electron from the HM^- ion. However, one cannot completely rule out the possibility that the missing additional splittings are relatively small, *i.e.*, less than 8 Mc. (due, possibly, to a small unpaired spin density on the carbonyl oxygens), and are not resolvable under the experimental conditions.

(18) Preliminary mass spectrometric analyses show that H_2 gas is evolved during the irradiation of KHM. H_2 and HD are given off by irradiated deuterated KHM. The presence of these gases lends support to the identity of the radical adopted in the present work.

determined by X-ray diffraction methods.[9,10] Moreover, the directions of the minimum principal values of protons H_2 and H_2' form an angle of 60° with each other, thus indicating a cis-configuration for the two C–H bonds in the radical. This, in turn, confirms a cis-structure for the parent molecule, assuming that no violent change in the orientation of the molecule occurs during the irradiation.

If the two C–H bonds in the radical were to have a trans-relationship to each other, the angle between the directions of the 6 Mc. values of H_2 and H_2' would have been close to 0°. In fact, the directions of all the principal values of H_2 and H_2' would have been very nearly parallel to each other. In such a case, the e.m.r. spectrum shown in Fig. 2C, in which the splitting due to one proton is 22.5 Mc. and that due to the other is 12.5 Mc., could not have occurred.

Arguments similar to the ones presented here were utilized previously in the study of the structure of an allyl-type radical HOOC–ĊH=CH–·CH–COOH found in X-irradiated glutaconic acid, HOOC–CH=CH—CH₂—COOH. In that case, the e.m.r. results have established that the stable isomer of glutaconic acid is the trans-isomer.

Acknowledgments.—We wish to thank A. Cote of this laboratory for assisting with the taking of the spectra, and M. Valukonis for assisting with some of the computations.

The Secondary Deuterium Effect in CH₃ and CF₃ Addition Reactions

By M. FELD, A. P. STEFANI AND M. SZWARC

The secondary deuterium effect was investigated for the CH₃ and CF₃ addition reactions. The results obtained for the relevant k_D/k_H were

CD₂=CD₂	1.05 for CH₃, 1.07 for CF₃	PhCD=CD₂	1.11 for CH₃, 1.10 for CF₃
CH₃CH=CD₂	1.12 for CH₃, 1.07 for CF₃	CD₂=CDCD=CD₂	1.20 for CH₃, 1.09 for CF₃
CD₃CD=CD₂	1.17 for CH₃, 1.09 for CF₃		

It is concluded that the incipient CH₃ (or CF₃)–C bonds in the respective transition states are relatively long, and that the remaining groups around the reactive center retain their original planar configuration. This conclusion does not appear to be invalidated by the recent argument of Wolfsberg.

The addition of a radical R to an olefinic or aromatic molecule A yields an adduct radical, as shown by the equation R· + A → RA·. The relative rate constant of the addition process k_2 may be related to the atom localization energy of the most reactive center of the substrate. For example, in the addition of CH₃ radicals to aromatic non-substituted hydrocarbons, a linear relation was observed for $\log(k_2/n)$,—n being the number of reactive centers— and the respective atom localization energy.[1] Such a relation was previously reported for the addition of CCl₃ radicals to aromatic hydrocarbons[2] and more recently for the CF₃ radical addition to the same series of substrates.[3] A linear relation between the rate constant and localization energy was also observed for the addition of CH₃ radicals to ethylene, styrene, butadiene, vinyl naphthalene, etc.[4,5] The existence of such relations was interpreted as an indication of the formation of an incipient, covalent R–C bond in the transition state of the addition.

The formation of an incipient bond between the radical R and the reactive carbon center of the substrate eventually leads to a rearrangement around this center; i.e., its original planar trigonal configuration is transformed into a tetrahedral one. The question arises, however, to what extent does such a change take place in the transition state. If the incipient R–C bond is relatively long, the configuration of the other groups around the reaction center should remain planar, but if its length approaches that characterizing the C–R of the final state, then the configuration in the transition state will be tetrahedral.

In order to get some information pertinent to this problem, we decided to investigate the secondary deuterium effect in the radical addition reaction. It was pointed out by Streitwieser[6,7] that the relatively soft out of plane C–H vibration of a trigonal carbon is transformed into a harder bending vibration in a tetrahedral carbon. For such a change, one calculates the ratio k_D/k_H for a reaction involving a $=C\begin{smallmatrix}H\\H\end{smallmatrix}$ center to be 1.82 at 65°. One may expect, therefore, that a value of k_D/k_H close to unity would indicate a planar transition state and a long R–C bond, whereas if k_D/k_H is close to 1.82, the configuration around the reactive center in the transition state should be essentially tetrahedral.

The first attempt to utilize this technique for the study of the transition state of radical addition reactions was reported by Matsuoka and Szwarc.[8] They determined the k_D/k_H ratio for the addition

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