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ELECTRON SPIN RESONANCE SPECTRA OF FREE RADICALS  
TRAPPED IN  $\gamma$ -IRRADIATED HYDROGEN BONDED SYSTEMS

KEY WORDS: Electron Spin Resonance, oriented free radicals.

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INTRODUCTION

A number of acid salts of simple dicarboxylic acids crystallize with their molecules linked into infinite chains by "very short" hydrogen bonds. In this type of H-bond two oxygen atoms, belonging to adjacent molecules are related by a centre of symmetry or by other symmetry element, and the proton lies on the symmetry element. These structures have been referred to as Type A<sub>2</sub> structures and present a characteristic i.r. spectrum of Hadzi's type <sup>1</sup>. Examples of salts showing

this behaviour are given by the potassium hydrogen malonate (KHM)<sup>2</sup>, potassium hydrogen succinate (KHS)<sup>3</sup> and potassium hydrogen glutarate (KHG)<sup>4</sup>, whose crystal structures have been studied by J.C. Speakman and his coworkers.

Information about the nature of the hydrogen bond may be obtained from the ESR and ENDOR spectra of single crystals in which some of the molecular units are substituted by free radicals. This can be obtained as result of  $\gamma$  or X ray irradiation and KHM has been studied by these techniques<sup>5</sup>.

In this paper we report the results of an ESR investigation of  $\gamma$ -irradiated single crystals of KHS and KHG which present some interesting aspects we will discuss; in particular the ESR investigation shows that in contrast to several other cases the damaged molecule re-orientates itself in the crystal lattice and the stable free radical which is formed upon irradiation does not occupy the expected position. In KHS and KHG the C-H bond of the stable radical which is formed upon irradiation is not as usually along the direction which bisects the angle  $\widehat{HCH}$  of the undamaged molecule. The possible causes of this rearrangement will be also discussed.

EXPERIMENTAL

Single crystals of KHG and KHS were grown from an aqueous solution; they were irradiated at room temperature by  $\gamma$  rays from  $^{60}\text{Co}$  source at a dose of 2 Mrad (KHG) and 10 Mrad (KHS).

The ESR spectra were recorded with a JEOL PE-3X spectrometer by mounting the crystal on a simple goniometer which allowed the crystal to be rotated around an axis perpendicular to the direction of the magnetic field.

The crystallographic axes a, b and c, were used as reference frame in both cases.

RESULTS AND DISCUSSION

The ESR spectrum of  $\gamma$ -irradiated single crystals of KHS consists of eight lines due to the hyperfine splitting by a single proton with an anisotropic coupling and by other two protons with slightly different and almost isotropic interaction. The spectrum is consistent with the presence of  $\text{--OOC-CH-CH}_2\text{-COO--}$  radicals having an  $\alpha$  proton and two unequivalent  $\beta$  protons.

At arbitrary orientations the spectrum is complicated by the presence of two unequivalent sites in the

crystal lattice whose splittings coincide when the field is along the monoclinic twofold axis *b* or it is perpendicular to *b*.

The  $\alpha$  proton tensor in the abc system, its principal values and principal directions are reported in the Table 1.

$\gamma$ -irradiated single crystals of KHG give ESR spectra due to the superposition of spectral lines due to two different radicals I and II (Fig. 1A).

The spectrum with the largest hyperfine splittings (I) is attributed to the radical  $-\text{OOC-CH-CH}_2-\text{CH}_2-\text{COO}-$ ; it consists of an anisotropic doublet ( $\alpha$  proton) of triplets 1:2:1 (two equivalent  $\beta$  protons). When the crystal is rotated around *a* and *b* crystallographic axes, the spectrum due to a single site is recorded; when the crystal is rotated around *c*, two magnetically inequivalent sites are detected. The presence of two different radicals in the crystal lattice makes difficult to measure the small anisotropy of the  $\beta$  proton coupling. The measure of h.c.c.'s along the three crystallographic axes allows to get the isotropic part of h.c.c., reported in Table 1.

The  $\alpha$  proton tensor, its principal values and principal directions of the radical  $-\text{OOC-CH-CH}_2-\text{CH}_2-\text{COO}-$  are collected in Table 1.

TABLE I  
Proton Tensors (MHz) and Direction Cosines from ESR Data

Proton	Isotropic value	Diagonal Elements	Direction Cosines in the abc System		
KHS α proton	-59.5	-26.6	0.668	±0.666	0.332
		-93.8	0.237	±0.235	-0.943
		-58.2	-0.675	±0.675	0.000
KHG I radical α proton	-57.8	-26.0	±0.156	0.350	0.923
		-91.6	±0.984	0.025	0.176
		-55.7	±0.085	0.936	-0.341
KHG I radical β proton	-97.2				
KHG II radical triplet h.c.c.		±17.1	0.000	0.730	0.684
		±35.0	1.000	0.000	0.000
		±35.3	0.000	-0.684	0.730

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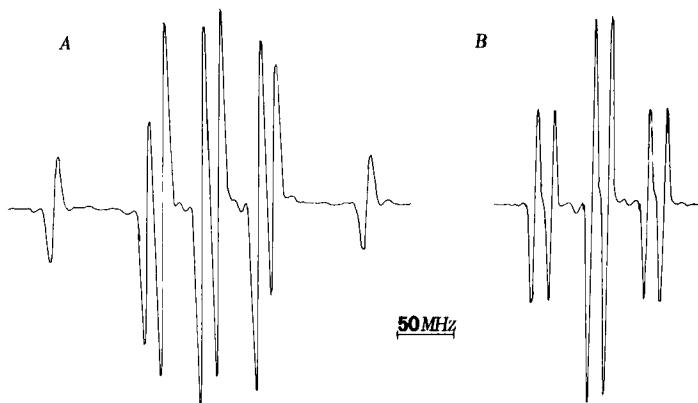


FIG. 1

ESR spectrum of room temperature  $\gamma$ -irradiated single crystal of K-H glutarate, the magnetic field is along the b axis of the crystal structure; A) just after a 2 Mrad dose irradiation; B) after aging.

Radical II has a spectrum which consists of a triplet 1:2:1 of doublets, the latter with a small ( $\sim 2$  G) splitting which for most orientations is not resolved. Radical II is the most stable radical, which is the only one one left in crystals aged for months (Fig. 1B). The hyperfine tensor of the triplet is reported in Table 1.

In the crystal structures of both KHS and KHG the molecules are planar, i.e. the carbon and oxygen atoms lie in the same plane, they are bonded by hydrogen bonds into infinite chains. For KHG all the molecules of a chain are coplanar while in KHS successive residues form an angle of  $79^\circ$ .

Quite generally the carbon centered  $\pi$  radicals formed in a molecular crystal by abstraction of a hydrogen atom from a methylene group, occupy in the crystal lattice the same position as the undamaged molecules. The only difference consists in a rearrangement of the bonds around the carbon atom which changes its hybridization from  $sp^3$  to  $sp^2$ . In particular the C-H bond is found in the direction bisecting the  $\widehat{HCH}$  angle in the undamaged molecule<sup>6</sup>. Fig. 2 shows for KHS the expected position of the  $-\text{OOC-CH-CH}_2\text{-COO}^-$  radical according to the above criteria (open circles).

As it is well known the principal directions of the  $\alpha$  proton hyperfine tensor corresponding to the prin-

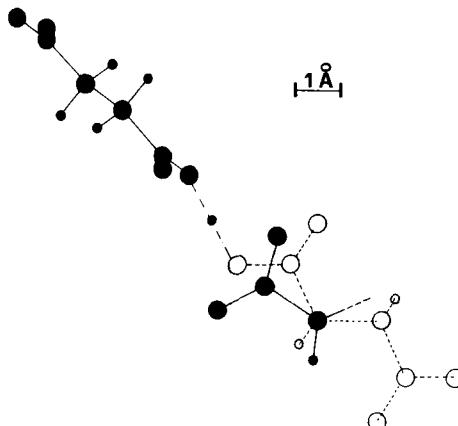


FIG. 2

Relative positions of the KHS radical and the neighbour molecule, projected on the plane of the radical. Open circles represent the expected position of the radical, full circles the position of  $-\text{CH-COO}^-$  determined by ESR assuming the  $sp^2$  carbon atom in the same position as in the undamaged molecule.

cipal values (-30, -60, -90 MHz) are to be attributed to the directions of the C-H bond, the  $p_z$  orbital and a direction perpendicular to both. It is then possible to have from ESR the orientation of the free radical which is shown also in Fig. 2 for KHS (full circles).

Fig. 3 shows the same features for KHG.

In both cases the  $p_z$  orbital is as expected perpendicular to the molecular plane and the C-H bond is in this plane; however the latter makes an angle of  $22 \pm 5^\circ$  for KHG and  $30 \pm 5^\circ$  for KHS with the expected direction. We believe that this effect is due to the perturbation

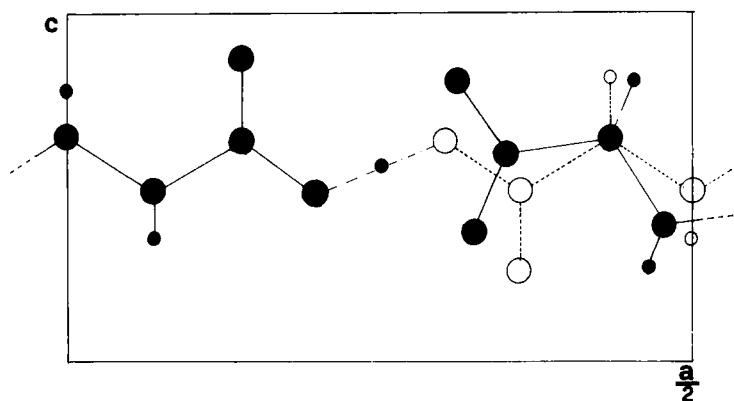


FIG. 3

Relative positions of the KHG radical and the neighbour molecule, in the ac crystallographic plane. Open circles represent the expected position of the radical, full circles the position of  $-\text{CH}-\text{COO}^-$  fragment as determined by ESR assuming the  $\text{sp}^2$  carbon in the same position as in the undamaged molecule.

of the "very short" hydrogen bond between adjacent molecules. The small rearrangement of  $sp^2$  bonds around the carbon carrying the unpaired electron, would force the carboxylic group and hence the oxygen atom to move from his position. This would destroy the symmetry of the "very short" hydrogen bond and the flat potential energy well typical of symmetric H bonds would be distorted<sup>7</sup>.

The lowest energy conformation compatible with the new hybridisation is then achieved. In the hypothesis that the  $sp^2$  carbon atom occupies the same position as in the undamaged molecules, in the conformations of both radicals the two oxygen atoms of the carboxylic group are nearly symmetrically placed with respect to the oxygen atom of the adjacent undamaged molecule.

protons anisotropic h.c.c.s. could give detailed information on the structures of the residue of the radicals. We got only the isotropic h.c.c. of protons of the KHG I radical. From the well known relation

$$A_H^\beta = B_0 + B \cos^2 \theta$$

using for  $B_0$  and B the values of 9 and 122 MHz as for the similar radical produced in glutaric acid<sup>8</sup> we get a

dihedral angle of 30° between the  $p_z$  orbital axis and the C-H bonds.

Therefore in the KHG radical the coplanarity of the heavy atoms is conserved. On the contrary the two different h.c.c's of protons of KHS radical prove that in this case the coplanarity is not conserved. The ENDOR spectra of free radicals produced by x irradiation of glutaric acid<sup>8</sup>, showed that two radicals are formed also in that case. The two radicals have the same structure, the only difference being the different angle formed between the carboxylic group and the skeleton of the radical. This is not the case for the KHG I and II radicals. Radical I has the structure similar to that of the two radicals in glutaric acid, while II has a completely different structure, as shown by the magnitude and anisotropy of h.c.c's.

ENDOR spectroscopy allowing to measure small h.c.c's could provide the key for the determination of the nature of the radical.

Furthermore it could provide further information about the nature of the hydrogen bond from the measure of the hyperfine interaction of the proton of the H-bond with the unpaired electron. An ENDOR investigation is hence in program.

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