

## ESR Study of OH Radicals in Irradiated Lithium Acetate Dihydrate Single Crystals

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The OH radicals originating from water of crystallization were identified in an irradiated single crystal of lithium acetate dihydrate. The OH radicals in two sites are related by the crystal symmetry. The principal values of the  $g$  tensor were determined to be (2.0038, 2.0071, 2.0457) and of the hyperfine tensor to be (-22.3, -45.8, +7.2) G. From the principal directions OH radicals appear to be formed from the water of crystallization located between the two planes of acetate ions in the crystal. The  $g_{\max}$  value indicates that a strong interaction of the trapped radical with the surrounding molecules exists. The energy separation of the two OH oxygen  $p\pi$  orbitals was estimated to be  $1.3 \cdot 10^{-10}$  erg.

### INTRODUCTION

Few reports of hydroxyl radicals OH in irradiated hydrate crystals have appeared. Such radicals were first observed by Gunter (1) in irradiated  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{LiSO}_4 \cdot \text{H}_2\text{O}$ . More recently, Toriyana and Iwasaki (2) found OH radicals in single crystals of irradiated alkaline metal salts of maleic and fumaric acids. We now report observation of these radicals in irradiated lithium acetate dihydrate ( $\text{LiAc} \cdot 2\text{H}_2\text{O}$ ), the first example of OH radical formation in hydrated salts of saturated carboxylic acids. In contrast to irradiated sodium hydrogen maleate trihydrate (2), there is only a single kind of OH radicals present in two sites related by crystal symmetry. It is assumed that OH radicals are formed from the water of crystallization located between the two planes of acetate ions. In  $\text{LiAc} \cdot 2\text{D}_2\text{O}$ , the OD species has not definitely been identified although the spectrum is altered by isotopic substitution.

### EXPERIMENTAL

Single crystals of  $\text{LiAc} \cdot 2\text{H}_2\text{O}$  were grown from aqueous solution by slow evaporation at room temperature. Deuterated crystals were obtained by the same procedure from a heavy water solution. The unit cell of the  $\text{LiAc} \cdot 2\text{H}_2\text{O}$  is orthorhombic (3), space group  $Cmm$ , dimensions  $a = 6.82 \cdot 10^{-8}$  cm,  $b = 10.83 \cdot 10^{-8}$  cm,  $c = 6.62 \cdot 10^{-8}$  cm. The unit cell contains four molecules. Crystals used for the experiments had well defined faces. The axes were identified by analysis of X-ray diffraction patterns.

Single crystals were irradiated at 77°K in a  $^{60}\text{Co}$  source to doses of 1-10 Mrad. The ESR spectra were recorded at 77°K using a Varian V4502 X-band spectrometer operated at 100 KHz modulation. The angular dependence of the spectra was measured

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at  $5^\circ$ – $10^\circ$  intervals by rotation of the crystals about the three orthogonal axes. The signals of  $Mn^{2+}$  in ZnS, or DPPH were used to calibrate accurately the magnetic field.

#### RESULTS AND DISCUSSION

The ESR spectra measured at low microwave power (22 mW) were complex and included the species  $CH_3\cdot$  and  $\dot{C}H_2CO_2^-$  (4). However, those obtained at high microwave power (20 mW) were simplified due to the shorter spin-lattice relaxation time of the OH radicals. Figure 1 shows the ESR spectrum of a single crystal of  $LiAc \cdot 2H_2O$

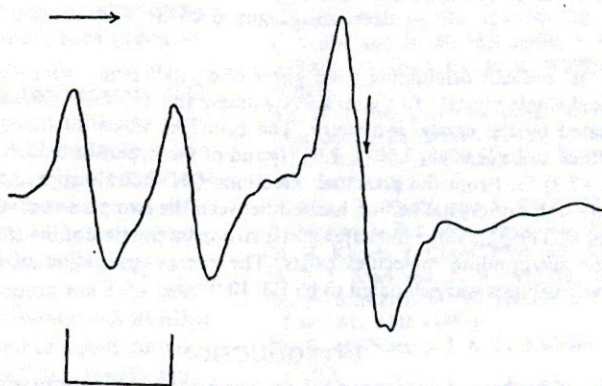


FIG. 1. ESR Spectrum of a single crystal of  $LiAc \cdot 2H_2O$   $\gamma$ -irradiated at  $77^\circ K$ . Measurements were made with magnetic field perpendicular to the  $b$  axis and with an angle ca.  $120^\circ$  from the  $c$  axis. The microwave power was 20 mW. The vertical arrow indicates the position of the signal of DPPH. The single line near the position of DPPH is the spectrum due to the other unidentified radical. The length of the horizontal arrow corresponds to 20 G.

irradiated at  $77^\circ K$ , the magnetic field being applied perpendicular to the  $b$  crystallographic axis with an angle of ca.  $120^\circ$  from the  $c$  crystallographic axis. The strong two-line spectrum analyzed as a doublet hyperfine splitting (indicated by the solid lines), is due to the OH radicals. Note that an additional species (as yet unidentified) with a single line spectrum occurs several gauss to the low field of the DPPH signal. The principal values and directions of the  $g$  and hyperfine tensors were obtained by the first order perturbation treatment with the least-squares fitting of the observed data (5). The results are listed in Table 1. The two inequivalent sites of OH radicals are revealed by the two sets of signs of the principal axes of the  $g$  and hyperfine tensors with respect to the  $a$  and  $b$  crystallographic axes. The principal values of the  $g$  and hyperfine tensors are very close to those previously reported for OH radicals in hydrated crystals (1, 2) and of water in ice (6).

It is well known that for OH radicals the  $g$  and hyperfine tensors have the same principal axes (1, 2, 6), accordingly the  $g_{max}$  and  $A_{min}$  are to be along O–H bond, the  $g_{min}$  and  $A_{int}$  axis along the  $O_{2p}$  unpaired electron orbital, and the  $g_{int}$  and  $A_{max}$  axis perpendicular to the O–H bond and the  $O_{2p}$  orbital. The data in Table 1 within an experimental error of  $\pm 5^\circ$  confirm the analysis of the OH radical.

Although the analysis of the angular dependence gives a sufficiently accurate hyperfine principal value (45.8 G) and the direction of the maximum element, smaller principal

TABLE 1

THE PRINCIPAL VALUES AND DIRECTIONS OF THE  $g$  AND HYPERFINE TENSORS FOR THE OH RADICALS IN  $\gamma$ -IRRADIATED LITHIUM ACETATE DIHYDRATE<sup>a</sup>

Principal values <sup>b</sup>	Direction cosines ( $a, b, c$ )		
	$l$	$m$	$n$
$g_{\max} = 2.0457$	$\pm 0.80$	$\pm 0.60$	0.00
$g_{\min} = 2.0038$	$\mp 0.60$	$\pm 0.80$	0.00
$g_{\text{int}} = 2.0071$	0.00	0.00	0.00
$A_{\min} = +7.2$	$\pm 0.80$	$\pm 0.60$	0.00
$A_{\text{int}} = -22.3$	$\mp 0.80$	$\pm 0.80$	0.00

<sup>a</sup> The errors are  $\pm 2$  G for the hyperfine splitting,  $\pm 0.001$  for the  $g$  values, and  $\pm 8^\circ$  for the directions.

<sup>b</sup> Theoretical sign is indicated for principal values of the hyperfine tensor.

values including their signs and directions are hard to determine accurately from these experiments, since the resolution of spectra at the  $ab$  orientation of the crystal is rather poor and the spectra of the other radical species interfere.

The small observed  $g_{\max}$  value indicates a large difference in the energy separation between the unpaired electron orbital  $2p_x$ , and the lone pair orbital  $2p_y$ , of the oxygen atom. The energy separation was estimated at  $1.3 \cdot 10^{-10}$  erg for  $g_{\max} = 2.0457$ , using the spin-orbital coupling constant of  $139.7 \text{ cm}^{-1}$  for oxygen (7). This value should be compared with  $0.98 \cdot 10^{-10}$  erg ( $g_{\max} = 2.0618$ ) and  $0.47 \cdot 10^{-10}$  erg ( $g_{\max} = 2.1198$ ). For OH radicals in sodium hydrogen maleate trihydrate (2) the increase in energy separation indicates that the OH radicals in  $\text{LiAc} \cdot 2\text{H}_2\text{O}$  are trapped in the lattice with a strong interaction with the surrounding molecules.

In the  $\text{LiAc} \cdot 2\text{H}_2\text{O}$  crystal, one hydrate molecule lies between the two acetate ion planes and forms hydrogen bonds with the second kind of water molecule which is in the acetate ion plane itself. These latter water molecules are hydrogen bonded to the oxygen atoms of two acetate ions (3).

The direction cosines of the  $g$  and hyperfine tensors (Table 1) indicate that the OH radicals lie in the  $ab$  crystallographic plane and hence perpendicular to the plane of the acetate ions. From the principal directions it can be ascertained that the OH bonds in these two sites make an average angle of  $60^\circ$  ( $120^\circ$ ). Furthermore, the OH bonds of the radical are only displaced  $17^\circ$  away from the OH bonds in the undamaged  $\text{H}_2\text{O}$  molecules that lie between the acetate planes. If the OH bond "relaxation" is assumed to occur in a position only somewhat displaced from the original water molecule,<sup>1</sup> a direct hydrogen oxygen bond fission is a reasonable model. Accordingly we postulate that the OH radicals observed in irradiated  $\text{LiAc} \cdot 2\text{H}_2\text{O}$  arise by scission of the two unequivalent OH bonds of the water molecules that lie in the  $ab$  plane of the crystal

<sup>1</sup> Note that the temperature of the irradiated crystals did not rise significantly above  $77^\circ\text{K}$  (liquid nitrogen) in rapid transfer from irradiation dewar to the dewar in the ESR cavity.

lattice, leading to two different sites for hydroxyl radicals. In this location the OH radicals will be strongly hydrogen bonded as predicted by the relatively large energy separation of the OH<sub>oxygen</sub> unpaired electron and lone pair orbitals.

The complexity of the spectrum from the deuterated crystals even at high power (20 mW) has so far made it impossible to analyze the expected triplet splittings. However, there is a distinct change of the hyperfine structure which can be explained by the replacement of H by D atoms in the OH radicals.

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