ESR AND OPTICAL SPECTRAL STUDIES
OF γ-IRRADIATED LITHIUM ACETATE DIHYDRATE

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Gamma irradiation of lithium acetate dihydrate single crystals at room temperature reveals initially an intense ESR signal due to $\dot{C}H_2CO_2^-$ radicals. On standing, these radicals disappear and $R\dot{C}HCO_2^-$ radicals are formed. UV and IR absorption spectra of irradiated crystal samples are discussed and correlated with the postulated $\dot{C}H_2CO_2^-$ and $R\dot{C}HCO_2^-$ radicals.

1. Introduction

Extensive studies of the ESR spectra of paramagnetic fragments resulting from radiation damage in metallic acetates have been reported for several systems. Irradiated sodium acetate [1–5] and zinc acetate [5–8] form methyl radicals at liquid nitrogen temperatures. In zinc acetate this radical disappears with the concomitant appearance of $\dot{C}H_2CO_2^-$ as a product of hydrogen abstraction from an acetate ion [6]. In all metallic acetates which have been investigated, the $\dot{C}H_2CO_2^-$ radical is relatively stable and does not undergo further transformation.

The present ESR investigation confirms the existence of the $\dot{C}H_2CO_2^-$ radical in irradiated $CH_3COOLi \cdot 2H_2O$ and $CH_3COOLi \cdot 2D_2O$. However, in these crystals $\dot{C}H_2CO_2^-$ is unstable and is readily transformed to $R\dot{C}HCO_2^-$, which has not been observed in other metal acetates. The ESR spectra of the light water and deuterated crystals do not differ in their essentials. The UV and IR absorption spectra support the presence of $\dot{C}H_2CO_2^-$ and $R\dot{C}HCO_2^-$ radicals.

The unit cell of the lithium acetate dihydrate is orthorhombic [9], space group C_{MMM}; dimensions are $a = 6.82$ Å, $b = 10.88$ Å, $c = 6.02$ Å. The unit cell con-

tains four molecules. Single crystals were irradiated at room temperature by a ^{60}Co γ-source to a dose of 1–5 Mrads. Over this range, the shapes of ESR spectra recorded at room temperature as first derivative absorption curves using a Varian V4502 X-band spectrometer with a variable temperature accessory were independent of dose. The ESR data used were defined with a least squares treatment. Calculations were made on a CDC-3600 computer.

Both UV and IR observations were performed at room temperature. The UV absorption spectra were obtained on a Beckmann DK-1A spectrophotometer, using a non-irradiated single crystal as a reference in the double beam technique. The IR measurements were made on a double beam Zeiss Model UR-10 spectrophotometer, using the KBr disks technique and the procedure given by Hartman and Hisatsune [10].

2. The $\dot{C}H_2CO_2^-$ radical

Irradiation of single crystals of $CH_3COOLi \cdot 2H_2O$ and $CH_3COOLi \cdot 2D_2O$ at room temperature produces an intense 1:2:1 triplet, observed at room temperature in all orientations. This triplet is attributed to the $\dot{C}H_2CO_2^-$ radical, which also is found in other metal acetates [1–8,11]. At room temperature, the two protons of the methylene group are equivalent because of the rapid rotation of that group around the C–C bond.

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Table 1

Proton hyperfine interaction and g-tensors in $\dot{C}H_2CO_2^-$ and $R\dot{C}HCO_2^-$ radicals in γ-irradiated lithium acetate dihydrate

Radical	Principal values [a]	Isotropic value	Anisotropy	Principal axes direction cosines		
$\dot{C}H_2CO_2^-$	27.1 [a] (G)		(−) 0.55	1.00	0.00	0.00
	(−)20.8 [a] (G)	(−) 21.6 (G)	(+) 0.08	0.00	1.00	0.00
	16.8 [a] (G)		(+) 0.48	0.00	0.00	1.00
	2.0030 [b]			1.00	0.00	0.00
	2.0024 [b]	2.0028		0.00	1.00	0.00
	2.0031 [b]			0.00	0.00	1.00
$R\dot{C}HCO_2^-$	27.7 [a] (G)		(−) 0.97	±0.83	0.00	±0.56
	(−)16.6 [a] (G)	(−) 18.0 (G)	(−) 0.14	0.00	1.00	0.00
	9.9 [a] (G)		(+) 0.81	±0.56	0.00	∓0.83
	2.0044			1.00	0.00	0.00
	2.0025	2.0036		0.00	1.00	0.00
	2.0038			0.00	0.00	1.00

[a] Theoretical signs are indicated for the tensor components.

[b] All principal values, except the intermediate one, and the corresponding direction cosines are approximate because of small anisotropy.

The proton hyperfine tensor of the $\dot{C}H_2CO_2^-$ radical in lithium acetate dihydrate is given in table 1. Its calculated isotropic value is in good agreement with those reported for the α-proton [12]. However, all reported values are slightly below 22.5 G, established for an ideal σ-π interaction [13]. The difference indicates that the spin density on the methylene C-atom is approximately 0.9.

Taking into account that the C–C bond direction of the $\dot{C}H_2CO_2^-$ radical is in the direction of the b-axis, and using the calculation valid for an ideal sp^2 structure, the principal values of 16.8 G and 27.1 G from table 1 can be transformed into the in-plane values [5] of the individual protons: A_H = 6.6 G and A'_H = 33.0 G. Here, A_H and A'_H are components along and perpendicular to the CH bond, respectively.

The ESR spectra of lithium acetate dihydrate, observed at a temperature below 230°K immediately after irradiation, reveal a 1:1:1:1 quartet instead of the 1:2:1 triplet found at room temperature. This transformation is due to the completely hindered rotation of the methylene group in $\dot{C}H_2CO_2^-$ radicals.

3. The $R\dot{C}HCO_2^-$ radical

Fig. 1b shows the ESR spectrum of the same sample as in fig. 1a, in the same orientation, but after four days standing at room temperature. It can be seen that two intense lines with an intensity ratio 1:1 appear, in addition to the faint lines of the triplet 1:2:1 of the $\dot{C}H_2CO_2^-$ radical. We postulate that the radical responsible for the long-lived two line spectrum is the planar species $R\dot{C}HCO_2^-$ with the hydrogen atom in the plane of acetate ions.

In table 1 the proton hyperfine tensor in the $R\dot{C}HCO_2^-$ radical is given.

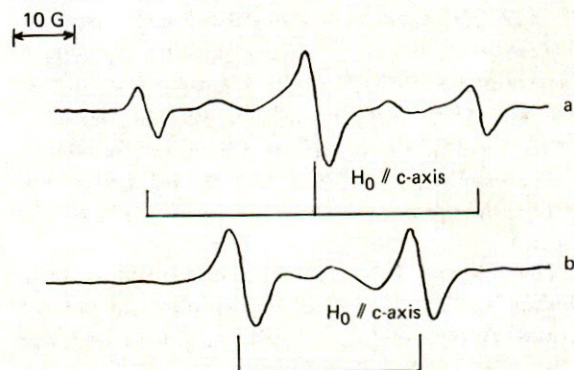The angular dependence of the proton hyperfine tensor (table 1) was readily interpreted in terms of the

Fig. 1. ESR spectra of lithium acetate dihydrate, γ-irradiated at room temperature, (a) immediately after irradiation, (b) four days after irradiation.

α-proton in an $R\dot{C}HCO_2^-$ radical which has two magnetically nonequivalent CH bonds. These CH bonds lie in the bc plane and make an angle of $124°$ with the C–C bond along the b axis which is in agreement with the value of $120°$ for an ideal sp^2 structure.

The observed isotropic value of 18.0 G indicates that the electron spin density of the CH carbon is reduced to approximately 70% of its full value.

The nature of the group R cannot be specified as no hyperfine structure is produced by this group. We submit that R might be CO_2^-. This is the only group which can arise in the solid system without assuming a too complicated radical formation mechanism or suggesting a very complex radical structure. The relatively simple shape of the ESR spectrum in fig. 1b is not inconsistent with a CO_2^- group. Thus, the radical responsible for the observed doublet could be the $\dot{C}H(CO_2^-)_2$ species. A comparison of the spin density on the CH fragment in several similar solid systems supports this assumption. For example, the spin density on the CH fragment in $HOOC\dot{C}HCOOH$ (1 M) [14] is approximately 90% of its full value. In the case of $^-OOC\dot{C}HCOOH$ the spin density decreases to about 80% [15], so that a further decrease could be expected for $^-OOC\dot{C}HCOO^-$. Thus, the spin density value in the observed radical, about 70% of the full value, is a reasonable result for $\dot{C}H(CO_2^-)_2$. However, the group R does affect the spin density at the CH-carbon as is seen from a comparison with the $\dot{C}H_2CO_2^-$ radical.

4. Formation of the $CH(CO_2^-)_2$ radical

To obtain information about the formation of the $R\dot{C}HCO_2^-$ radical, we observed the ratio $\dot{C}H_2CO_2^-$ / $R\dot{C}HCO_2^-$ as a function of time. In the course of several days after irradiation the ESR spectra were recorded at low power levels. From the doubly integrated spectra we deduced that about one (1 ± 0.2) $R\dot{C}HCO_2^-$ radical is formed for each $\dot{C}H_2CO_2^-$ which disappears.

For comparison we observed the ESR spectra of zinc acetate dihydrate and sodium acetate trihydrate single crystals. In contrast to the ESR spectra of lithium acetate no evidence of the presence of the $R\dot{C}HCO_2^-$ was found. This notable difference between the ESR spectra is probably due to the different crys-
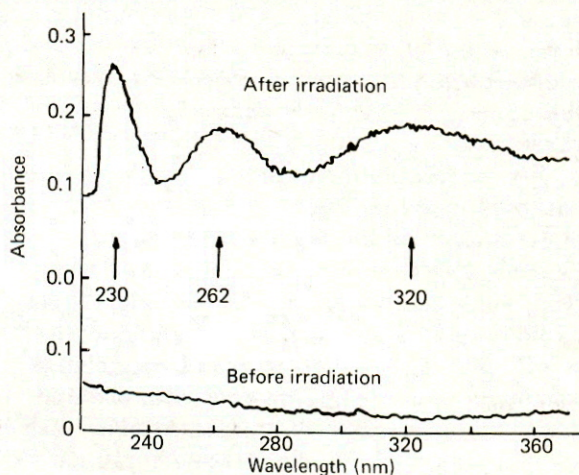

Fig. 2. UV absorption spectra of γ-irradiated lithium acetate dihydrate single crystal.

tal structures of the acetates [9,16]. A similar effect has been noted when secondary radicals are formed in the three crystal forms of glycine [17,18]. It is felt that the exceptional behaviour of lithium acetate among other acetates (i.e., $R\dot{C}HCO_2^-$ formation) is due to the fact that the C–C bonds in all acetate ions are co-linear with the b axis [9].

5. Optical spectra

5.1. UV spectra

The UV absorption spectra of irradiated single crystals were recorded in order to obtain additional information on the species formed. The intensities of all three bands in fig. 2 increase when the absorbed dose increases, but decrease when the temperature is increased. These facts indicate that all three bands belong to the same radical species. We attributed these bands to the trapped radicals $\dot{C}H_2CO_2^-$ and $R\dot{C}HCO_2^-$. In both $\dot{C}H_2CO_2^-$ and $R\dot{C}HCO_2^-$ electrons from the carboxyl carbon and oxygen conjugate with the unpaired electron of the α-carbon to form a π-electron system.

The absorption peak at 230 nm is attributed to a transition from the ground state of this π-system to an excited state ($\pi \rightarrow \pi^*$). On the other hand, in the carboxylate anion $-C\langle{}^O_{O^-}$, in analogy with isoelectronic nitro group, there is an interaction between the n-orbitals in the isolated oxygen atoms. This interac-

tion is caused by the proximity of the oxygen atoms and leads to symmetric and antisymmetric combinations, n_s and n_a, which have slightly different energies because of non-bonding interactions [19].

The absorption peaks at 262 and 320 nm might be due to the transitions of the electrons from the n_s and n_a orbitals, respectively, to an excited state ($n_s \rightarrow \pi^*$, $n_a \rightarrow \pi^*$). Therefore, we concluded that three optical absorptions near 230, 260 and 320 nm may be used to characterize trapped radicals of the form $R_1 R_2 \dot{C} COO^-$ in nonconjugated organic solids. This interpretation is consistent with that of Shields et al. [20] of the spectra of X-irradiated amino acids; they suggested it for the absorptions near 250 and 350 nm for the acid form $R_1 R_2 \dot{C} COOH$. In the $-COOH$ group there is only one n-orbital, because no combination of the orbitals of the isolated oxygen atoms are possible [19]. Therefore, in the radicals of the $R_1 R_2 \dot{C} COOH$ type only the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions are anticipated [20].

In order to verify our deduction, we have also recorded the spectrum of γ-irradiated glycine. The irradiated sample of glycine contains $\dot{C}H_2 CO_2^-$ and $R\dot{C}HCO_2^-$ radicals [17,18]. Thus, one would expect all three peaks in the UV spectrum as in lithium acetate. Indeed, the spectrum of irradiated glycine with peaks at 232, 260 and 315 nm, is very similar to that of lithium acetate. Shields et al. [20] reported only two peaks (at 240 and 365 nm) in the UV spectrum of X-irradiated glycine. It might be that in the latter case, because of different irradiation conditions, only the $\dot{C}H_2 COOH$ radicals are formed and their spectrum overlaps that of the radical $\overset{+}{N}H_3 \dot{C}HCOO^-$. The fact that the absorption spectra remain unchanged if the irradiated samples are left four days at room temperature is in agreement with the hypothesis derived from the ESR data on the transformation of the $\dot{C}H_2 CO_2^-$ into the $R \cdot \dot{C}HCO_2^-$ radicals.

5.2. IR spectra

Fig. 3 shows the IR spectrum of γ-irradiated lithium dihydrate (A). For comparison the spectra of glycine (B) and sodium formate (C) are also given. There is no new peak at the position of the $\dot{C}O_2^-$ absorption in the spectrum of irradiated lithium acetate or in that of irradiated glycine. If the three peaks observed in the corresponding UV spectra originate from
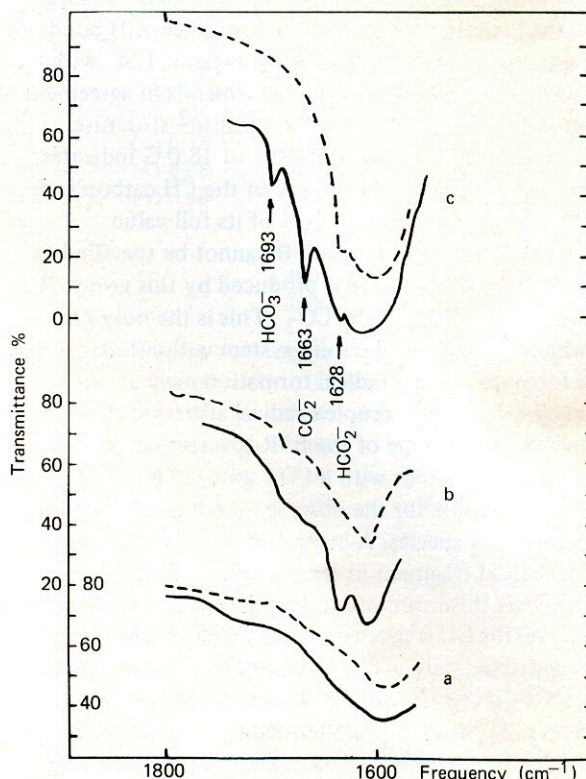

Fig. 3. IR absorption spectra of γ-irradiated (a) lithium acetate dihydrate, (b) glycine and (c) sodium formate. Dotted lines correspond to the unirradiated samples. The spectra are shifted downwards for each successive spectrum.

the $\dot{C}O_2^-$ radical, one can then expect to observe the peak near 1660 cm^{-1} in the IR spectra. On the other hand, the absence of the CO_2^- peak is consistent with our finding as its presence is not detected by the more sensitive ESR measurements.

Acknowledgement

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