

# Electron Spin Resonance Study of $\gamma$ -Irradiated Single Crystals of Ammonium Oxalate Monohydrate

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Free radicals produced in a single crystal of ammonium oxalate monohydrate by  $\gamma$  irradiation have been investigated with the method of electron spin resonance. At 77°K three different species are found: B,  $^{-}\text{O}_2\text{CCO}_2$ ; C,  $[\text{HOCCO}_2]^{-}\cdot$ ; and radical pairs (D). The spin-spin interaction comes from different radicals B and C. On heating, the radical pairs vanish first. At temperatures above 190°K concentration of species C decays. At room temperature, two radical species are detected: A,  $^{-}\text{O}_2\text{CCOH}^{-}$ , and B. Radicals denoted as A are more stable than species B.

## Introduction

Dicarboxylic acids and their salts are suitable model systems for studying the influence of hydrogen bonds in the radiation damage processes in solids. Particular interest in oxalic acid arises from the fact that it is a parent compound of many derivatives and metal salts and that it is the first member of a homologous series of dicarboxylic acids. This interest is enhanced by the fact that both chemical forms of oxalic acid (anhydrous and dihydrated) and many oxalate salts can be readily obtained as pure crystals of known structure.

Radiolytic behavior of oxalic acid in aqueous solution is a useful tool for large-dose dosimetry, and to some extent this is also the case with solid oxalic acid and oxalates. These compounds in the solid state can be used even in the more difficult dosimetric conditions (multimegarad doses of mixed-pile radiations), although the chemistry of the solid compounds is less studied, and also less understood, than that of their aqueous solution.

Our earlier esr work<sup>2</sup> was concerned with the general considerations on the radiation processes in oxalates. Several authors have already studied single crystals of some of these substances, like oxalic acid, anhydrous and dihydrate,<sup>3a</sup> urea oxalate,<sup>3b,4</sup> sodium hydrogen oxalate,<sup>5</sup> and hydrazinium hydrogen oxalate.<sup>6</sup> The present work is an attempt to understand better the paramagnetic species formed in ammonium oxalate monohydrate (Am-Ox) and the processes in this substance upon irradiation.

## Experimental Section

Single crystals of Am-Ox were grown from aqueous solution by slow evaporation at room temperature. Deuterated crystals were obtained by the same procedure from a heavy water solution. A typical configuration and crystal axes are shown in Figure 1. The crystal is orthorhombic with space group  $P2_12_12$ ,

the unit cell dimensions being  $a = 8.06$ ,  $b = 10.27$ , and  $c = 3.82$  Å.<sup>7</sup> A right-handed set of the orthogonal crystallographic axes  $a$ ,  $b$ , and  $c$  is used as the reference coordinate system for the esr measurements. The axes have been identified by optical goniometer and X-ray diffraction analysis. The crystals were irradiated with a <sup>60</sup>Co  $\gamma$  source at liquid nitrogen and room temperature. Absorbed doses were between 1 and 15 Mrads. ESR spectra at both temperatures were recorded using a Varian E-3 (X-band) spectrometer.

The esr parameters were evaluated by the procedure of Schonland<sup>8</sup> and Lund and Vanngard.<sup>9</sup> Calculations were made by a CDC 3600 computer.

## Results

*Low-Temperature Measurements.* Three distinct paramagnetic species, denoted for convenience as B, C, and D, were observed at 77°K after irradiation at the same temperature. Species B and C have a single-line resonance, while species D shows a doublet with a strong anisotropic splitting. Essentially the same spectra were observed for the crystals grown from regular and heavy water solutions. The esr parameters were measured on a deuterated crystal, because in this case the lines were sharper, particularly that belonging to species C.

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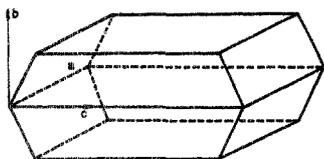


Figure 1. The appearance of the single crystal of ammonium oxalate monohydrate and the crystallographic and coordinate axes.

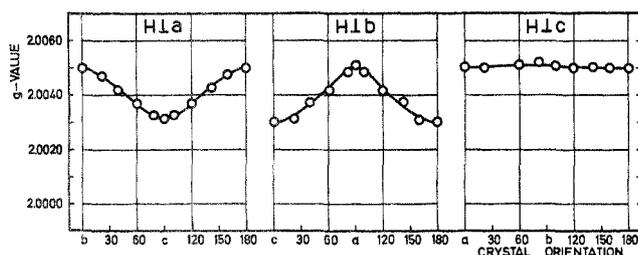


Figure 2. Variation of the  $g$  value for radical B in the three perpendicular coordinate planes.

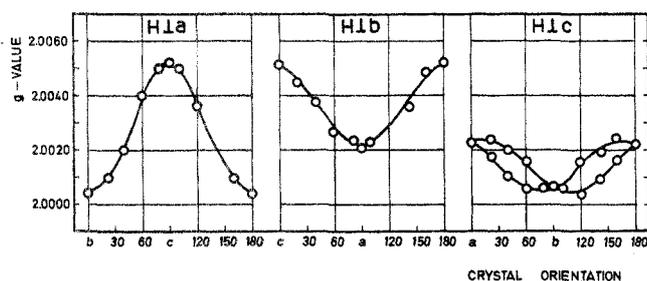


Figure 3. Variation of the  $g$  value for radical C in the three perpendicular coordinate planes.

Figures 2 and 3 give the variations of the  $g$  factor in the three planes for species B and C, respectively. Table I gives principal values of the  $g$  tensor and the direction cosines for the species. In Figure 3 the  $g$  value as a function of angle in the  $ab$  plane shows two magnetically nonequivalent sites per unit cell (site splitting) for species C. The magnetically nonequivalent sites of species B in the same plane cause unresolved site splitting. Here only "average"  $g$  values (Figure 2) are observed.

The separation  $D = 2(H - H_0)$  of the doublet of species D (Figure 4) follows the equation  $D = D_0(3 \cos^2 \theta - 1)$ . This behavior is characteristic of the dipolar magnetic coupling between two like spins, and species D can be identified as radical pairs with the average distance  $R$  between the two unpaired electrons<sup>10</sup>

$$R = \frac{3}{D} \beta (3 \cos^2 \theta - 1)^{1/3}$$

where  $\theta$  is the angle between  $R$  and  $H$ . The maximum value  $D_{\parallel}$ , obtained for  $H$  parallel to  $a$ , gives  $R = (6\beta/D_{\parallel})^{1/3} = 8.5 \text{ \AA}$ .

After heating the samples, the radical pairs D vanish

Table I

Species	Principal values	Direction cosines		
		$a$	$b$	$c$
<b>A</b>				
$A_1, G(-)$	6.2	$\pm 0.77$	$\mp 0.64$	0
$A_2, G(-)$	22.0	$\pm 0.64$	$\pm 0.77$	0
$A_3, G(-)$	12.8	0	0	1
$g_1$	2.0058	$\pm 0.50$	$\mp 0.87$	0
$g_2$	2.0048	$\pm 0.87$	$\pm 0.50$	0
$g_3$	2.0028	0	0	1
<b>B</b>				
$g_1$	2.0050	1	0	0
$g_2$	2.0052	0	1	0
$g_3$	2.0026	0	0	1
<b>C</b>				
$g_1$	1.9995	$\pm 0.94$	$\pm 0.33$	0
$g_2$	2.0021	$\mp 0.33$	$\pm 0.94$	0
$g_3$	2.0051	0	0	1
<b>D</b>				
$D_{\parallel}, G$	90.0	1	0	0
$D_{\perp}, G$	44.0			

first. At temperatures above  $190^\circ\text{K}$  the concentration of species C decays with a simultaneous change of the spectrum. This process has not been studied in detail.

**Room-Temperature Measurement.** The room-temperature spectrum obtained immediately after irradiation at room temperature consists of a singlet and a doublet. The same is true for the crystal irradiated at  $77^\circ\text{K}$  if the spectrum is recorded at  $300^\circ\text{K}$ . The singlet attributed to species B remains unchanged after heating. At room temperature the radical species denoted as A, corresponding to the doublet, is more stable than species B (Figure 5). Figure 6 gives the variation of the doublet splitting in the three crystallographic planes. The principal value of the hyperfine splitting tensor,  $g$  tensor, and the direction cosines are listed in Table I. The variation of the splitting and  $g$  factor in the  $ab$  plane indicates two magnetically nonequivalent sites of species A. For the crystal grown from heavy

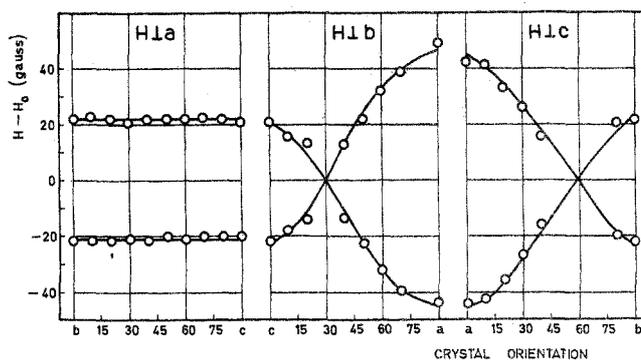


Figure 4. The angular variation of the spin-spin coupling for radical pairs (species D).

(10) Y. Kurita, *Nippon Kagaku Zasshi*, **85**, 842 (1964).

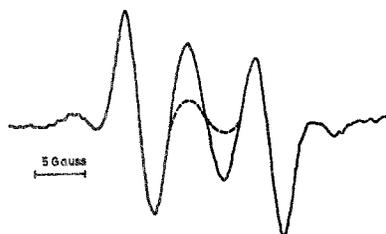


Figure 5. The room-temperature esr spectra (first derivative) recorded immediately after irradiation (—) and after several weeks (---).

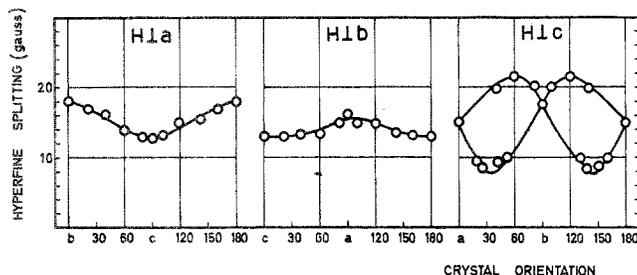


Figure 6. Angular variation of the hyperfine splitting for radical species A.

water the doublet is replaced by a 1:1:1 triplet with the hyperfine splitting smaller than that of the doublet by a factor of about 6.5.

### Discussion

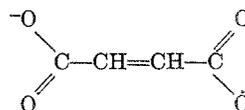
A great deal of the primary effect of  $\gamma$  radiation is ionization of either cation or anion species, or both. The high-energy secondary electrons make further ionizations until they reach thermal energies; then they are trapped. Thus, as a consequence of irradiation, one might expect species bearing one electron more or less than in the undamaged crystal. One can also expect species formed by the breaking of some of the covalent bonds in either cation or anion.

Unfortunately, species B and C detected at 77°K are characterized only by the  $g$  values. This fact makes the identification of the radicals more difficult. However, there exist already a number of precise measurements both of the principal values and direction cosines of  $g$  tensor for similar radicals in other matrices, and a comparison of the present values with those reported earlier offers a possibility for identification of the radical species in the present system.

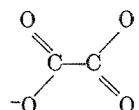
In oxalates one expects to observe the  $\text{CO}_2^-$  radicals upon irradiation. In the present case, we have to exclude that possibility, because the observed  $g$  values of the present radicals (Table I) differ significantly from the known values of  $\text{CO}_2^-$ .<sup>11</sup>

For species B the direction of the minimum principal value of the  $g$  tensor is perpendicular to the  $ab$  plane, and the  $g$  value in that plane varies very little. We assume radical B to be planar, in the  $ab$  plane, although in the undamaged crystal the strong hydrogen bonds

cause twisting of carboxyl groups out of the  $ab$  plane.<sup>7</sup> The  $g$  values of radical B agree very well in size and direction with respect to the parent molecule with those reported for the radical.<sup>12</sup>

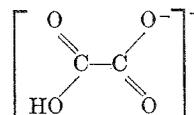


It has been shown both theoretically and experimentally that the direction of the minimum value of the  $g$  tensor in such a radical is perpendicular to the plane of the radical. Based on the above considerations and on the fact that this kind of radical is expected to be formed as a primary event upon irradiation, radical species B is assumed to be



A rough calculation in the Hückel approximation indicates that for such a radical about 80% of the spin density should be localized on oxygen atoms. The presence of considerable spin density on oxygen explains the somewhat higher principal values of the  $g$  tensor for radical B than for the radicals in dicarboxylic acids.<sup>13-15</sup> The larger  $g$  value is due to the larger spin-orbit coupling constant of oxygen ( $\lambda \approx 139 \text{ cm}^{-1}$ ) in comparison to that of carbon ( $\lambda \approx 28 \text{ cm}^{-1}$ ).<sup>16</sup>

For species C the direction of the minimum  $g$  value is in the C-C direction, *i.e.*, in the  $ab$  plane, while the direction of the maximum value is perpendicular to the  $ab$  plane. We propose radical C to be of the form



The reasons are as follows.

(a) The Hückel calculation for this radical indicates a higher spin density on the carbon atoms than on the oxygen atoms. In this case one expects the direction of the C-C bond to be preferred in esr parameters. That is really the case: the C-C bond is the direction of the minimum principal value of the  $g$  tensor.

(b) The narrowing of the resonance line of this radical upon the H  $\rightarrow$  D replacement is much more pronounced than that for radical B. Such a change of the line width is due to the change of the hyperfine coupling of the unpaired electron with the paramag-

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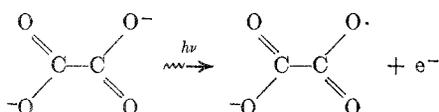
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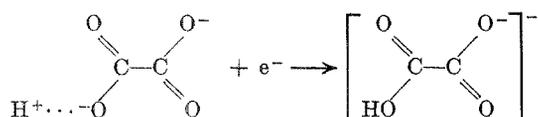
netic nuclei (protons or deuterons). Since for radical B one expects much larger spin density on oxygens than on carbons, and for radical C the opposite, the observation that radical C is much more sensitive to the hydrogen isotope present suggests that the hyperfine interaction responsible for the line width must be intramolecular rather than intermolecular. That is in accordance with the suggested radical structures. The small spin density on oxygens for radical C is the reason that one does not see a resolved hyperfine coupling. Besides, two magnetically distinct species make it even more unresolved.

A possible mechanism for the formation of radicals B and C is

(B)



(C)



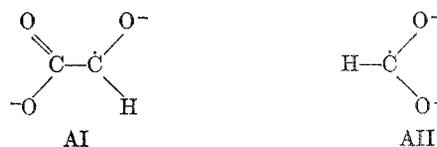
Radical species B is formed by the loss of an electron from the oxalate anion in the crystal. Radicals C are formed by trapping an electron with a subsequent transfer of a proton. The above mechanism corresponds to the primary radiolytic process<sup>2</sup> in which the ionic precursors of the more stable secondary radicals are formed. While radical C disappears before room temperature is reached, the half-life of radical B at room temperature is several days.

The nature of the radical pairs (species D) remains unexplained. From the direction of  $D_{\parallel}$  and from the calculated distance of 8.5 Å between the spins, it is obvious that the spin-spin coupling comes from two neighboring radicals in the  $a$  direction. The separation between the molecules in that direction is 8.06 Å.<sup>7</sup> From the spin-spin coupling of delocalized identical radicals one expects to get an "effective" interspin distance smaller than the crystallographic value of 8.06 Å. For two different radicals, like B and C in our case, the "effective" interspin distance is expected to be larger than the actual intermolecular distance. That is the only argument in support of the assumption that in ammonium oxalate the spin-spin interaction comes from two different radicals, namely radicals B and C.

For radical species A the hyperfine splitting tensor, as presented in Table I, is characteristic for an  $\alpha$ -proton coupling. In elucidating the nature of this radical we may rule out any structure associated with the ammonium cation, since such a structure would give a much more complex resonance pattern. Also, the observed proton coupling cannot be due to a hydroxyl

proton, because such a proton would have the principal values of the coupling tensor not all of the same sign,<sup>17-19</sup> which is in contrast to the present observation. Therefore, we conclude that we deal with the C-H fragment in radical species A.

The actual structure of the radical is not easily determined. We considered two structures, AI and AII.



AI is in much better agreement with the observed tensor parameters. The principal  $g$  values (Table I) are almost the same as those reported for very similar radicals  $\text{HO}\dot{\text{C}}\text{H}-\text{COOH}$ <sup>4,17</sup> and  $\text{HO}\dot{\text{C}}\text{H}-\text{COO}^-$ .<sup>18</sup> The directions of the principal elements are very similar with respect to molecular skeleton in all of these radicals. The coupling parameters for radical A are slightly smaller than those for the  $\text{HO}\dot{\text{C}}\text{H}-\text{COOH}$  and  $\text{HO}\dot{\text{C}}\text{H}-\text{COO}^-$  radicals, but the relative magnitudes of the components are similar in all of these radicals. The orientation of the smallest value of the coupling,  $A_3$ , is  $\pm 39^\circ$  from the  $a$  axis. If one supposes that the orientation of the radical in the crystal matrix is the same as the orientation of the undamaged molecule, this direction is exactly in the  $\text{sp}^2$  hybrid orbital of carbon in the oxalate ion. That is, again, in accordance with the expectation for radical AI.

Slightly larger  $g$  values and smaller proton coupling components for radical species A as compared with the values for similar oxalate radicals<sup>4,17,18</sup> can be justified by the fact that in the present case both hydroxyl protons are missing. The tendency of increasing  $g$  values and decreasing coupling parameters with the removal of these protons can be noticed from the data reported by Atherton and Whiffen.<sup>17,18</sup>

The only problem with structure AI is the lack of an obvious way of its formation. At present we are unable to visualize any reasonable mechanism leading to structure AI. Similar reasons led Bales<sup>3b</sup> to assume that in some oxalates a structure of type AII rather than AI was present. In our case structure AII seems less probable. By assuming that serious reorientation of the  $-\text{COO}^-$  group does not take place upon radical formation, for radicals AII one expects minimum proton coupling in the former C-C direction, *i.e.*,  $\pm 19^\circ$  from the  $a$  axis, which is far from the observed direction. In addition, the stability observed for radical species A is strongly against the doubly charged structure AII. All the above considerations make us be-

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lieve that we deal with radical AI. The observation that these radicals are not detectable at low temperatures, but only at room temperature, may account for a rather complicated mechanism which must be involved in the radical formation.

*Acknowledgments.* We are grateful to Dr. B. Radak and Dr. I. Draganić for their interest during the progress of the work. We are also indebted to Dr. R. Herak and Mr. B. Prelesnik for checking the unit cell dimensions of our crystal.

## The Electrode Reduction Kinetics of Carbon Dioxide in Aqueous Solution

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The electrolytic reduction of CO<sub>2</sub> in neutral, aqueous solution at a mercury pool cathode has been studied to establish the mechanism and to obtain the kinetic parameters by the steady-state galvanostatic method. The log current *vs.* potential curves show two Tafel regions of different slope which is indicative that different, *i.e.*, consecutive, steps are rate determining in the two regions. The most plausible steps considered are (1) CO<sub>2</sub> + H<sub>2</sub>O + e ⇌ HCO<sub>2</sub>·(ads) + OH<sup>-</sup> and (2) HCO<sub>2</sub>·(ads) + e → HCO<sub>2</sub><sup>-</sup>. Reaction orders with respect to the partial pressure of the CO<sub>2</sub> and the Tafel slopes are considered as the criteria for the proposed mechanism. The Langmuir and Temkin conditions for the adsorption of the reaction intermediate are considered and compared. The experimental results show that the Temkin condition is the more suitable and hence there is an appreciable change in the heat of adsorption with the surface coverage of the reaction intermediate.

### Introduction

The cathodic reduction of carbon dioxide in an aqueous solution has been the subject of investigations by several authors.<sup>1-13</sup> Through the above works, the principal reaction product in aqueous solution has been found to be the formate ion. Although some of the previously published papers<sup>10-13</sup> have proposed mechanisms for the reaction, certain salient points have been overlooked and it is necessary to reconsider and clarify some aspects of the kinetics. Therefore we have proposed and formulated a mechanism, as was done in some previous papers,<sup>10-13</sup> but have more carefully considered the form of the rate equations in order to apply reaction order differentials as a criteria of our mechanism. In particular, the influence of the partial pressure of CO<sub>2</sub> on the pH and the reversible potential, and thus on the form of the rate equations, has been taken into account. Also the adsorption of the reaction intermediate and its influence on the rate equations have been more fully and explicitly investigated than had been previously. Finally, the effect of temperature on the rate has been studied.

### Experimental Section

The details of the experimental setup can be found elsewhere.<sup>14</sup> An H-type cell was used which consisted of an anode and cathode compartment in a thermo-

stated jacket. The cathode, which was separated by a glass frit from the anode, consisted of a pool of polarographic grade mercury of 2.98-cm diameter which was connected by a tube of Hg to a Pt wire lead located

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