



## Calhoun: The NPS Institutional Archive

---

Faculty and Researcher Publications

Faculty and Researcher Publications Collection

---

1971-02-15

# EPR investigation of irradiated strontium and zinc acetate single crystals

Tolles, W.M.

American Institute of Physics

---

W.M. Tolles, R.A. Sanders & R.G. Gisch. EPR investigation of irradiated strontium and zinc acetate single crystals, *Journal of Chemical Physics*, v.54 (1971) pp. 1532-1535



Calhoun is a project of the Dudley Knox Library at NPS, furthering the precepts and goals of open government and government transparency. All information contained herein has been approved for release by the NPS Public Affairs Officer.

**Dudley Knox Library / Naval Postgraduate School**  
**411 Dyer Road / 1 University Circle**  
**Monterey, California USA 93943**

<http://www.nps.edu/library>

## EPR Investigation of Irradiated Strontium and Zinc Acetate Single Crystals\*

W. M. TOLLES, R. A. SANDERS, AND R. G. GISCH†

*Department of Chemistry, Naval Postgraduate School, Monterey, California 93940*

(Received 5 October 1970)

X-ray irradiation of strontium acetate hemihydrate produces  $\text{CH}_3\dot{\text{C}}\text{O}_2^-$  and not the methyl radical as in other acetates. At higher temperatures this spectrum is replaced with two magnetically distinct  $\cdot\text{CH}_2\text{CO}_2^-$  radicals. In the presence of the propionate ion, further reaction proceeds at about  $-30^\circ\text{C}$  to yield one rotamer of one magnetically distinct  $\text{CH}_3\dot{\text{C}}\text{HCO}_2^-$  radical. The ratio of propionate/acetate damage at room temperature is found to be 700:1 in strontium acetate, indicating some mechanism for the delocalization of the damage. This same reaction with a substituted propionate ion occurs in zinc acetate with a ratio of 20:1. The coupling tensors for all species are presented.

## I. INTRODUCTION

Paramagnetic fragments resulting from radiation damage in metallic acetates have recently been reported for several systems. Irradiated sodium acetate<sup>1-3</sup> and zinc acetate<sup>4-7</sup> show the appearance of a methyl radical at liquid-nitrogen temperatures. In zinc acetate this radical disappears with the concomitant appearance of  $\cdot\text{CH}_2\text{CO}_2^-$  as a product of hydrogen abstraction from an acetate.<sup>4</sup> In cupric<sup>8,9</sup> and nickel<sup>10</sup> acetates the observed paramagnetic changes indicate that an electron transfer yields a spin-one-half species.

The present investigation demonstrates that  $\text{CH}_3\text{CO}_2^{2-}$  is the precursor to  $\cdot\text{CH}_2\text{CO}_2^-$  in strontium acetate hemihydrate. In the presence of trace amounts of propionate ion a preferential attack of the secondary hydrogens yields  $\text{CH}_3\dot{\text{C}}\text{HCO}_2^-$  as a major product.

## II. EXPERIMENTAL

Single crystals of zinc acetate dihydrate and strontium acetate hemihydrate were grown by slow evaporation of an aqueous solution. It was found that excess acetic acid in this solution improved the ease by which single crystals could be grown. The amount of propionate impurity in strontium acetate was sufficient in many samples (greater than 0.01%) to mask the  $\cdot\text{CH}_2\text{CO}_2^-$  species. The source of relatively pure strontium acetate was K and K Laboratories, Incorporated, Hollywood, California. For investigation of impurity effects, the corresponding propionate salt was added in amounts up to 2 mole %. Trace amounts of propionate in a given acetate were analyzed by forming a slurry of the acetate crystals with concentrated sulfuric acid, then collecting under vacuum the acetic acid and propionic acid vapors. Analysis of the resulting acid mixture was accomplished by passage over a 10-ft  $\times$   $\frac{1}{4}$ -in. fatty acid gas-chromatograph column with a flame ionization detector. As little as 0.005% propionate could be detected with this technique.

Single crystals were exposed to x-ray radiation using a copper target at 45 kV and 35 mA for from 1-4 h. The ESR spectra were taken using 100-kHz modulation. Temperatures were continually monitored

with a copper-constantan thermocouple. Rotation of single crystals was performed according to previously employed methods<sup>4</sup>.

The coupling tensors were determined with data obtained from 30 to 180 crystal orientations depending on the number required to be certain of the values obtained. The data used was refined with a least squares treatment. The standard deviation after such a treatment was typically on the order of the accuracy with which the center of a transition could be measured. The estimated errors reported here represent the 68% confidence levels.

Since the crystal structure of strontium acetate hemihydrate has not been reported, the direction cosines of the principal axes of the coupling tensors are reported in the coordinate system shown in Fig. 1. The direction cosines for the zinc acetate dihydrate monoclinic structure are given in the  $a^*bc$  axis system reported previously.<sup>4</sup>

## III. RESULTS AND DISCUSSION

A.  $\text{CH}_3\dot{\text{C}}\text{O}_2^-$  in Strontium Acetate Hemihydrate

Single crystals of strontium acetate hemihydrate, when irradiated in liquid nitrogen and observed at 160°K, showed a 1:3:3:1 quartet with a cylindrically symmetric coupling constant (Table I). At lower temperatures and favorable orientations eight lines of the three inequivalent nuclei observed were resolved (Fig. 2). These characteristics identify it as the acetate dianion, previously reported by Sevilla<sup>11</sup> in a frozen basic aqueous solution containing potassium ferrocyanide and sodium acetate after photolysis and subsequent photobleaching. The previously reported coupling constant of approximately 32 MHz (taken from Fig. 1 of Ref. 11) in the sample with random orientations agrees well with the isotropic value of 33.15 MHz reported here.

The barrier to internal rotation for the species is noticeably less in the strontium acetate single crystal than in the frozen aqueous solution. The spectrum reported by Sevilla<sup>11</sup> undergoes a transformation from slow to rapid exchange at temperatures ranging from

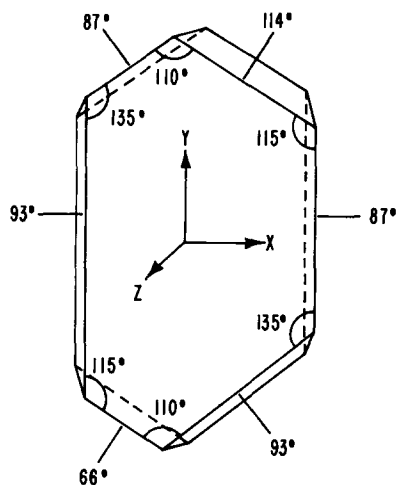


FIG. 1. Crystal form and axis system chosen for strontium acetate hemihydrate single crystals. Internal angles on each edge are given with respect to top surface.

150–180°K, whereas the corresponding temperature range in strontium acetate is between 100–150°K. The free energy of activation for the internal rotation process is determined to be 2.3 kcal/mole by comparison with computer-simulated spectra.

#### B. $\cdot\text{CH}_2\text{CO}_2^-$ in Strontium Acetate Hemihydrate

Several samples of strontium acetate hemihydrate were examined at higher temperatures showing a

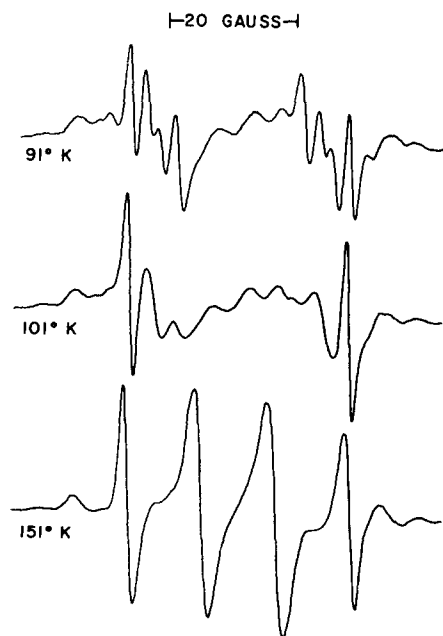


FIG. 2. The  $\text{CH}_3\text{CO}_2^-$  ion in strontium acetate hemihydrate with the magnetic field along the (0.612, 0.612, -0.500) direction.

TABLE I. Coupling tensors observed in irradiated strontium acetate.

Species	Principal values (MHz)	Direction cosines		
		<i>x</i>	<i>y</i>	<i>z</i>
$\text{CH}_3\text{CO}_2^-$ (150°K)				
$a_{  }$	$39.56 \pm 0.05$	0.370	-0.165	-0.914
$a_{\perp}$	$29.95 \pm 0.05$			
$\cdot\text{CH}_2\text{CO}_2^-$ (233°K)				
$\text{H}_1$	$-90.94 \pm 0.3$	0.986	-0.157	0.055
	$-58.57 \pm 0.4$	0.157	0.988	0.006
	$-29.24 \pm 0.4$	-0.055	0.002	0.998
$\text{H}_2$	$-91.47 \pm 0.3$	0.519	-0.088	-0.850
	$-55.05 \pm 0.4$	0.187	0.982	0.013
	$-31.37 \pm 0.6$	0.834	-0.166	0.527
$\text{H}_1'$	$-88.40 \pm 0.4$	0.444	0.485	-0.753
	$-57.88 \pm 0.5$	0.733	-0.680	-0.007
	$-30.62 \pm 0.6$	0.516	0.549	0.658
$\text{H}_2'$	$-90.64 \pm 0.3$	0.201	0.237	0.951
	$-56.66 \pm 0.5$	0.740	-0.673	0.011
	$-31.31 \pm 0.9$	0.642	0.701	-0.310
$\text{CH}_3\text{CHCO}_2^-$ (room temperature)				
$a_{\text{H}}$	$-86.6 \pm 0.8$	0.676	0.098	-0.730
	$-54.1 \pm 1.2$	0.085	0.974	0.209
	$-31.3 \pm 1.9$	0.732	-0.203	0.650
$a_{\text{CH}_3}$				
$a_{  }$	$74.78 \pm 0.14$	-0.373	-0.220	0.901
$a_{\perp}$	$67.64 \pm 0.10$			

TABLE II. Coupling tensors observed in irradiated zinc acetate dihydrate.

Species	Principal values (MHz)	Direction cosines		
		$a^*$	<i>b</i>	<i>c</i>
$\cdot\text{CH}_2\text{CO}_2^-$ <sup>a</sup>				
$\text{H}_1$	$-26.80 \pm 0.74$	$\pm 0.547$	0.722	$\pm 0.423$
	$-59.59 \pm 0.44$	$\mp 0.768$	0.634	$\mp 0.088$
	$-92.15 \pm 0.13$	$\mp 0.332$	-0.276	$\pm 0.902$
$\text{H}_2$	$-26.41 \pm 0.99$	$\pm 0.048$	-0.081	$\mp 0.996$
	$-58.98 \pm 0.45$	$\mp 0.768$	0.634	$\mp 0.088$
	$-92.78 \pm 0.20$	$\pm 0.638$	0.769	$\mp 0.032$
$\text{CH}_3\text{CHCO}_2^-$				
$\text{H}$	$-29.95 \pm 1.2$	$\mp 0.061$	-0.064	$\mp 0.996$
	$-52.92 \pm 0.5$	$\mp 0.702$	0.713	$\mp 0.003$
	$-86.22 \pm 0.5$	$\pm 0.710$	0.697	$\mp 0.088$
$\text{CH}_3$				
$a_{  }$	$76.15 \pm 0.13$	$\pm 0.667$	0.708	$\pm 0.231$
$a_{\perp}$	$69.90 \pm 0.20$			

<sup>a</sup> Taken from Ref. 4.

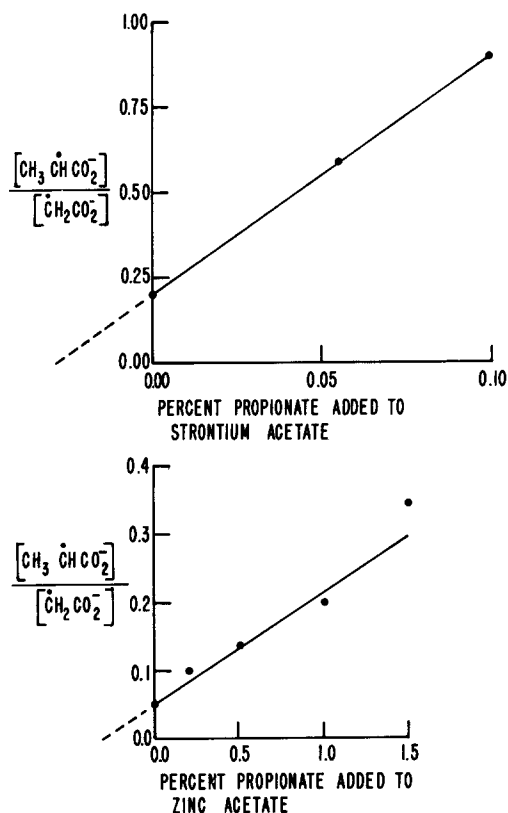


FIG. 3. Ratio of damaged propionate to damaged acetate as a function of propionate ion added to solution from which single crystals were grown.

very complex pattern. It was only after realizing that a trace impurity was responsible for a second spectrum having an intensity comparable with the  $\cdot\text{CH}_2\text{CO}_2^-$  species that an interpretation was possible. Relatively pure strontium acetate gave a spectrum which could be interpreted as being due to two magnetically distinct  $\cdot\text{CH}_2\text{CO}_2^-$  radicals. The coupling tensors in Table I were obtained after rotating by  $15^\circ$  increments about eight different axes.

The experimentally determined principal axes for the intermediate coupling constants of two protons on the same radical are colinear to within  $2^\circ$  for each species. In the limit of a radical having  $C_{2v}$  symmetry in free space, of course, these axes would be colinear. The direction cosines of the smallest coupling constant give the HCH bond angles of  $118.64^\circ$  and  $120.81^\circ$  as compared to  $116.0^\circ \pm 0.3^\circ$  in zinc acetate.<sup>4</sup>

### C. $\text{CH}_3\dot{\text{C}}\text{HCO}_2^-$ in Strontium and Zinc Acetates

A zinc acetate crystal which, when left at room temperature for 1 month after irradiation, shows another spectrum after the decay of  $\cdot\text{CH}_2\text{CO}_2^-$ . This resulting species has a spectrum of a doublet of quartets, and is due to the  $\text{CH}_3\dot{\text{C}}\text{HCO}_2^-$  ion as a

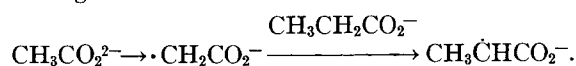
result of damage to trace amounts of propionate present as an impurity. This same species is present in irradiated strontium acetate crystals and may be enhanced by the addition of small amounts of propionate ion to each crystal (Fig. 3). The slope of the ratio of damaged propionate, acetate vs concentration of propionate, gives the selectivity ratio between propionate and acetate ions. In strontium acetate this ratio is 700; in zinc acetate it is 20. It is well known in organic reactions that the abstraction of a secondary substituent is much easier than a primary substituent. The reason for the marked difference in the selectivity ratios between the two acetates has not been explained.

The coupling tensors for this species (Tables I and II) are nearly identical with this species as reported in irradiated disodium succinate.<sup>12</sup> The coupling parameters may be compared with those of  $\cdot\text{CH}_2\text{CO}_2^-$  in the same crystalline lattice. In strontium acetate there is only one magnetically distinct site for the damaged propionate ion. The direction cosines indicate that only one of the two acetate sites is occupied by a propionate ion, and within this site, only one rotamer of the damaged propionate ion is thermally populated. This is good evidence for the fact that the two acetate ions are not related by symmetry in the strontium acetate lattice. In addition, the orientation of the  $\text{CH}_3\dot{\text{C}}\text{H}$  group is almost identical with that of the  $\cdot\text{CH}_2$  group from the damaged acetate ion.

In zinc acetate there are two magnetically distinct sites for the damaged propionate radical, but again only one rotamer is thermally populated. If both rotamers were equally populated, this spectrum would be quite difficult to analyze. The orientation of the  $\text{CH}_3\dot{\text{C}}\text{H}$  group again is almost the same as the  $\cdot\text{CH}_2$  group. The direction cosine for  $a_{11}$  for the coupling with the methyl group gives the C-CH<sub>3</sub> bond direction. Assuming that the acetate skeleton is in the same position as for the undamaged species, the additional methyl group is found to lie between adjacent planes which are hydrogen bonded to one another.

### D. Damage Mechanisms

In zinc acetate dihydrate, previous measurements<sup>4</sup> show that the methyl radical is a precursor to the  $\cdot\text{CH}_2\text{CO}_2^-$  radical. However, for strontium acetate no evidence of the methyl radical has been observed. The acetate dianion disappears with the simultaneous appearance of  $\cdot\text{CH}_2\text{CO}_2^-$  at about  $173^\circ\text{K}$  (this does not rule out a short-lived methyl radical as an intermediate). If sufficient propionate is present, a further reaction is evident at about  $243^\circ\text{K}$  where the damaged propionate appears with the concomitant disappearance of  $\cdot\text{CH}_2\text{CO}_2^-$ . The energy of activation for this process is found to be 7.4 kcal/mole from an Arrhenius plot. Thus, in strontium acetate the following chain of events is observed:



The mechanism for the actual transference of damage from  $\cdot\text{CH}_2\text{CO}_2^-$  to a propionate ion must include considerable delocalization of the initial damage. Otherwise selectivity ratios of 700 would not be observed. The mechanism for this delocalization has not been explained.

\* Supported by the Office of Naval Research.

† LTJG, U.S. Navy, Present address: Director of Division Reactors Office, Atomic Energy Commission, Navy Department, Washington, D.C. 20360.

<sup>1</sup> M. T. Rogers and L. D. Kispert, *J. Chem. Phys.* **46**, 221 (1967).

<sup>2</sup> D. G. Cadena, Jr., V. Mendez, and J. R. Rowlands, *Mol. Phys.* **13**, 157 (1967).

<sup>3</sup> S. Abbas and A. K. Roy, *Dacca Univ. Studies* **17**, 17 (1969).

<sup>4</sup> W. M. Tolles, L. P. Crawford, and J. L. Valenti, *J. Chem. Phys.* **49**, 4745 (1968).

<sup>5</sup> H. Ohigashi and Y. Kurita, *Bull. Chem. Soc. Japan* **41**, 275 (1968).

<sup>6</sup> M. T. Rogers and L. D. Kispert, *Advan. Chem. Ser.* **82**, 327 (1968).

<sup>7</sup> R. G. Hayes, D. J. Steible, Jr., W. M. Tolles, and J. W. Hunt, *J. Chem. Phys.* **53**, 4466 (1970).

<sup>8</sup> F. Apaydin and S. Clough, *Proc. Phys. Soc. (London) Solid State Phys. Ser.* **2**, 2, 1536 (1969).

<sup>9</sup> D. A. Morton-Blake, *J. Phys. Chem.* **74**, 1508 (1970).

<sup>10</sup> D. A. Morton-Blake, *J. Phys. Chem.* **73**, 2964 (1969).

<sup>11</sup> M. D. Sevilla, *J. Phys. Chem.* **74**, 669 (1970).

<sup>12</sup> B. L. Bales, R. N. Schwartz, and M. W. Hanna, *J. Chem. Phys.* **51**, 1974 (1969).

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 54, NUMBER 4 15 FEBRUARY 1971

## Ultraslow Hydrogen Motion in $\text{KH}_2\text{PO}_4$ and $\text{NaH}_3(\text{SeO}_3)_2$ Type Crystals

R. BLINC AND J. PIRŠ

*University of Ljubljana and Institute "J. Stefan," Ljubljana, Yugoslavia*

(Received 13 October 1970)

Ultraslow reorientational motions of the  $\text{H}_2\text{PO}_4$  and  $\text{H}_2\text{SeO}_3$  groups have been studied in  $\text{KH}_2\text{PO}_4$ ,  $\text{RbH}_2\text{PO}_4$ ,  $\text{CsH}_2\text{PO}_4$ ,  $\text{LiH}_3(\text{SeO}_3)_2$ ,  $\text{NaH}_3(\text{SeO}_3)_2$ ,  $\text{KH}_3(\text{SeO}_3)_2$ , and  $\text{CsH}_3(\text{SeO}_3)_2$  by dipolar and rotating frame proton spin-lattice relaxation measurements. The measured values of the reorientational correlation times change from about  $10^{-3}$  sec at room temperature to about  $10^{-5}$  sec at  $100^\circ\text{C}$ . The activation energies for the hindered rotation of the  $\text{H}_2\text{PO}_4$ , respectively,  $\text{H}_2\text{SeO}_3$  groups are controlled by the size of the cation rather than by the strength of the  $\text{O}-\text{H}\cdots\text{O}$  bonds, and vary from 0.4 to 1.4 eV. In contrast to the case of ice this slow reorientational process dominates the dc protonic conductivity of both the  $\text{KH}_2\text{PO}_4$  and the  $\text{NaH}_3(\text{SeO}_3)_2$  group of hydrogen bonded crystals.

### I. INTRODUCTION

Deuteron spin-lattice relaxation time measurements in  $\text{KD}_2\text{PO}_4$  type hydrogen bonded ferroelectrics have shown<sup>1</sup> the existence of two basic reorientation mechanisms in the paraelectric phase: a *very fast one* occurring in the frequency range of  $10^9$ - $10^{12}$  Hz which shows a critical slowing down<sup>2</sup> on approaching the ferroelectric transition temperature, and a *low frequency one* ( $10^3$ - $10^5$  Hz) which shows no anomaly in the vicinity of  $T_c$  but dominates the proton and deuteron conductivity of these compounds. Uehling and Schmidt<sup>1</sup> were the first to demonstrate that in  $\text{KD}_2\text{PO}_4$  the high frequency motion is connected with deuteron motion between the two equilibrium sites *within* an  $\text{O}-\text{H}\cdots\text{O}$  bond, whereas the low frequency motion results in an effective exchange of deuterons between *different* hydrogen bonds. The deuteron exchange could be due to either spatial diffusion of deuterons or hindered rotation of the  $\text{H}_2\text{PO}_4$  groups.

In order to throw some additional light on the nature of the low frequency reorientation process we decided to investigate  $\text{KH}_2\text{PO}_4$ ,  $\text{RbH}_2\text{PO}_4$ , and  $\text{CsH}_2\text{PO}_4$ , as well as  $\text{LiH}_3(\text{SeO}_3)_2$ ,  $\text{NaH}_3(\text{SeO}_3)_2$ ,  $\text{KH}_3(\text{SeO}_3)_2$ , and  $\text{CsH}_3(\text{SeO}_3)_2$ . The aim of this work was to elucidate the dependence of the slow interbond motion on the size of the cation and the strength of the  $\text{O}-\text{H}\cdots\text{O}$  bonds.

Crystals of the  $\text{NaH}_3(\text{SeO}_3)_2$  family were included in this study as deuteron spin-lattice relaxation measurements in  $\text{NaD}_3(\text{SeO}_3)_2$  showed the same general behavior—and in particular the existence of both intrabond and interbond deuteron motion—as in  $\text{KD}_2\text{PO}_4$ . In view of the fact that the proton Zeeman spin-lattice relaxation times were found to be, except in the vicinity of the Curie points in rather pure samples, dominated by spin diffusion to paramagnetic impurities, we decided to investigate the proton motion by rotating frame,  $T_{1\rho}$ , and local dipolar field energy relaxation time,  $T_{1D}$ , measurements, performed in the absence of fields.

### II. EXPERIMENTAL PROCEDURE

The spin Hamiltonian of our problem is the sum of a Zeeman term and of the secular part of the magnetic dipolar term

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_{D'} \quad (1)$$

It is well known<sup>3</sup> that the density matrix of the proton spin system reaches in a time  $T_2$  a quasiequilibrium form

$$\rho = 1 - \alpha \mathcal{H}_Z - \beta \mathcal{H}_{D'} \quad (2)$$

The inverse Zeeman and dipolar spin temperatures  $\alpha$  and  $\beta$  tend towards the inverse lattice temperature  $\beta_L$  with time constants  $T_{1Z}$  and  $T_{1D}$ . They also tend to