

# Acetyl Radical Formation in X-Irradiated Acetic Acid Single Crystals Studied by ESR Spectroscopy

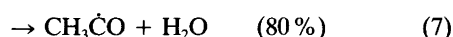
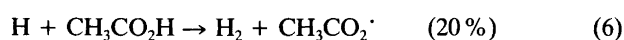
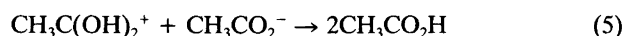
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Single crystals of CH<sub>3</sub>CO<sub>2</sub>H, CH<sub>3</sub>CO<sub>2</sub>D, CD<sub>3</sub>CO<sub>2</sub>D and CD<sub>3</sub>CO<sub>2</sub>Li · 2D<sub>2</sub>O have been irradiated with X-rays and investigated by ESR spectroscopy with the purpose of comparing the fragmentation pattern of the molecular anion radicals. CD<sub>3</sub>CO<sup>·</sup> was identified as the radical product in the decay of CD<sub>3</sub>CO<sub>2</sub>D<sup>-</sup> in CD<sub>3</sub>CO<sub>2</sub>D, and CO<sub>2</sub><sup>·-</sup> was similarly identified in the decay of CD<sub>3</sub>CO<sub>2</sub><sup>2-</sup> in CD<sub>3</sub>CO<sub>2</sub>Li · 2D<sub>2</sub>O, confirming an earlier observation [LoBrutto, R., Budzinski, E. E. and Box, H. C. *J. Chem. Phys.* 73 (1980) 6349]. The mechanism is discussed.

The purpose of this work was to study a difference that exists in the radiolysis mechanism of carboxylic acids on the one hand and their salts on the other. In the former case acetyl radicals have been observed, while in the latter case CO<sub>2</sub><sup>·-</sup> radical ions have been detected after irradiation in the solid state.<sup>1</sup> The radiation chemistry of carboxylic acids has been most thoroughly studied in the case of acetic acid.<sup>2</sup> A radiolysis mechanism for liquid acetic acid includes steps (1)–(8). The major final products are CO<sub>2</sub> and CH<sub>4</sub>.



Many of the free-radical intermediates in acetic acid and acetates have been identified by ESR spectroscopy in the solid state.<sup>1–10</sup> The radicals identified so far are  $\dot{\text{C}}\text{H}_3$ , CH<sub>3</sub>CO<sub>2</sub>H<sup>·-</sup>, CH<sub>3</sub>CO<sup>·</sup>,  $\dot{\text{C}}\text{H}_2\text{CO}_2\text{H}$  and CO<sub>2</sub><sup>·-</sup>. Of these, CH<sub>3</sub>CO<sub>2</sub>H<sup>·-</sup>, the primary anion, and  $\dot{\text{C}}\text{H}_2\text{CO}_2\text{H}$  are observed at 77 K in the dry acid.<sup>6,11,12</sup> The molecular cation CH<sub>3</sub>CO<sub>2</sub>H<sup>+</sup> is not stable at 77 K, but the  $\dot{\text{C}}\text{H}_3$  radicals

observed in acetic acid containing water are thought to be decomposition products, together with CO<sub>2</sub>. In dry CH<sub>3</sub>CO<sub>2</sub>H  $\dot{\text{C}}\text{H}_3$  is not observed.  $\dot{\text{C}}\text{D}_3$  is, however, present after irradiation of dry CD<sub>3</sub>CO<sub>2</sub>D at 77 K.<sup>6</sup> Evidently, in the former case  $\dot{\text{C}}\text{H}_3$  reacts further and produces  $\dot{\text{C}}\text{H}_2\text{CO}_2\text{H}$ . Evidence that CH<sub>3</sub>CO<sup>·</sup> is a secondary radical formed by the decomposition of the anion has been obtained.<sup>6</sup> The measurements were made using polycrystalline samples, and the ESR spectrum overlapped the  $\dot{\text{C}}\text{H}_2\text{CO}_2\text{H}$  spectrum. In this paper we have used single crystals of CD<sub>3</sub>CO<sub>2</sub>D in order to obtain a better resolution, and have obtained resolved spectra from CD<sub>3</sub>CO<sup>·</sup> subsequent to the thermal decay of the anion. A comparison has been made with the results obtained with crystals of CD<sub>3</sub>CO<sub>2</sub>Li · 2D<sub>2</sub>O, in which CD<sub>3</sub>CO<sup>·</sup> has not been observed. CO<sub>2</sub><sup>·-</sup> has been observed, both as the isolated radical and as triplet radical pairs in irradiated single crystals of CH<sub>3</sub>CO<sub>2</sub>Li · 2H<sub>2</sub>O. The anion is also present in this compound and has been characterized using <sup>13</sup>C-labelled CH<sub>3</sub><sup>13</sup>CO<sub>2</sub>Li · 2H<sub>2</sub>O.<sup>13–15</sup> Thus further evidence for a difference in the mechanism of the anion radical decomposition in acids and salts is provided for simple model systems.

## Experimental

CH<sub>3</sub>CO<sub>2</sub>H was dried over anhydrous magnesium sulphate and degassed on a vacuum line. CH<sub>3</sub>CO<sub>2</sub>D purchased from Sigma and CD<sub>3</sub>CO<sub>2</sub>D from Merck, Sharp and Dohme were used without further treatment except for degassing. The crystals were grown directly in the Suprasil quartz tubes used for the ESR measurements. The technique used to grow single crystals at subambient temperature has been described.<sup>16</sup> Transparent samples could be obtained at a temperature slightly below the melting point of acetic acid,

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Table 1. Radicals observed in acetic acid and in lithium acetate after irradiation.

Sample	Radical	T/K	g-factors and coupling constants/mT	Comments
CH <sub>3</sub> CO <sub>2</sub> H	CH <sub>3</sub> CO <sub>2</sub> H <sup>-</sup>	77	$g = 2.0032, a_{\beta 1} = 3.2$	Refs. 6 and 11
CH <sub>3</sub> CO <sub>2</sub> D	CH <sub>3</sub> CO <sub>2</sub> D <sup>-</sup>	77	$a_{\beta 1} = 3.2, a_{\beta 2} = 0.65, a_{\beta 3} = 0$	Ref. 12
	CH <sub>2</sub> CO <sub>2</sub> D	77	$a_{\alpha} = 1.4-3.4$ (2H)	Ref. 12
CD <sub>3</sub> CO <sub>2</sub> D	CD <sub>3</sub> C <sup>o</sup>	77	$g = (1.9954, 1.9968, 2.0018), A_0 = 0.092$	This work
CH <sub>3</sub> COCl/K	CH <sub>3</sub> C <sup>o</sup>	77	$A = (0.46, 0.46, 0.60)$	Ref. 21
CD <sub>3</sub> CO <sub>2</sub> D	CD <sub>3</sub>	111	$a_D = 0.355$	Ref. 6
CD <sub>3</sub> COCl/K	CD <sub>3</sub> C <sup>o</sup>	77	$g = (1.9960, 1.9960, 2.0036)$	Ref. 21
CD <sub>3</sub> CO <sub>2</sub> Li · 2D <sub>2</sub> O	CO <sub>2</sub> <sup>-</sup> ··· CO <sub>2</sub> <sup>-</sup>	77	$g = (1.9965, 2.0016, 2.0027), D = -8.77$	This work
	CO <sub>2</sub> <sup>-</sup>	77	$g = (1.9972, 2.0026, 2.0039)$	This work

16.6°C. Crystals of CD<sub>3</sub>CO<sub>2</sub><sup>6</sup>Li · 2D<sub>2</sub>O were obtained by mixing CD<sub>3</sub>CO<sub>2</sub>D and <sup>6</sup>Li<sub>2</sub>CO<sub>3</sub> followed by crystallization in D<sub>2</sub>O. The samples were cooled to 77 K and irradiated at that temperature for 5–10 min using an X-ray tube with an Au anode operated at 70 kV and 20 mA. ESR spectra were recorded immediately after irradiation at 77 K, and also after heat treatment at 280 K. In addition, spectra were examined at variable temperatures between 100 and 280 K. Single-crystal data were recorded in three crystal planes. For CD<sub>3</sub>CO<sub>2</sub>Li · 2D<sub>2</sub>O measurements were made with respect to the crystallographic axes. The orientation of the acetic acid crystals in the tubes was not determined, and arbitrary orthogonal axes were used in the measurements. The total yield of free radicals was determined by double integration of the first-derivative ESR spectra from weighed amounts of polycrystalline samples irradiated under the same conditions.

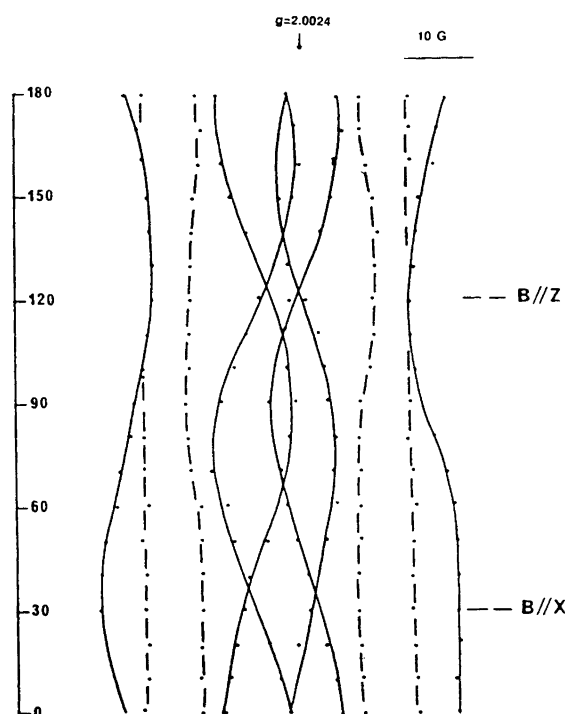


Fig. 1. ESR line positions in a CH<sub>3</sub>CO<sub>2</sub>D single crystal (in-plane) showing good resolution. Lines due to CH<sub>3</sub>CO<sub>2</sub>D<sup>-</sup> and CH<sub>2</sub>CO<sub>2</sub>D are marked. Irradiation and measurements were made at 77 K.

## Results

In previous papers ESR single-crystal data for CH<sub>3</sub>CO<sub>2</sub>H and CH<sub>3</sub>CO<sub>2</sub>D have been briefly reported.<sup>11,12</sup> The formation of CD<sub>3</sub>C<sup>o</sup> in CD<sub>2</sub>CO<sub>2</sub>D was mentioned in a conference report.<sup>17</sup> Radical formation in acetates has been described by several authors.<sup>3,4,8,10</sup> The results are summarized in Table 1. The total yields of free radicals in acetic acid and in lithium acetate dihydrate were determined to be in the ratio 1.3:1, i.e. approximately equal within the error limits. An account of the results obtained for the individual compounds follows.

*CH<sub>3</sub>CO<sub>2</sub>H and CH<sub>3</sub>CO<sub>2</sub>D.* At 77 K the spectra contain two components.<sup>11,12</sup> The first is nearly isotropic and is assigned to the molecular anion. At 77 K the hyperfine couplings of the three protons are different. At higher temperatures the CH<sub>3</sub> group starts to rotate and the couplings become equal at 173 K. The second has two anisotropic hyperfine couplings and is assigned to the radicals CH<sub>2</sub>CO<sub>2</sub>H and CH<sub>2</sub>CO<sub>2</sub>D, respectively. A plot of the line positions in a plane giving good spectral resolution is shown in Fig. 1. A spectrum containing the two components is shown in Fig. 2. Because of spectral overlap in the two other orthogonal planes the coupling tensors were not obtained. The

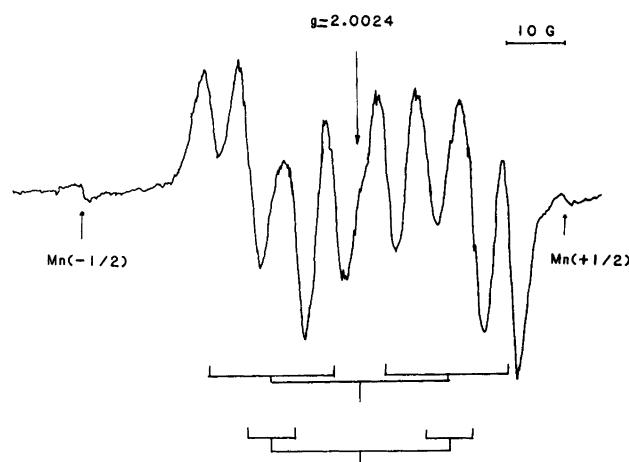


Fig. 2. ESR spectrum of a CH<sub>3</sub>CO<sub>2</sub>D crystal X-irradiated and measured at 77 K. The orientation corresponds to an angle of rotation of 30° in Fig. 1. Lines due to CH<sub>3</sub>CO<sub>2</sub>D<sup>-</sup> and CH<sub>2</sub>CO<sub>2</sub>D are indicated by stick spectra.

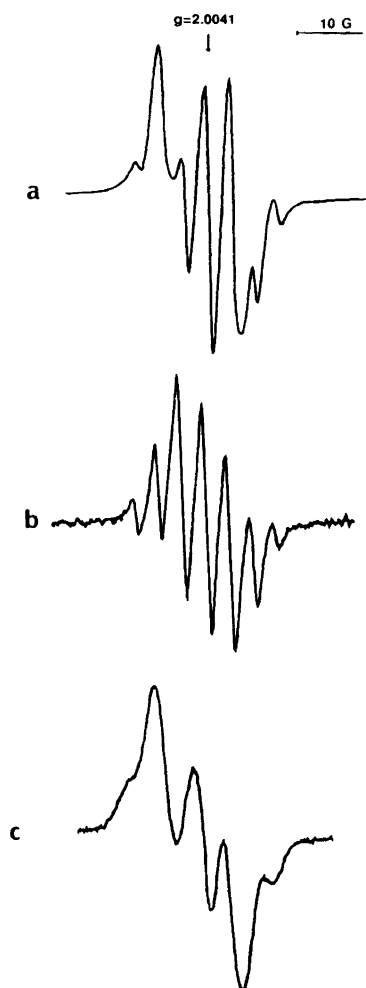


Fig. 3. ESR spectra of a  $\text{CD}_3\text{CO}_2\text{D}$  crystal irradiated at 77 K and measured at (a) 77 K, (b) 111 K before annealing with lines due to  $\dot{\text{C}}\text{D}_3$ , and (c) 77 K after annealing at 150 K showing features due to  $\text{CD}_3\dot{\text{C}}\text{O}_2\text{D}^-$ .

anion decayed at about 173 K. The spectra were then analysed again in search of the secondary  $\text{CH}_3\dot{\text{C}}\text{O}$  radicals expected from the decomposition reaction (7). Measurements were made at X- and Q-bands to take advantage of the larger  $g$ -factor anisotropy of  $\text{CH}_3\dot{\text{C}}\text{O}$  compared to radicals such as  $\dot{\text{C}}\text{H}_2\text{CO}_2\text{H}$ . The spectra were complex, and it was not easy to identify the radicals. The radicals in  $\text{CD}_3\text{CO}_2\text{D}$  were therefore investigated.

**$\text{CD}_3\text{CO}_2\text{D}$ .** In agreement with the results obtained from polycrystalline samples two species, identified as  $\text{CD}_3\text{CO}_2\dot{\text{D}}^-$  and  $\dot{\text{C}}\text{D}_3$ , were observed at 77 K.<sup>6</sup> The two components could be separated by thermal treatment. Fig. 3a was obtained when the sample was irradiated and measured at 77 K. The septet assigned to  $\dot{\text{C}}\text{D}_3$  in Fig. 3b has narrow lines at 111 K and dominates the spectrum. It disappears irreversibly on thermal annealing at 150 K. The spectrum in Fig. 3c was obtained when the annealed sample was measured at 77 K. It is dominated by the triplet assigned to  $\text{CD}_3\text{CO}_2\dot{\text{D}}^-$ . Above 173 K  $\text{CD}_3\text{CO}_2\dot{\text{D}}^-$  disappeared irreversibly and a new signal occurred. We sug-

gest that  $\text{CD}_3\dot{\text{C}}\text{O}_2\text{D}^-$  has then been converted into  $\text{CD}_3\dot{\text{C}}\text{O}$ . This suggestion is based upon evidence presented below.

The spectra obtained after warmup were anisotropic. The most clear data were obtained when the crystal was rotated about the tube axis. An example of a spectrum is shown in Fig. 4. The spectrum corresponds to an orientation at which radicals trapped at the two crystallographic sites give coinciding spectra (see Ref. 18 for a description of the crystal structure). It is proposed that two radicals are present centered at positions marked by arrows in Fig. 4. Thus the singlet observed at  $g = 1.9971$  is less readily saturated than the component centered at  $g = 2.0044$ . A  $g$ -tensor was obtained from measurements in three mutually perpendicular planes with principal values 1.9954, 1.9968 and 2.0018. These values suggest that the radical is either  $\text{CD}_3\dot{\text{C}}\text{O}_2^-$  or  $\dot{\text{C}}\text{O}_2^-$ . The symmetry of the  $g$ -tensor was used to differentiate between the two cases.<sup>19,20</sup> We have compared the  $g$ -tensor obtained here with that from  $\dot{\text{C}}\text{O}_2^-$  in  $\text{CD}_3\text{CO}_2\text{Li} \cdot 2\text{D}_2\text{O}$  and from the acetyl radical (Table 1). For  $\text{CD}_3\dot{\text{C}}\text{O}$  in  $\text{CD}_3\text{COCl}$  axial symmetry was observed with  $g_{\perp} = 1.9960$  and  $g_{\parallel} = 2.0036$ . In  $\text{CO}_2^-$  there is one value less than the free-electron value  $g_e = 2.0023$  and two approximately equal values greater than  $g_e$ . The comparison favours  $\text{CD}_3\dot{\text{C}}\text{O}$  in  $\text{CD}_3\text{CO}_2\text{D}$ . McCalley and

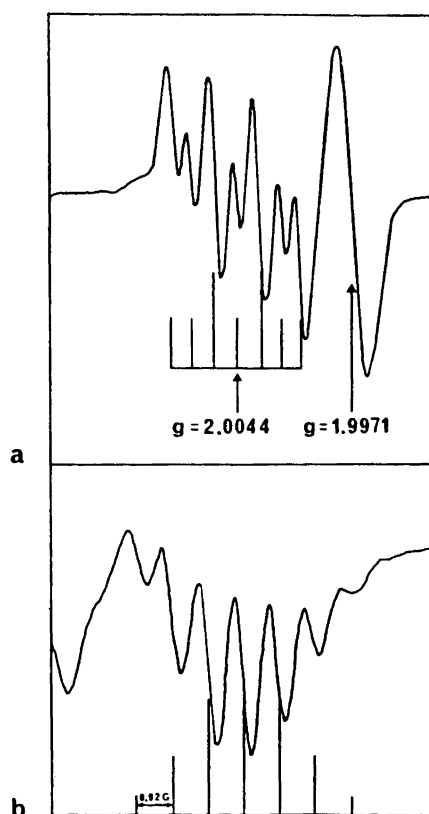


Fig. 4. (a) ESR spectrum of a  $\text{CD}_3\text{CO}_2\text{D}$  crystal, X-irradiated at 77 K at an orientation with resolved components of  $\dot{\text{C}}\text{D}_2\text{CO}_2\text{D}$  and  $\text{CD}_3\dot{\text{C}}\text{O}$  radicals (single line) indicated by stick spectra. The measurement was made at 77 K after thermal annealing at 278 K. (b) Expansion of the  $\text{CD}_3\dot{\text{C}}\text{O}$  radical spectrum with deuterium hyperfine structure as indicated by a stick spectrum centered at  $g = 1.9971$ .

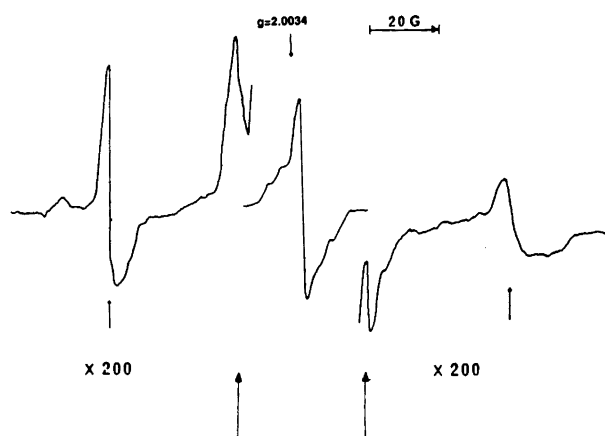


Fig. 5. ESR spectrum of a  $\text{CD}_3\text{CO}_2\text{D}$  powder sample. The outer lines and the lines marked by arrows indicate  $^{13}\text{C}$  splittings.

Kwiram<sup>20</sup> showed that two  $^{13}\text{C}$  hyperfine splittings can be resolved in a substituted acetyl radical,  $\text{RCH}_2\dot{\text{C}}\text{O}$ , with diagonalized tensors of (17.86, 13.71, 13.32) mT and (6.14, 4.75, 4.71) mT, respectively. Lines due to  $^{13}\text{C}$  hyperfine interaction were indeed detected at certain orientations of the crystal, and also from the powder. In the latter case evidence was obtained for two  $^{13}\text{C}$  hyperfine splittings (Fig. 5). There is, however, a possibility that the inner pair of lines (marked by arrows in Fig. 5) originates from  $^{13}\dot{\text{C}}\text{D}_2\text{CO}_2\text{D}$  or another unidentified species. As a final piece of evidence we therefore searched for resolved hyperfine structure from the  $\dot{\text{C}}\text{D}_3$  deuterons in  $\text{CD}_3\dot{\text{C}}\text{O}$ . This could be observed at certain orientations, as exemplified in Fig. 4b. Seven lines were resolved as expected for three equivalent deuterons with a coupling of  $a_{\text{D}} = 0.092$  mT. The hyperfine coupling for the methyl protons in  $\text{CH}_3\dot{\text{C}}\text{O}$  is nearly isotropic, with  $a_{\text{H}} = 0.46\text{--}0.6$  mT.<sup>21</sup> Thus one expects a value of  $a_{\text{D}} = 0.153a_{\text{H}} = 0.070\text{--}0.092$  mT from the ratio of the nuclear  $g$ -factors. The collected evidence shows that the species observed is  $\text{CD}_3\dot{\text{C}}\text{O}$ . The other component at  $g = 2.0044$  in Fig. 4a is probably due to  $\dot{\text{C}}\text{D}_2\text{CO}_2\text{D}$  by analogy with the case of  $\text{CH}_3\text{CO}_2$  investigated previously.<sup>6,11,12</sup> The same conclusion was reached by Ayscough *et al.* using polycrystalline  $\text{CD}_3\text{CO}_2\text{D}$ . The stick spectrum in Fig. 4a suggests an interpretation for this particular orientation.

#### Comparison with acetates.

$\text{CD}_3\text{CO}_2\text{Li} \cdot 2\text{D}_2\text{O}$ .  $\dot{\text{C}}\text{H}_3$  radicals or weak  $\dot{\text{C}}\text{H}_3 \cdots \text{CO}_2$  pairs have been identified in  $\text{CH}_3^{13}\text{CO}_2\text{Li} \cdot 2\text{D}_2\text{O}$  after X-irradiation at 77 K.<sup>15</sup> It is described as a 'positive hole centre' and presumably produced by one-electron loss from  $\text{CH}_3^{13}\text{CO}_2^-$ . In the same experiment the anion,  $\text{CH}_3^{13}\dot{\text{C}}\text{O}_2^{2-}$ , was observed. Triplet radical pairs of  $\dot{\text{C}}\text{O}_2^-$  and  $\dot{\text{C}}\text{H}_3$  radicals were observed at 77 K in irradiated  $\text{CH}_3\text{CO}_2\text{Li} \cdot 2\text{H}_2\text{O}$ .<sup>13</sup> After thermal annealing at room temperature  $\dot{\text{C}}\text{O}_2^-$  and  $\dot{\text{C}}\text{H}_2\text{CO}_2^-$  were observed. The latter radical might be formed according to reaction (8). The fate of the anion and the origin of  $\dot{\text{C}}\text{O}_2^-$  was less clear.

Experiments to investigate whether the acetyl radical is formed in this system gave the following results. The spectra of  $\text{CD}_3\text{CO}_2\text{Li} \cdot 2\text{D}_2\text{O}$  irradiated and measured at 77 K consisted of a doublet due to a triplet-state radical pair and a central component. The  $g$ -value and the zero-field splitting  $D$  of the radical pair (Table 1) were the same, within experimental error, as those reported for  $\text{CO}_2^-$  triplet radical pairs in  $\text{CH}_3\text{CO}_2\text{Li} \cdot 2\text{H}_2\text{O}$  (cf. Ref. 13).

The Li superhyperfine structure was not observed because the  $^6\text{Li}$  isotope used in our experiment has a smaller magnetic moment than  $^7\text{Li}$  used in Ref. 13. The intensity of the radical pair lines was relatively stronger by comparison to the central spectrum in  $\text{CD}_3\text{CO}_2\text{Li} \cdot 2\text{D}_2\text{O}$  than in  $\text{CH}_3\text{CO}_2\text{Li} \cdot 2\text{H}_2\text{O}$ ; compare Fig. 6 with Fig. 2 of Nunome *et al.*<sup>13</sup> The central spectrum in our case probably contains lines from  $\dot{\text{C}}\text{D}_3$  and  $\text{CD}_3\dot{\text{C}}\text{O}_2^{2-}$  by analogy with the case of  $\text{CH}_3\text{CO}_2\text{Li} \cdot 2\text{H}_2\text{O}$ . Upon gradual warm-up the radical pairs disappeared at 260 K.

At room temperature two radicals were observed. One of them is assigned to  $\dot{\text{C}}\text{D}_2\text{CO}_2^-$  by analogy with results obtained with  $\text{CH}_3\text{CO}_2\text{Li} \cdot 2\text{H}_2\text{O}$ .<sup>13</sup> The possibility that the latter radical was actually  $\text{CD}_3\dot{\text{C}}\text{O}$  was considered. The  $g$ -tensor was equal within experimental error to that obtained for  $\dot{\text{C}}\text{O}_2^-$  in  $\text{CH}_3\text{CO}_2\text{Li} \cdot 2\text{H}_2\text{O}$ . In the latter case the assignment was unambiguously made from measurements of the  $g$ - and  $^{13}\text{C}$  hyperfine coupling tensors.<sup>13</sup> There is therefore no evidence for acetyl radicals in lithium acetate.

*Anhydrous acetates.* Comparisons of the stable and free-radical products in anhydrous and hydrated acetates and acetic acid have been made, and some differences have been noted.<sup>2,4,21</sup> Potassium acetate is more stable towards radiation damage than acetic acid and, upon irradiation at 77 K, contains  $\dot{\text{C}}\text{H}_2\text{CO}_2^-$  and  $\dot{\text{C}}\text{H}_3$  as the trapped radicals, with a yield of paramagnetic species which is about 1/10 of the yield of radicals in acetic acid.<sup>21</sup> According to our measurements the total yield of free radicals is approximately the same in acetic acid and in lithium acetate dihydrate after irradiation at 77 K. Single-crystal ESR data

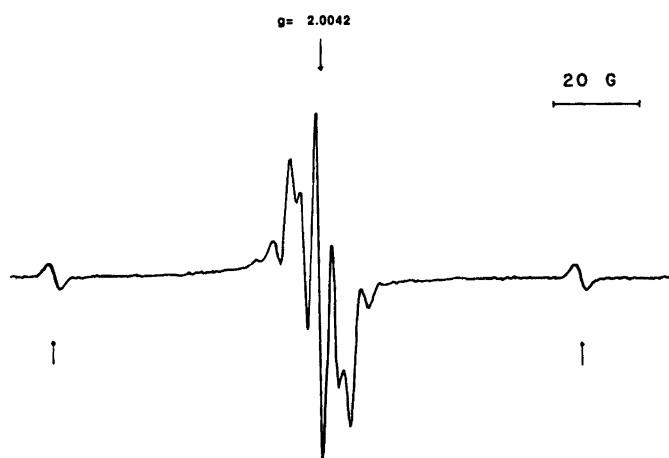


Fig. 6. ESR spectrum of a  $\text{CD}_3\text{CO}_2\text{Li} \cdot 2\text{D}_2\text{O}$  single crystal irradiated and measured at 77 K with  $B$  parallel to  $b$ . Lines on the wings are due to radical pairs.

are not available, and some radicals might have escaped detection in previous investigations. Unfortunately our attempts to grow single crystals of anhydrous systems like  $\text{CH}_3\text{CO}_2\text{K}$  and  $\text{CH}_3\text{CO}_2\text{TI}$  have so far failed.

## Discussion

The proposed scheme for formation and conversion of radicals in the radiolysis of acetic acid in the liquid state is mostly in agreement with the observations on solid samples. According to this scheme the primary steps are ionisation and electron attachment. The positive and negative ions decompose according to reactions (2) and (5) and (5) and (6), respectively. The radicals detected after irradiation and measurement at 77 K in  $\text{CH}_3\text{CO}_2\text{H}$  are  $\dot{\text{C}}\text{H}_2\text{CO}_2\text{H}$  and  $\text{CH}_3\text{CO}_2\text{H}^-$ . In addition to the hypothesis in the scheme,  $\dot{\text{C}}\text{H}_2\text{CO}_2\text{H}$  and analogously  $\dot{\text{C}}\text{D}_2\text{CO}_2\text{H}$  may also be formed by an alternative abstraction process, reaction (9). Since the hydrogen atoms were not detected in



either case, and the methyl radical was only seen in  $\text{CD}_3\text{CO}_2\text{D}$ , the mechanisms are tentative. Previously  $\text{CH}_3\dot{\text{C}}\text{O}$  has been observed in irradiated  $\text{CH}_3\text{CO}_2\text{H}$  by ESR spectroscopy in polycrystalline samples after thermal annealing to decompose the anion.<sup>6</sup> The radicals found in  $\text{CD}_3\text{CO}_2\text{D}$  after irradiation and measurement at 77 K are  $\dot{\text{C}}\text{D}_3$  and  $\text{CD}_3\text{CO}_2\text{D}^-$ . The observation of  $\text{CD}_3\dot{\text{C}}\text{O}$  after the decay of the anion in irradiated  $\text{CD}_3\text{CO}_2\text{D}$  single crystals is new and is in agreement with the proposed scheme for the decomposition of the negative ion in radiolysis of carboxylic acids.<sup>19,20</sup> According to the observations by Toriyama *et al.*, the methyl radical is formed by the fragmentation of the positive ion.<sup>4,15</sup>  $\dot{\text{C}}\text{H}_3$  was not observed in irradiated dry  $\text{CH}_3\text{CO}_2\text{H}$  or  $\text{CH}_3\text{CO}_2\text{D}$ , but appears if 20% or more water is present.  $\dot{\text{C}}\text{D}_3$  has been observed in dry irradiated  $\text{CD}_3\text{CO}_2\text{D}$  by Ayscough *et al.*<sup>6</sup> and by us. Evidently the hydrogen abstraction reaction (8) occurs more easily with  $\dot{\text{C}}\text{H}_3$  than with  $\dot{\text{C}}\text{D}_3$ , in agreement with previous experiments and theory.<sup>22,23</sup> Our measurements show that  $\dot{\text{C}}\text{D}_3$  can be observed at least up to 111 K (Fig. 3). They have disappeared at about 140 K, probably forming  $\dot{\text{C}}\text{D}_2\text{CO}_2\text{D}$  according to reaction (8). According to this scheme,  $\dot{\text{C}}\text{D}_2\text{CO}_2\text{D}$  and  $\text{CD}_3\dot{\text{C}}\text{O}$  may be regarded as secondary oxidation and reduction products, respectively.

One issue, namely the fragmentation of the molecular anion, has not been discussed much before. LoBrutto *et al.* have investigated radiation effects in zinc acetate and observed that the anion decomposes to give  $\dot{\text{C}}\text{O}_2^-$  and a diamagnetic product by cleavage of the carbon-carbon bond.<sup>1</sup>  $\dot{\text{C}}\text{O}_2^-$  has been observed as a relatively stable species in lithium acetate dihydrate, whereas it has not been detected in acetic acid or anhydrous acetates. Molecular anions of carboxylic acids are found to have an extra proton abstracted by the anion from its environment.<sup>24</sup> Acetic acid forms hydrogen-bonded chains in the crystal,<sup>18</sup> and the

anion can be protonated through the hydrogen bonds. Also in acetates containing water of crystallisation the anion is probably protonated. In this case, however, reactions (4) and (7) cannot occur, explaining why acetyl is not formed. Instead reaction (10) might take place.



Reaction (10) is analogous to the scheme proposed for the succinic acid anion.<sup>25</sup> It was later found that the succinic acid anion decomposes to an acetyl radical.<sup>19,20</sup> The mechanism may be correct for the hydrated acetates, however.

## Conclusions

(a) There is a difference between the decomposition reactions of the anion radical in acetic acid on the one hand and in hydrated metal ion acetates on the other. The anion of the former decomposes by ultimately forming an acetyl radical. In the latter case  $\dot{\text{C}}\text{O}_2^-$  is the major anion radical. The difference is probably not unique for the acetic acid/acetate systems. The carboxyl radical has been considered by radiation chemists as an important species in oxalic acid, but the mechanism of formation<sup>2</sup> by cleavage of the C-C bond does not seem applicable to monocarboxylic systems. In anhydrous acetate systems the mechanism of free radical formation is less well investigated, and single-crystal ESR studies are desirable.

(b) The hydrogen atom [reactions (4) and (6)] is not observed in the ESR experiments. Either the reactions occur too rapidly, or the decomposition of the anion to acetyl radicals occurs in a single step. One possible future test of the mechanism would be to add an unsaturated acid to observe hydrogen addition types of radicals.

(c) The cation radical decomposes [reactions (1)–(3)] to give methyl and  $\text{CO}_2$ . Under our conditions (irradiation and observation at 77 K)  $\dot{\text{C}}\text{D}_3$  has been identified in  $\text{CD}_3\text{CO}_2\text{D}$ , whereas  $\dot{\text{C}}\text{H}_3$  in  $\text{CH}_3\text{CO}_2\text{H}$  was not observed, probably because of an isotope effect in reaction (8). This agrees with the observations of Ayscough *et al.*<sup>6</sup> in acetic acid and by Williams and Sprague<sup>22</sup> in related systems.

(d) The secondary radical  $\dot{\text{C}}\text{H}_2\text{CO}_2\text{D}$  is definitely present at 77 K in  $\text{CH}_3\text{CO}_2\text{D}$ , as shown here and in previous ESR single-crystal studies.<sup>11,12</sup> The failure to detect it in polycrystals is attributed to overlap by lines from the anion.

(e) The reaction scheme proposed for acetic acid fails to account for the formation of  $\dot{\text{C}}\text{O}_2^-$  in, for example,  $\text{CD}_3\text{CO}_2\text{Li} \cdot 2\text{D}_2\text{O}$ , where  $\dot{\text{C}}\text{O}_2^-$  triplet radical pairs have been observed at 77 K, and  $\dot{\text{C}}\text{O}_2^-$  radicals after thermal annealing. Further comparisons of the decomposition of anions in carboxylic acids and the corresponding salts should be made to clarify the issue.

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