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

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Single crystals of CH₃CO₂H, CH₃CO₂D, CD₃CO₂D and CD₃CO₂Li·2D₂O have been irradiated with X-rays and investigated by ESR spectroscopy with the purpose of comparing the fragmentation pattern of the molecular anion radicals. CD₃CO was identified as the radical product in the decay of CD₃CO₂D⁺ in CD₃CO₂D, and CO₂⁻ was similarly identified in the decay of CD₃CO₂⁺ in CD₃CO₂Li·2D₂O, confirming an earlier observation [LoBrutto, R., Budzinski, E. E. and Box, H. C. J. Chem. Phys. 72 (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 CO₂⁻ radical ions have been detected after irradiation in the solid state. The radiation chemistry of carboxylic acids has been most thoroughly studied in the case of acetic acid. A radiolysis mechanism for liquid acetic acid includes steps (1)–(8). The major final products are CO₂ and CH₄.

\[
\begin{align*}
\text{CH₃CO₂H} & \rightarrow \text{CH₃CO₂H}^+, \text{CH₃CO₂H}^-, e^- & (1) \\
\text{CH₃CO₂H}^+ + \text{CH₃CO₂H} & \rightarrow \text{CH₃C(OH)₂}^+ + \text{CH₃CO₂}^- & (2) \\
\text{CH₃CO₂}^- & \rightarrow \text{CH₃} + \text{CO₂} & (3) \\
\text{CH₃CO₂H} + e^- & \rightarrow \text{CH₃CO₂H}^- \rightarrow \text{CH₃CO₂}^- + \text{H} & (4) \\
\text{CH₃C(OH)₂}^+ + \text{CH₃CO₂}^- & \rightarrow 2\text{CH₃CO₃H} & (5) \\
\text{H} + \text{CH₃CO₂H} & \rightarrow \text{H₂} + \text{CH₃CO₂}^- & (20\%) & (6) \\
& \rightarrow \text{CH₃CO₃H} + \text{H₂O} & (80\%) & (7) \\
\text{'CH₃} + \text{CH₃CO₂H} & \rightarrow \text{CH₄} + \text{CH₃CO₂H} & (8) 
\end{align*}
\]

Many of the free-radical intermediates in acetic acid and acetates have been identified by ESR spectroscopy in the solid state. The radicals identified so far are CH₃, CH₃CO₂H⁺, CH₃CO₂, CH₃CO₂H and CO₂⁻. Of these, CH₃CO₂H⁺, the primary anion, and CH₃CO₂H are observed at 77 K in the dry acid. The molecular cation CH₃CO₂H⁺ is not stable at 77 K, but the CH₃ radicals observed in acetic acid containing water are thought to be decomposition products, together with CO₂. In dry CH₃CO₂H CH₃ is not observed. CD₃ is, however, present after irradiation of dry CD₃CO₂D at 77 K. Evidently, in the former case CH₃ reacts further and produces CH₃CO₂H. Evidence that CD₃CO is a secondary radical formed by the decomposition of the anion has been obtained. The measurements were made using polycrystalline samples, and the ESR spectrum overlapped the CH₃CO₂H spectrum. In this paper we have used single crystals of CD₃CO₂D in order to obtain a better resolution, and have obtained resolved spectra from CD₃CO subsequent to the thermal decay of the anion. A comparison has been made with the results obtained with crystals of CD₃CO₂Li·2D₂O, in which CD₃CO has not been observed. CO₂⁻ has been observed, both as the isolated radical and as triplet radical pairs in irradiated single crystals of CD₃CO₂Li·2H₂O. The anion is also present in this compound and has been characterized using ¹³C-labelled CH₃¹³CO₂Li·2H₂O. 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

CH₃CO₂H was dried over anhydrous magnesium sulphate and degassed on a vacuum line. CH₃CO₂D purchased from Sigma and CD₃CO₂D 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. 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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Radical</th>
<th>T/K</th>
<th>$g$-factors and coupling constants/mT</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CO$_2$H</td>
<td>CH$_3$CO$_2$H$^-$</td>
<td>77</td>
<td>$g = 2.0032$, $a_{1s} = 3.2$</td>
<td>Refs. 6 and 11</td>
</tr>
<tr>
<td>CH$_3$CO$_2$D</td>
<td>CH$_3$CO$_2$D$^-$</td>
<td>77</td>
<td>$a_{1s} = 3.2$, $a_{2s} = 0.65$, $a_{3s} = 0$</td>
<td>Ref. 12</td>
</tr>
<tr>
<td>CD$_3$CO$_2$D</td>
<td>CD$_3$CO</td>
<td>77</td>
<td>$g = 1.4-3.4$ (2H)</td>
<td>Ref. 12</td>
</tr>
<tr>
<td>CH$_3$COCl/K</td>
<td>CH$_3$CO</td>
<td>77</td>
<td>$g = 1.9954, 1.9968, 2.0018$, $A = 0.992$</td>
<td>This work</td>
</tr>
<tr>
<td>CD$_3$CO$_2$D</td>
<td>CD$_3$</td>
<td>77</td>
<td>$a_0 = 0.355$</td>
<td>Ref. 6</td>
</tr>
<tr>
<td>CD$_3$COCl/K</td>
<td>CD$_3$CO</td>
<td>77</td>
<td>$g = 1.9960, 2.0036$</td>
<td>Ref. 21</td>
</tr>
<tr>
<td>CD$_3$CO$_2$Li·2D$_2$O</td>
<td>CO$_2^-$</td>
<td>77</td>
<td>$g = 1.9965, 2.0016, 2.0027$, $D = -8.777$</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$g = 1.9972, 2.0026, 2.0039$</td>
<td></td>
</tr>
</tbody>
</table>

16.6°C. Crystals of CD$_3$CO$_2$Li·2D$_2$O were obtained by mixing CD$_3$CO$_2$D and $^4$Li$_2$CO$_3$ followed by crystallization in D$_2$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$_3$CO$_2$Li·2D$_2$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.

#### Results

In previous papers ESR single-crystal data for CH$_3$CO$_2$H and CH$_3$CO$_2$D have been briefly reported.\textsuperscript{11,12} The formation of CD$_3$CO in CD$_3$CO$_2$D was mentioned in a conference report.\textsuperscript{17} Radical formation in acetates has been described by several authors.\textsuperscript{3,4,8,10} 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$_3$CO$_2$H and CH$_3$CO$_2$D. At 77 K the spectra contain two components.\textsuperscript{11,12} 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$_3$ 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$_3$CO$_2$H and CH$_3$CO$_2$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. 1](image1.png)

**Fig. 1.** ESR line positions in a CH$_3$CO$_2$D single crystal (in-plane) showing good resolution. Lines due to CH$_3$CO$_2$D$^-$ and CH$_3$CO$_2$D are marked. Irradiation and measurements were made at 77 K.

![Fig. 2](image2.png)

**Fig. 2.** ESR spectrum of a CH$_3$CO$_2$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$_3$CO$_2$D$^-$ and CH$_3$CO$_2$D are indicated by stick spectra.
suggest that CD₃CO₂D⁻ has then been converted into CD₃CO. 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 CD₃CO⁻ or CO⁻. The symmetry of the g-tensor was used to differentiate between the two cases.²⁰ We have compared the g-tensor obtained here with that from CO⁻ in CD₃CO₂Li·2D₂O and from the acetyl radical (Table 1). For CD₃CO in CD₃COCl axial symmetry was observed with g₁ = 1.9960 and g₃ = 2.0036. In CO⁻ there is one value less than the free-electron value gₑ = 2.0023 and two approximately equal values greater than gₑ. The comparison favours CD₃CO in CD₃CO₂D. McCalley and

Fig. 3. ESR spectra of a CD₃CO₂D crystal irradiated at 77 K and measured at (a) 77 K, (b) 111 K before annealing with lines due to CD₃, and (c) 77 K after annealing at 150 K showing features due to CD₃CO₂D⁻.

anion decayed at about 173 K. The spectra were then analysed again in search of the secondary CH₃CO 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 CH₃CO compared to radicals such as CH₃CO₂H. The spectra were complex, and it was not easy to identify the radicals. The radicals in CD₃CO₂D were therefore investigated.

CD₃CO₂D. In agreement with the results obtained from polycrystalline samples two species, identified as CD₃CO₂D⁻ and CD₃, were observed at 77 K.⁶ 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 CD₃ 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 CD₃CO₂D⁻. Above 173 K CD₃CO₂D⁻ disappeared irreversibly and a new signal occurred. We sug-

Fig. 4. (a) ESR spectrum of a CD₃CO₂D crystal, X-irradiated at 77 K at an orientation with resolved components of CD₃CO₂D and CD₃CO radicals (single line) indicated by stick spectra. The measurement was made at 77 K after thermal annealing at 278 K. (b) Expansion of the CD₃CO radical spectrum with deuterium hyperfine structure as indicated by a stick spectrum centered at g = 1.9971.
ACETYL RADICAL FORMATION

Experiments to investigate whether the acetyl radical is formed in this system gave the following results. The spectra of CD₃CO₂Li·2D₂O 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 CO₂⁻ triplet radical pairs in CH₃CO₂Li·2H₂O (cf. Ref. 13).

The Li superhyperfine structure was not observed because the ⁶Li isotope used in our experiment has a smaller magnetic moment than ⁷Li used in Ref. 13. The intensity of the radical pair lines was relatively stronger by comparison to the central spectrum in CD₃CO₂Li·2D₂O than in CH₃CO₂Li·2H₂O; compare Fig. 6 with Fig. 2 of Nunome et al.¹³ The central spectrum in our case probably contains lines from CD₃ and CD₃CO₂⁻ by analogy with the case of CH₃CO₂Li·2H₂O. Upon gradual warm-up the radical pairs disappeared at 260 K.

At room temperature two radicals were observed. One of them is assigned to CD₇CO₂⁻ by analogy with results obtained with CH₃CO₂Li·2H₂O.¹³ The possibility that the latter radical was actually CD₆CO was considered. The g-tensor was equal within experimental error to that obtained for CO₂⁻ in CH₃CO₂Li·2H₂O. In the latter case the assignment was unambiguously made from measurements of the g- and ¹³C hyperfine coupling tensors.¹³ There is therefore no evidence for acetyl radicals in lithium acetate.

Anhydrous acetas. 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.²,⁴,²¹ Potassium acetate is more stable towards radiation damage than acetic acid and, upon irradiation at 77 K, contains CH₃CO₂⁻ and CH₃ as the trapped radicals, with a yield of paramagnetic species which is about 1/10 of the yield of radicals in acetic acid.²¹ 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

Comparison with acetates.

CD₃CO₂Li·2D₂O. CH₃ radicals or weak CH₃···CO₂ pairs have been identified in CH₃CO₂Li·2D₂O after X-irradiation at 77 K.⁵ It is described as a ‘positive hole centre’ and presumably produced by one-electron loss from CH₃CO₂⁻. In the same experiment the anion, CH₃CO₂⁻, was observed. Triplet radical pairs of CO₂⁻ and CH₃ radicals were observed at 77 K in irradiated CH₃CO₂Li·2H₂O.¹³ After thermal annealing at room temperature CO₂⁻ and CH₃CO₂⁻ were observed. The latter radical might be formed according to reaction (8). The fate of the anion and the origin of CO₂⁻ was less clear.

Fig. 5. ESR spectrum of a CD₃CO₂D powder sample. The outer lines and the lines marked by arrows indicate ¹³C splittings.

Fig. 6. ESR spectrum of a CD₃CO₂Li·2D₂O 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 CH₃CO₂K and CH₃CO₂Ti 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 CH₃CO₂H are CH₃CO₂⁺ and CH₃CO₂H⁻. In addition to the hypothesis in the scheme, CH₃CO₂⁻ and analogously CD₃CO₂⁻ 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 CD₃CO₂D, the mechanisms are tentative. Previously CH₃CO₂⁻ has been observed in irradiated CH₃CO₂H by ESR spectroscopy in polycrystalline samples after thermal annealing to decompose the anion. The radicals found in CD₃CO₂D after irradiation and measurement at 77 K are CD₃ and CD₃CO₂D⁻. The observation of CD₃CO after the decay of the anion in irradiated CD₃CO₂D single crystals is new and is in agreement with the proposed scheme for the decomposition of the negative ion in radiolysis of carboxylic acids. According to the observations by Toriyama et al., the methyl radical is formed by the fragmentation of the positive ion. CH₃H was not observed in irradiated dry CH₃CO₂H or CH₃CO₂D, but appears if 20% or more water is present. CD₃ has been observed in dry irradiated CD₃CO₂D by Ayscough et al. and by us. Evidently the hydrogen abstraction reaction (8) occurs more easily with CH₃H than with CD₃H, in agreement with previous experiments and theory. Our measurements show that CD₃ can be observed at least up to 111 K (Fig. 3). They have disappeared at about 140 K, probably forming CD₃CO₂D according to reaction (8). According to this scheme, CD₃CO₂D and CD₃CO can 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 CO₂⁻ and a diamagnetic product by cleavage of the carbon-carbon bond. CO₂⁻ 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. Acetic acid forms hydrogen-bonded chains in the crystal, 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.

\[
\text{CH₃CO₂⁻}(\text{H}^+ \rightarrow \text{CH₄ + CO}_₂⁻) \tag{10}
\]

Reaction (10) is analogous to the scheme proposed for the succinic acid anion. It was later found that the succinic acid anion decomposes to an acetyl radical. 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 CO₂⁻ 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 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 CO₂. Under our conditions (irradiation and observation at 77 K) CD₃ has been identified in CD₃CO₂D, whereas CH₃H in CH₃CO₂H was not observed, probably because of an isotope effect in reaction (8). This agrees with the observations of Ayscough et al. in acetic acid and by Williams and Sprague in related systems.

(d) The secondary radical CH₃CO₂D is definitely present at 77 K in CH₃CO₂D, as shown here and in previous ESR single-crystal studies. 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 CO₂⁻ in, for example, CD₃CO₂Li·2D₂O, where CO₂⁻ triplet radical pairs have been observed at 77 K, and CO₂⁻ 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.

**References**

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