# Electron Spin Resonance Spectra of Ester Radical Cations; Evidence for Hydrogen Atom Migration

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Exposure of  $CH_3CO_2CHD_2$  in dilute solutions in  $CFCI_3$  to  ${}^{60}Co \gamma$ -rays at 77 K or to X-rays at *ca*. 4 K gave only the rearranged cation  $CH_3C(=OH^+)-OCD_2$ , as detected by e.s.r. spectroscopy. This result is discussed in the light of current ideas concerning the structures of ester radical cations.

There has been a recent spate of e.s.r. spectroscopic studies of primary organic radical cations, following the discovery that various cations which had proven impossible to prepare by other methods were readily formed by radiolysis of dilute solutions of molecular precursors in various fluorinated solvents.<sup>1-5</sup> In many cases, the e.s.r. results proved to be reasonably unambiguous despite the fact that only 'powder' spectra are available. However, in certain cases, ambiguities have arisen, perhaps the most notable being for the ester cations.

The problem for ester cations is two-fold: on the one hand, theory shows that two quite different orbitals are potential SOMOs (semi-occupied molecular orbitals),<sup>6–8</sup> the calculated energies being so close that no clear selection can be made on the basis of theory, and on the other, gas-phase studies show that rearrangements such as (1) take place readily.<sup>9</sup>



E.s.r. results obtained from dilute solutions, especially in  $CFCl_3$ , have not been clear-cut. Rearrangements such as (1) clearly occur for various higher esters, a well defined example being the formation of (1) from isopropyl acetate.<sup>10</sup> However,



this is clearly facilitated by the stabilising effect of the two methyl groups and we would expect that methyl esters should be less likely to undergo reaction (1) at low temperatures. For methyl formate, another complication arose, since the primary cation formed a well defined solvent complex (2), showing strong hyperfine coupling to chlorine.<sup>11,12</sup>

It was surmised that this complex was derived from the  $\sigma(nb)$  structure (3) rather than the alternative  $\pi$ -structure (4).



Evidence for this is based on the observation of a well defined hyperfine coupling (17 G) to the formyl proton, <sup>11,12</sup> but, as we

have stressed, this is a relatively small coupling and there is no compelling reason for accepting this limiting structure.<sup>10</sup>

On annealing to *ca.* 110 K this complex underwent an irreversible change to give a species having a proton coupling of *ca.* 25 G to two equivalent protons both belonging to the methyl group.<sup>11,12</sup> Whilst this result suggested the rearranged complex formed as in (1), we rejected this conclusion in favour of the  $\pi$ -cation (4) for the following reasons: (i) the proton coupling seemed to be slightly too large for the rearranged cation; (ii) INDO calculations of the <sup>1</sup>H coupling for the  $\pi$ -cation were in good agreement with experimental results; (iii) the anisotropy of the proton coupling seemed to be less than that usually observed for H<sub>2</sub>Č-X radicals.<sup>10</sup>

None of these arguments is compelling and Iwasaki *et al.* have come down firmly in favour of reaction (1) for the radical formed from the solvent adduct of the methyl formate cation.<sup>13</sup> However, the results of Sevilla and his co-workers for deuterium-substituted ethyl formate [DC(O)CH<sub>2</sub>CD<sub>3</sub>] seemed to provide conclusive evidence in favour of the  $\pi$ -cation formulation (4).<sup>14</sup> Thus the non-deuteriated radical showed couplings of 22.5 G (2 H) and 10–11 G (2 H), whilst that from the deuteriated ester showed couplings to only 2 H (22.5 G). These results seemed to be reasonable for the  $\pi$ -cation. However, for the rearranged species (5), coupling to only one  $\alpha$ proton and almost certainly three equivalent  $\beta$ -protons was expected, whilst for (6), although the data for the normal ester



could be accommodated, with two  $\alpha$ -H giving 22.5 G and two  $\beta$ -H giving 10—11 G, the deuteriated species  $DC(=OD^+)^2$ -CH<sub>2</sub>CD<sub>2</sub> was expected to exhibit an 11 G triplet rather than a 22.5 G triplet. It seemed reasonable to argue, therefore, that hydrogen atom migration had not occurred and hence that it had also not occurred for the methyl derivative.

Our approach to solving this problem was to use  $Me-C(O)OCD_2H$  in the expectation that the  $\pi$ -cation would display a doublet species with  $A(^1H) \ge 23$  G, whilst formation of the rearranged species would involve migration of <sup>1</sup>H rather than <sup>2</sup>H, and hence this species would not exhibit any large doublet splitting. We selected the acetate rather than the formate since this avoided the complication arising from the solvent complex formed by the latter cation. The results, described later, clearly favour the occurrence of reaction (1) at both 77 K and *ca.* 4 K.

An alternative approach was taken by Sevilla *et al.*<sup>15</sup> They concentrated on the problem posed by the ethyl esters and, in particular, probed the effect of the alternative deuteriation, in which the methylene group was deuteriated and not the methyl



Figure 1. First-derivative X-band e.s.r. spectra obtained from (a)  $CH_3CO_2CH_3$  and (b)  $CH_3CO_2CHD_2$  in CFCl<sub>3</sub> after exposure to <sup>60</sup>Co  $\gamma$ -rays at 77 K, showing features assigned to (a)  $CH_3C(OH)OCH_2$  and (b)  $CH_3C(OH)OCD_2$  radical cations

group  $[DC(O)CD_2CH_3]$ . Their results, which again favour ready hydrogen atom transfer, are also described fully later.

### Experimental

Partially deuteriated methyl acetate was synthesised from  $CH_3C(=O)Cl$  and  $CD_2HOH$  (MSD isotopes) by standard procedures.

Degassed solutions in purified CFCl<sub>3</sub> were frozen as small beads in liquid nitrogen and exposed to <sup>60</sup>Co  $\gamma$ -rays in a Vickrad cell at 77 K to doses of up to 1 Mrad. Alternatively, samples were X-irradiated in Supracil tubes at *ca*. 4 K using an Oxford Instruments helium cryostat.

E.s.r. spectra were measured with a Varian E109 spectrometer in the temperature range ca. 10 to ca. 160 K using the liquid helium cryostat and a Varian variable-temperature accessory.

### **Results and Discussion**

A typical e.s.r. spectrum for  $CH_3CO_2CHD_2$  is shown in Figure 1. The triplet spectrum obtained from  $CH_3CO_2CH_3$ is included for comparative purposes. The spectra were almost invariant in the 10—77 K range. On annealing to *ca.* 145 K some resolution into a set of at least six features separated by *ca.* 4 G was obtained. The triplet features for  $CH_3CO_2CH_3$  also narrowed in this range and showed a quartet substructure of *ca.* 5 G splitting.

There is no sign of a doublet splitting  $\ge 23$  G. This strongly suggests that the hydrogen atom has indeed been transferred as

in equation (1), the species detected being  $CH_3C(OH^+)\dot{C}D_2$ . Coupling to the methyl protons should be *ca*. 5 G and that to the two <sup>2</sup>H nuclei *ca*. 3.5 G. Overlap of lines would give a poorly defined set of lines in the central region with a mean splitting in the region of 4 G, as observed.

The only way this result could be accommodated in terms of a  $\pi$ -cation with restricted rotation of the CHD<sub>2</sub> group would be for the proton to be close to the nodal plane, with the two deuterium atoms giving maximum overlap. This conformation is just the reverse of that expected, since it is well established that the lighter isotope favours the out-of-plane site.<sup>16,17</sup> Indeed, we would have predicted a conformation giving maximum coupling to the unique proton (*ca.* 46 G for the  $\pi$ -cation).

On the other hand, we expect almost complete preference for hydrogen atom transfer rather than deuterium transfer in reaction (1). This generalisation is backed by extensive e.s.r. studies, especially by Williams and his co-workers.<sup>18</sup> It is also supported by the results for the  $DCO_2CD_3$  cation-solvent complex discussed below. Thus we should obtain the radical  $CH_3C(OH^+)\dot{C}D_2$  and, in our view, this is indeed the species obtained.

It is significant that this is also the dominating species obtained after X-irradiation at ca. 4 K. The absence of any large temperature effect implies that there is a major contribution from quantum mechanical tunnelling in this rearrangement.<sup>18</sup> This leads us to support Sevilla's suggestion <sup>19</sup> that the species tentatively identified as the true  $\pi$ -cation of methyl formate<sup>13</sup> is really HC(OH<sup>+</sup>)CH<sub>2</sub>. In fact, the triplet spectrum is quite similar to that now clearly assignable to the rearranged radical. Even so, there remain interpretive problems with this system.

Further evidence in favour of this postulate stems from work on DCO<sub>2</sub>CD<sub>3</sub>.<sup>15</sup> This forms the normal solvent adduct (7) at 77 K, but the irreversible change observed for DCO<sub>2</sub>CH<sub>3</sub>, now clearly known to give DC(OH)<sup>+</sup>OCH<sub>2</sub> at *ca*. 110 K, does not, apparently, occur. Indeed, the complex is much more stable, in accord with our result of a major kinetic isotope effect favouring <sup>1</sup>H transfer. When reaction *does* occur, at *ca*. 150 K, Sevilla *et al.* are of the opinion that instead of forming DC(OD)<sup>+</sup>O CD<sub>2</sub> by <sup>2</sup>H transfer, the complex prefers to break down to give OCOCD<sub>3</sub> [equation (2)], where S is some proton-accepting



impurity. The evidence for this is primarily the small shift to a mean negative g value of 2.0017. This result is not absolutely compelling, since the average g value for this radical in other solvents is smaller,<sup>20</sup> but, for our purposes, the key result is the fact that no change occurs in the temperature range for which migration of <sup>1</sup>H is very rapid.

In summary, it seems that for these methyl esters, hydrogen atom migration involves a rapid tunnelling which takes place readily for the  $\sigma[O_{nb}]$  cation even at *ca.* 4 K. For the formate this is in competition with the formation of a solvent complex which inhibits the rearrangement. This occurs at *ca.* 110 K for the <sup>1</sup>H formate, but at > 150 K for the <sup>2</sup>H formate if it occurs at all.

In the light of these conclusions, we turn to the apparent paradox presented by the ethyl esters.

*Ethyl Ester Cations.*—In order to probe the apparently definitive results obtained from  $DCO_2CH_2CD_3$  which favour  $\pi$ -cation formation, Sevilla *et al.* turned to  $DCO_2CD_2CH_3$ .

Remarkably, the triplet spectrum obtained for the former was also obtained for the latter.<sup>15</sup> However, for the latter, this spectrum was obtained directly at 77 K, whereas for the former a 40 G doublet was initially obtained and it was necessary to warm to *ca.* 140 K before the triplet spectrum was irreversibly formed. This temperature effect had not been thought significant in previous discussions. The new interpretation is summarised in equations (3) and (4). These are based on the concept

$$DC = OCH_2CD_3 \longrightarrow DC = OCH_2CD_2$$
(3)

$$DC = OD^{+} OCH_{2}\dot{C}D_{2} - DC = OD^{+} OCD_{2}\dot{C}H_{2}$$
(4)

that one of the methyl hydrogen atoms migrates for the parent ester, to give the radical  $HC(OH)^+OCH_2\dot{C}H_2$ . This formulation satisfactorily explains the triplet of triplets obtained originally, provided there is a clear preference for the extreme out-of-plane site for the  $-OC(OH)^+H$  unit.

Although this sequence satisfactorily explains why, on annealing, the DCO<sub>2</sub>CH<sub>2</sub>CD<sub>3</sub> derivative gives the same e.s.r. spectrum as the DCO<sub>2</sub>CD<sub>2</sub>CH<sub>3</sub> derivative, both reactions (3) and (4) present difficulties. For (3), in view of the large kinetic isotope effect established for DCO<sub>2</sub>CD<sub>3</sub> cations, and the fact that MeCO<sub>2</sub>CHMe<sub>2</sub> gives MeC(OH<sup>+</sup>)OCMe<sub>2</sub>, we would have expected that DCO<sub>2</sub>CH<sub>2</sub>CD<sub>3</sub> would have given DC(OH<sup>+</sup>)-CHCD<sub>3</sub> in preference to DC(OD<sup>+</sup>)CH<sub>2</sub>CD<sub>2</sub>. This would, of course, block the rearrangement shown in (4). Also, it cannot explain the initial 40 G doublet. If (4) does occur, there are several problems associated therewith. One is the requirement that it be effectively irreversible, and the other that the normal, symmetrical cyclic transition state required for this rearrangement [(8) in equation (5)], cannot be formed because of the

$$R-C \stackrel{0}{\underset{OCH_{2}\dot{C}H_{2}}{\leftarrow}} R\dot{C} \stackrel{O-CH_{2}}{\underset{O-CH_{2}}{\leftarrow}} R-C \stackrel{OCH_{2}\dot{C}H_{2}}{\underset{O-CH_{2}}{\leftarrow}} (5)$$

(8)

extra deuteron, which also has to shift concurrently. That (5) takes place readily has been established in liquid-phase e.s.r. studies,<sup>21,22</sup> and it seems that the cyclic structure (8), although potentially stable, undergoes ring-opening at room temperature.<sup>21,22</sup> The suggestion that the fully formed cyclic radical (8) is actually an intermediate in the rearrangement has been questioned, but it is clear that it is readily produced. This supports the rearrangement postulated by Sevilla *et al.*,<sup>15</sup> but provides no explanation as to its apparent irreversibility for the O-CD<sub>2</sub>CH<sub>2</sub> derivative, or for its rapidity at *ca.* 140 K despite the extra requirement of concurrent proton transfer.

Another problem relates to the magnitudes of the  $\beta$ -proton coupling constants for the  $-OCH_2\dot{C}H_2$  and  $-OCH_2\dot{C}D_2$ radicals. In the former, the initial splittings of *ca.* 16 and 4 G readily change to give two equivalent protons of *ca.* 10—11 G splitting. We have found, however, that the unprotonated analogue CH<sub>3</sub>C(=O)OCH<sub>2</sub>\dot{C}H<sub>2</sub>, formed from CH<sub>3</sub>CO<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>Cl by electron capture in CD<sub>3</sub>OD at 77 K, has two equivalent  $\beta$ -protons with  $A(^{1}H)$  34 G (Figure 2). There was no sign of any change on annealing and, in particular, there was no tendency to form the cyclic structure. Thus, the species formed



Figure 2. First-derivative X-band e.s.r. spectrum obtained from  $CH_3CO_2CH_2CH_2CI$  after exposure to  $^{60}CO \gamma$ -rays at 77 K, showing features assigned to  $CH_3CO_2CH_2CH_2$  radicals

from the cation prefers structure (9) with  $\theta = 60^{\circ}$  but that formed from the chloride prefers the other extreme structure (10) with  $\theta = 30^{\circ}$ . It is possible that the presence of the OH<sup>+</sup> group changes the conformational preference, but it is more probable that structure (9) is formed simply because this is close to the required conformation for hydrogen atom transfer to the carbonyl oxygen (11). If this is correct, then why should



the radical  $-OCH_2\dot{C}D_2$  exhibit a very large coupling (40 G) to just one  $\beta$ -proton initially? This question needs to be added to that posed above: why does <sup>2</sup>H transfer occur readily at 77 K in this case?

We conclude that the ester  $HCO_2CH_2CH_3$  gives  $HC(OH)^+$ -OCH<sub>2</sub>CH<sub>2</sub> radicals at 77 K, but that there are many problems posed by the results for  $DCO_2CH_2CD_3$ , which as yet have no really satisfactory explanation.

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