

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

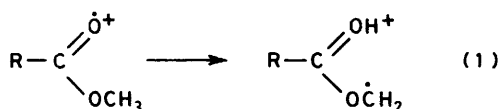
Jan Rideout and Martyn C. R. Symons\*

Department of Chemistry, The University, Leicester LE1 7RH

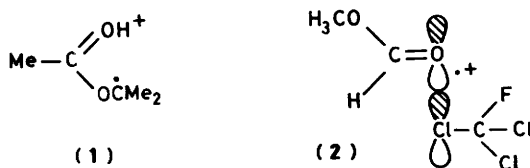
Exposure of  $\text{CH}_3\text{CO}_2\text{CHD}_2$  in dilute solutions in  $\text{CFCl}_3$  to  $^{60}\text{Co}$   $\gamma$ -rays at 77 K or to X-rays at *ca.* 4 K gave only the rearranged cation  $\text{CH}_3\text{C}(=\text{OH}^+)\text{O}\dot{\text{C}}\text{D}_2$ , as detected by e.s.r. spectroscopy. 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>

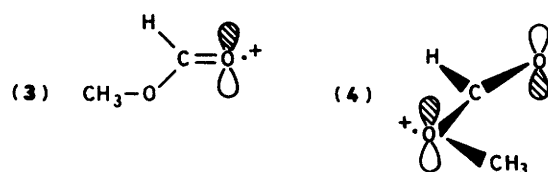


E.s.r. results obtained from dilute solutions, especially in  $\text{CFCl}_3$ , have not been clear-cut. Rearrangements such as (1) clearly occur for various higher esters, a well defined example being the formation of (1) from isopropyl acetate.<sup>10</sup> However,



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).

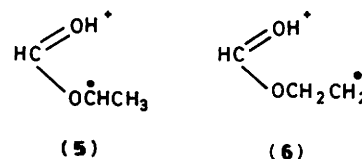


Evidence for this is based on the observation of a well defined hyperfine coupling (17 G) to the formyl proton,<sup>11,12</sup> but, as we

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  $^1\text{H}$  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  $\text{H}_2\dot{\text{C}}-\text{X}$  radicals.<sup>10</sup>

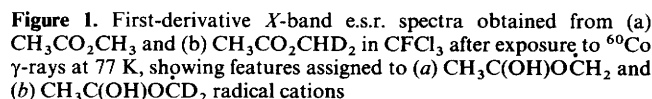
None of these arguments is compelling and Iwasaki *et al.* have come down firmly in favour of reaction (1) for the radical formed from the solvent adduct of the methyl formate cation.<sup>13</sup> However, the results of Sevilla and his co-workers for deuterium-substituted ethyl formate [ $\text{DC}(\text{O})\text{CH}_2\text{CD}_3$ ] 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  $\text{DC}(\text{O}=\text{OD}^+)^2-\text{CH}_2\dot{\text{C}}\text{D}_2$  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  $\text{Me}-\text{C}(\text{O})\text{OCD}_2\text{H}$  in the expectation that the  $\pi$ -cation would display a doublet species with  $A(^1\text{H}) \geq 23$  G, whilst formation of the rearranged species would involve migration of  $^1\text{H}$  rather than  $^2\text{H}$ , 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



## Experimental

Degassed solutions in purified  $\text{CFCl}_3$  were frozen as small beads in liquid nitrogen and exposed to  $^{60}\text{Co}$   $\gamma$ -rays in a Vickrad cell at 77 K to doses of up to 1 Mrad. Alternatively, samples were  $X$ -irradiated in Supracol tubes at *ca.* 4 K using an Oxford Instruments helium cryostat.

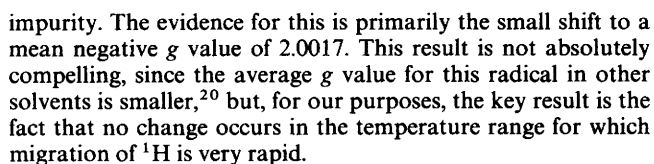
## Results and Discussion

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

The only way this result could be accommodated in terms of a  $\pi$ -cation with restricted rotation of the  $\text{CHD}_2$  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).

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  $\text{HC}(\text{OH}^+)\dot{\text{C}}\text{H}_2$ . 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.

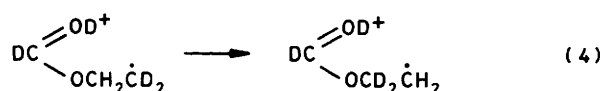
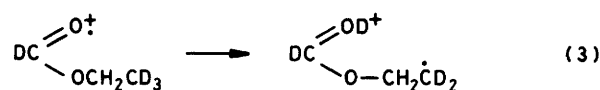
Further evidence in favour of this postulate stems from work on  $\text{DCO}_2\text{CD}_3$ .<sup>15</sup> This forms the normal solvent adduct (7) at 77 K, but the irreversible change observed for  $\text{DCO}_2\text{CH}_3$ , now clearly known to give  $\text{DC}(\text{OH})^+\text{OCH}_2$  at ca. 110 K, does not, apparently, occur. Indeed, the complex is much more stable, in accord with our result of a major kinetic isotope effect favouring  $^1\text{H}$  transfer. When reaction *does* occur, at ca. 150 K, Sevilla *et al.* are of the opinion that instead of forming  $\text{DC}(\text{OD})^+\text{O}\text{CD}_2$  by  $^2\text{H}$  transfer, the complex prefers to break down to give  $\text{OCOD}_3$  [equation (2)], where  $S$  is some proton-accepting



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

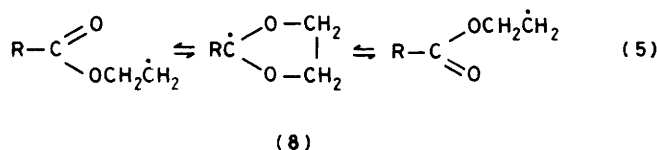
**Ethyl Ester Cations.**—In order to probe the apparently definitive results obtained from  $\text{DCO}_2\text{CH}_2\text{CD}_3$  which favour  $\pi$ -cation formation, Sevilla *et al.* turned to  $\text{DCO}_2\text{CD}_2\text{CH}_3$ .

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



that one of the methyl hydrogen atoms migrates for the parent ester, to give the radical  $\text{HC}(\text{OH})^+\text{OCH}_2\dot{\text{C}}\text{H}_2$ . 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  $-\text{OC}(\text{OH})^+\text{H}$  unit.

Although this sequence satisfactorily explains why, on annealing, the  $\text{DCO}_2\text{CH}_2\text{CD}_3$  derivative gives the same e.s.r. spectrum as the  $\text{DCO}_2\text{CD}_2\text{CH}_3$  derivative, both reactions (3) and (4) present difficulties. For (3), in view of the large kinetic isotope effect established for  $\text{DCO}_2\text{CD}_3$  cations, and the fact that  $\text{MeCO}_2\text{CHMe}_2$  gives  $\text{MeC}(\text{OH}^+)\text{O}\dot{\text{C}}\text{Me}_2$ , we would have expected that  $\text{DCO}_2\text{CH}_2\text{CD}_3$  would have given  $\text{DC}(\text{OH}^+)\text{CHCD}_3$  in preference to  $\text{DC}(\text{OD}^+)\text{CH}_2\dot{\text{C}}\text{D}_2$ . 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



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  $\text{O}-\text{CD}_2\dot{\text{C}}\text{H}_2$  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  $-\text{OCH}_2\dot{\text{C}}\text{H}_2$  and  $-\text{OCH}_2\dot{\text{C}}\text{D}_2$  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  $\text{CH}_3\text{C}(=\text{O})\text{OCH}_2\dot{\text{C}}\text{H}_2$ , formed from  $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_2\text{Cl}$  by electron capture in  $\text{CD}_3\text{OD}$  at 77 K, has two equivalent  $\beta$ -protons with  $A(^1\text{H})$  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

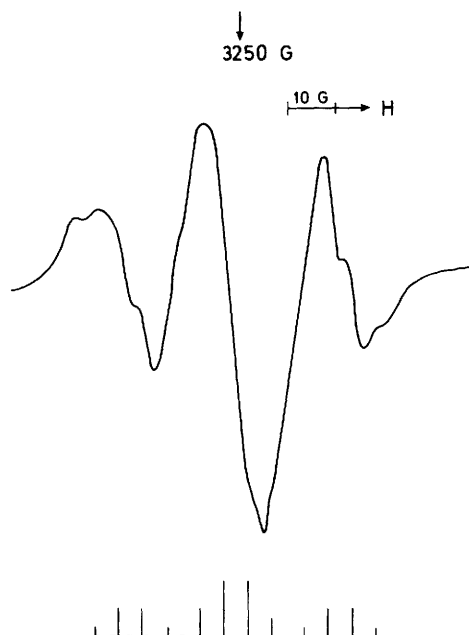
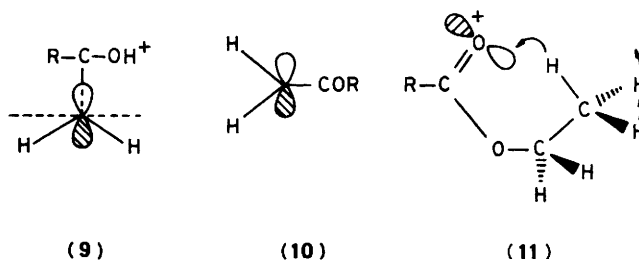


Figure 2. First-derivative X-band e.s.r. spectrum obtained from  $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_2\text{Cl}$  after exposure to  $^{60}\text{Co}$   $\gamma$ -rays at 77 K, showing features assigned to  $\text{CH}_3\text{CO}_2\text{CH}_2\dot{\text{C}}\text{H}_2$  radicals

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  $\text{OH}^+$  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  $-\text{OCH}_2\dot{\text{C}}\text{D}_2$  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  $^2\text{H}$  transfer occur readily at 77 K in this case?

We conclude that the ester  $\text{HCO}_2\text{CH}_2\text{CH}_3$  gives  $\text{HC}(\text{OH})^+\text{OCH}_2\dot{\text{C}}\text{H}_2$  radicals at 77 K, but that there are many problems posed by the results for  $\text{DCO}_2\text{CH}_2\text{CD}_3$ , which as yet have no really satisfactory explanation.

### Acknowledgements

We thank S.E.R.C. for a grant, and Professor M. D. Sevilla for discussions.

### References

- 1 T. Kato and T. Shida, *J. Am. Chem. Soc.*, 1979, **101**, 6869.
- 2 I. G. Smith and M. C. R. Symons, *J. Chem. Res. (S)*, 1979, 382.

- 3 K. Toriyama, K. Nunome, and M. Iwasaki, *J. Phys. Chem.*, 1981, **85**, 2151.
- 4 J. T. Wang and F. Williams, *Chem. Phys. Lett.*, 1981, **82**, 171.
- 5 M. C. R. Symons, *Chem. Soc. Rev.*, 1984, **12**, 393.
- 6 K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, and S. Iwata, 'Handbook of He<sup>+</sup> Photoelectron Spectra of Fundamental Molecules,' Jap. Sci. Soc. Press, 1972, vol. 94, p. 5592.
- 7 D. A. Sweigart and D. W. Turner, *J. Am. Chem. Soc.*, 1972, **94**, 5592.
- 8 T. A. Claxton, J. Rideout, and M. C. R. Symons, *J. Chem. Res. (S)*, 1986, 72.
- 9 H. Budzikiewicz, C. Djerassi, and H. O. Williams, 'Mass Spectrometry of Organic Compounds,' Holden-Day, San Francisco, 1967, p. 176.
- 10 D. N. R. Rao, J. Rideout, and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1221.
- 11 D. Becker, K. Plante, and M. D. Sevilla, *J. Phys. Chem.*, 1983, **87**, 1648.
- 12 G. W. Eastland, A. Hasegawa, J. Rideout, and M. C. R. Symons, *J. Chem. Res. (S)*, 1983, 258.
- 13 M. Iwasaki, H. Muto, K. Toriyama, and K. Nunome, *Chem. Phys. Lett.*, 1984, **105**, 586.
- 14 M. D. Sevilla, D. Becker, C. L. Sevilla, and S. J. Swarts, *J. Phys. Chem.*, 1984, **88**, 1701.
- 15 M. D. Sevilla, D. Becker, C. L. Sevilla, and S. Swarts, *J. Phys. Chem.*, 1985, **89**, 633.
- 16 D. A. Forsyth, P. Lucas, and R. M. Burk, *J. Am. Chem. Soc.*, 1982, **104**, 240.
- 17 V. J. Shiner, B. L. Murr, and G. Heinemann, *J. Am. Chem. Soc.*, 1963, **85**, 2413.
- 18 F. Williams and E. D. Sprague, *Acc. Chem. Res.*, 1982, **15**, 408.
- 19 M. D. Sevilla, *Faraday Discuss. Chem. Soc.*, 1984, **78**, 102.
- 20 M. D. Sevilla, K. M. Morehouse, and S. J. Swarts, *J. Phys. Chem.*, 1981, **85**, 923.
- 21 A. L. J. Beckwith and C. B. Thomas, *J. Chem. Soc., Perkin Trans. 2*, 1973, 861.
- 22 M. J. Perkins and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1975, 77.

Received 12th August 1985; Paper 5/1400