Radiolytically Generated Radical-cations of Simple Esters: an Electron Spin Resonance Study

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Exposure of dilute solutions of simple esters in fluorotrichloromethane to ^{60}Co γ-rays at 77 K gave the corresponding cations in several instances (methyl formate and acetate, ethyl formate and acetate). In all cases, the SOMO of the stable cation was π, with major spin density on the ester oxygen atom and low negative spin density on carbon. This result makes an interesting contrast with that from photoelectron spectroscopy. For the ethyl esters, a large hyperfine coupling (*ca.* 16 G) was observed for one of the γ-protons, in addition to the two β-protons (*ca.* 22 G). The first formed product obtained from methyl formate is thought to have the less stable σ-structure, comparable with those for ketones, stabilised by weak σ-bonding *via* the carbonyl oxygen to one chlorine atom in the solvent. This results in a large chlorine hyperfine splitting. This complex cation decomposed irreversibly on annealing to give the π-cation, with no chlorine hyperfine coupling. This result is discussed in terms of the mechanistic pathway leading to cation formation. The isopropyl and t-butyl esters gave unimolecular breakdown products, identified as the cation $(H_2C\overset{\bullet}{=}CMe_2)^+$ for t-butyl and as a mixture of $(H_2C\overset{\bullet}{=}CHMe)^+$ and $Me_2\dot{C}OC(OH)CH_3^+$ for the isopropyl derivative. Acetates with more remote hydrogen atoms in the alkyl groups gave alkyl radicals thought to be formed by internal attack of the carbonyl oxygen, resulting in hydrogen-atom transfer.

Although mass spectroscopy and photoelectron spectroscopy have been concerned with the study of radical-cations for many years, it is only in the last 2—3 years that they have been systematically studied by e.s.r. spectroscopy.[1–4] The special power of this technique is that besides offering positive identification, it usually provides detailed information about the SOMO (semi-occupied molecular orbital) of the radical. Also, unimolecular pathways for the decomposition of the primary cations are more discriminating at the low temperatures of these studies, and interesting matrix effects can sometimes be observed. Examples of unstable organic radical-cations recently studied by this technique include alkene cations,[5] aryl cations,[6] and nitroalkane cations.[7] These ions are prepared by exposing dilute solutions of the substrates in solvents such as fluorotrichloromethane, to ionizing radiation at 77 K. Under these conditions reactions (1)—(4) occur, resulting clearly in the formation of S^+ cations with no sign of electron-capture or neutral-radical products formed from bond homolysis. Fortunately the e.s.r. spectra for the electron-capture species, (2), are broad at low temperature and do not seriously interfere, and the mobility of $CFCl_3^{+\bullet}$ cations is so great, (3), that they are not detectable in the presence of S.

$$CFCl_3 \longrightarrow CFCl_3^{+\bullet} + e^- \quad (1)$$

$$e^- + CFCl_3 \longrightarrow (^{\bullet}CFCl_3)^- \longrightarrow {}^{\bullet}CFCl_2 + Cl^- \quad (2)$$

$$CFCl_3^{+\bullet} + CFCl_3 \longrightarrow CFCl_3 + CFCl_3^{+\bullet} \quad (3)$$

$$CFCl_3^{+\bullet} + S \longrightarrow CFCl_3 + S^{+\bullet} \quad (4)$$

Recently, Sevilla and his co-workers,[8] and ourselves,[9] have reported details of the e.s.r. spectra of methyl formate cations. The spectrum at 77 K shows a major splitting assigned to the hyperfine coupling to a chlorine nucleus, but this was lost irreversibly on annealing to give the expected π-cation. Coupling to solvent nuclei is fairly common for certain types of cations in these solvents,[9] but this result is exceptional in that the structure of the cation in the solvent complex differs markedly from that of the normal π-cation.

Experimental

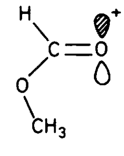
All chemicals used in these studies were of highest grade available. They were generally used as supplied but standard purification procedures were carried out when required. Solutions were prepared by dissolving the ester in fluorotrichloromethane in the ratio 1:1000 (w/w) and they were frozen in liquid nitrogen. They were exposed to γ-rays in a ^{60}Co Vickrad cell with doses of *ca.* 1 Mrad.

E.s.r. spectra were recorded on a Varian E 109 X-band spectrometer calibrated with a Hewlett–Packard 5246L frequency counter and a Bruker BH-12E field probe, which were standardised with a sample of diphenylpicrylhydrazyl. Samples were annealed using a Varian variable-temperature accessory or simply by decanting liquid nitrogen from the insert Dewar and re-cooling to 77 K whenever significant changes were observed.

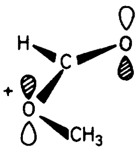
Results and Discussion

According to the results of photoelectron spectroscopy (p.e.s.), and theory,[10,11] ester cations are expected to have the σ (n.b) structure (I) (methyl formate), the SOMO being largely confined to the in-plane $2p$ orbital on the carbonyl oxygen. In all cases except for the primary product from methyl formate, our results are not in accord with this formulation. Instead the SOMO corresponds to the first fully occupied orbital in the proposed energy levels.[10,11] This is the π-structure (II), the spin density being fairly evenly divided between the two oxygen atoms. The former, (I), is the SOMO for the simple carbonyl cations, $R_2C\dot{O}^+$, the sequence being inverted when R is replaced by OR. We stress that it is not a necessary result that the ground state of the matrix-isolated cations be the same as that deduced from p.e.s. This is largely because major distortions from the parent molecular structure can occur under our conditions, but not under p.e.s. conditions. Also matrix perturbations could invert structures when orbitals are in close proximity. However, this is one of the first examples of such an inversion studied by e.s.r. spectroscopy.

Methyl Formate.—As has been reported previously,[8,9] the e.s.r. spectrum for the first formed cation is dominated by features due to hyperfine coupling to a single chlorine nucleus



(I)



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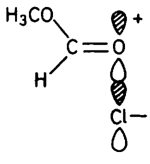

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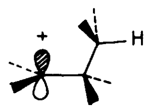
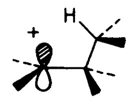
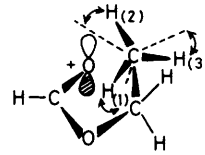


(IV)



(V)



(VI)

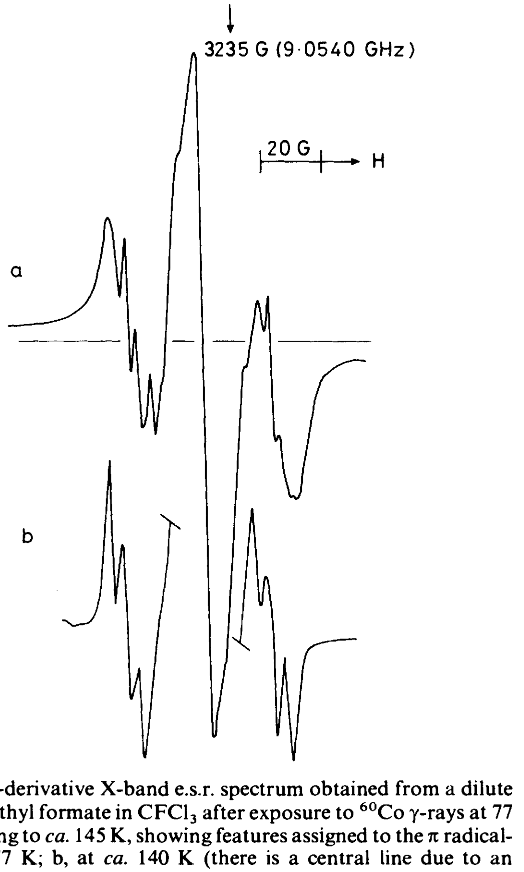


Figure 1. First-derivative X-band e.s.r. spectrum obtained from a dilute solution of methyl formate in CFCl$_3$ after exposure to ^{60}Co γ-rays at 77 K and annealing to *ca.* 145 K, showing features assigned to the π radical-cation: a, at 77 K; b, at *ca.* 140 K (there is a central line due to an impurity which obscures the 10> features)

(see Figure 1 of refs. 8 and 9). Each feature is split into a doublet, due to hyperfine coupling to the formyl proton. On annealing from 77 to *ca.* 140 K the spectrum changed irreversibly, with complete loss of the chlorine coupling, and the appearance of a major triplet assigned to coupling to two equivalent protons. Each line is further split into a triplet at 140 K (Figure 1). It seems that the methyl group is rigidly held in a conformation having two strongly overlapping C–H bonds, the third being close to the nodal plane. The other weakly coupled proton (*ca.* 5 G) must then be the formyl proton, and this has been confirmed by deuterium substitution (these weakly coupled protons have different coupling constants at 77 K: see Figure 1a). It is a noteworthy fact that, for many radical cations, methyl groups exhibit well defined, fixed conformations, rather than exhibiting free rotation in the 77 K temperature region, as is normally observed for the neutral radicals. This may in some cases be an electronic preference rather than being caused by purely steric considerations. These results confirm the π-structure for the annealed cation. The spin density on the acyl carbon is clearly small and probably negative. INDO calculations for the π-cation[8] suggest a spin density of −0.42 in the carbon p_z orbital, leading to a calculated proton coupling of 8.2 G. This is clearly an overestimate, but establishes the expected negative sign. INDO calculations also predict the observed inequivalence of the methyl protons, the theoretical coupling constants being 23, 20, and 0.4 G, in remarkably good agreement with experimental values. Using the average methyl proton coupling of *ca.* 15 G and a *Q* value of 23, we estimate an oxygen *p* (π) spin density of *ca.* 65%. The INDO value of 78% is remarkably high for the small values of the proton coupling constants, especially when the positive charge effect is considered. Thus, for (CH$_3$OCH$_3$)$^+$, A_{iso} is *ca.* 43 G.[4] If a reasonable allowance is made for a partial positive charge, our estimate falls from 65% to, say, *ca.* 50%. We would expect a clear reduction in spin density on X in X-CHO on going from X = NMe$_2$ to X = OMe. From our e.s.r. data for *NN*-dimethylformamide cations we estimated a spin density of *ca.* 78% on nitrogen. Hence values in the region 50—60% seem reasonable for oxygen. This comparison is also interesting in that both methyl groups for the *NN*-dimethylformamide cations were apparently equivalent, and freely rotating at 77 K, which is surprising in the light of our results for methyl formate. The average proton coupling for the amide cation is *ca.* 32 G.[12]

The structure of the solvent adduct clearly differs from that of the π-cation. Thus there is no detectable coupling to the methyl protons, but that to the formyl proton has increased to 17 G. Our original interpretation of these differences was that the first formed cation has a σ (n.b) structure (I) rather than the normal π-structure (II). As with the acetaldehyde cation, this might be expected to form a weak σ* bond to chlorine.[9,13,14] However if this structure (III) is correct, the coupling (17 G) for the formyl hydrogen is remarkably low, compared with that for the acetaldehyde cation (*ca.* 136 G).[15] Furthermore the chlorine coupling is much greater than that for the aldehyde complex.

An alternative is that bonding between the carbonyl oxygen and the chlorine lies more along the π-axis, but in that case why is complexing not observed for the normal π-cation? We therefore favour the σ (n.b) structure, but the proton coupling is smaller than expected.

Methyl Acetate.—The e.s.r. spectrum (Figure 2) is readily interpretable in the light of the above results. When CH$_3$CO$_2$CD$_3$ was used, the major triplet was lost. It is noteworthy that the methoxy methyl group exhibits the same rigid conformation, whereas the acid methyl group appears to be freely rotating even at 77 K. Otherwise the results are very similar to those for the π-cation of methyl formate. As with the formate, rotation of the ester methyl group did not occur even at the maximum temperature available (*ca.* 160 K). This means that the barrier to rotation is ≥4 kcal mol^{-1}. It is interesting that in this case there was no evidence for the initial formation of a solvent adduct. This may be due to a steric factor, but must also reflect the fall in ionization potential on going from the

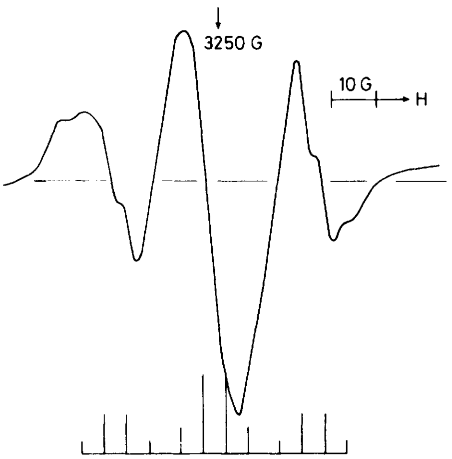


Figure 2. First-derivative X-band e.s.r. spectrum obtained from a dilute solution of methyl acetate in $CFCl_3$ after exposure to ^{60}Co γ-rays at 77 K and annealing to *ca.* 120 K, showing features assigned to the π radical-cation

formate (10.815 eV) to the acetate (10.27 eV).[16] As we have already stressed,[9] we find a marked fall in the chlorine hyperfine coupling as the ionization potential falls, and at some stage this must result in no tendency to form a complex. However, from Figure 2 of ref. 9, we would predict a chlorine parallel coupling of *ca.* 10—20 G for the acetate, which is about equal to that observed for acetaldehyde cations (10.2 eV). Probably the structural switch from (n.b) to π occurs with greater facility for the weaker complex, and it may be that irradiation at 4 K would yield the solvent adduct.

As with other ester cations, when more concentrated solutions were studied, intermolecular hydrogen transfer occurred, to give $H_2\dot{C}OCOCH_3$ radicals.

Ethyl Formate and Acetate.—The results for these cations are most interesting (Figure 3). The spectra are best analysed in terms of two strongly coupled protons (*ca.* 22 G for the formate) which are assigned to the two β-protons, and one other proton (*ca.* 16 G). This must be due to one specific proton from the methyl group. This is confirmed by the fact that there is a reversible change on annealing which changes the 16 G doublets into 10 G triplets (Figure 3b). These assignments have been confirmed by suitable deuteriation. Coupling to the formyl proton is lost in the line widths, and must be less than *ca.* 4 G.

Two aspects of these results are unexpected. One is that motional averaging only interchanges two of the three methyl protons, and the other is the large magnitude of the γ-proton coupling. Large γ-proton coupling for alkyl radicals in specific conformations have been predicted by Ellinger *et al.*[17] and observed by Ingold and his co-workers.[18] The results show that only for the very specific conformation shown in (IV), the so-called W conformation,[19] is the coupling large. For all other structures, including the *anti*-W structure (V), the coupling is predicted to be relatively small. This type of structure has been invoked to explain the large coupling constants for the δ-protons formed for certain cations of aldehydes and ketones,[20,21] but unfortunately it cannot be applied in the present case. This is because the large coupling (22 G) to the two β-protons requires that the C–CH_3 bond lies close to the nodal plane of the SOMO, which is 90° away from the optimum angle required for the W structure (IV). Thus theory predicts only small coupling to all three methyl protons, whatever the orientation of the methyl group.

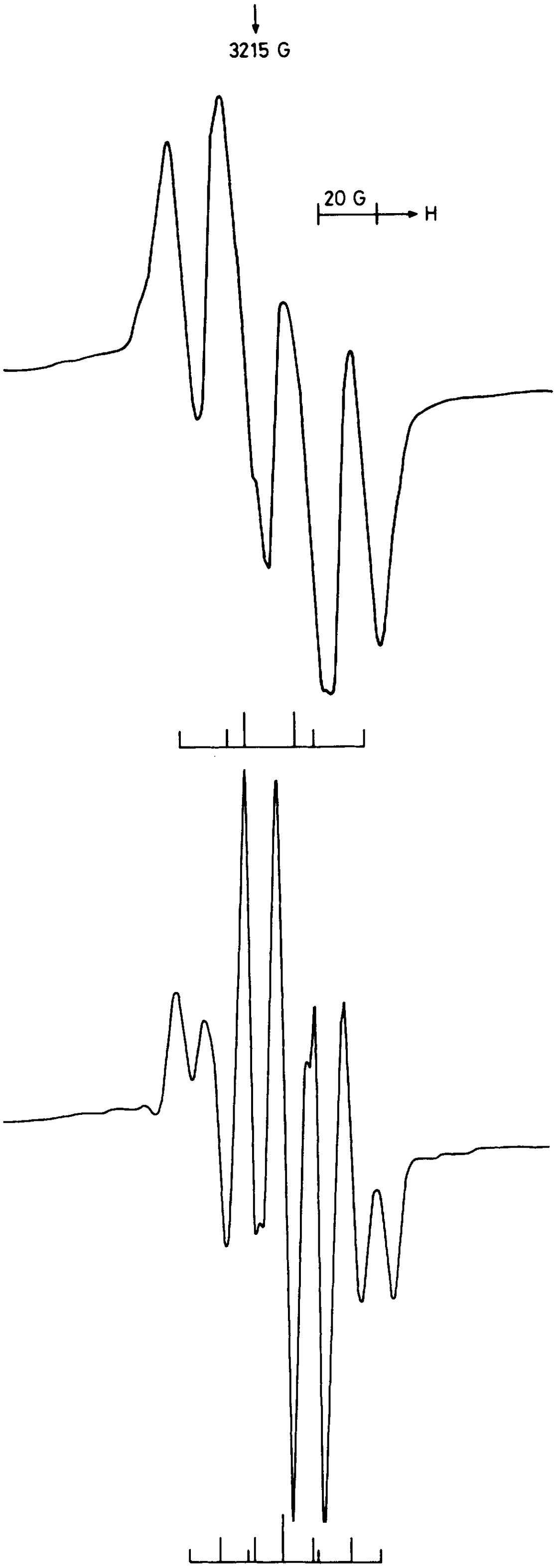


Figure 3. First-derivative X-band e.s.r. spectrum obtained from a dilute solution of ethyl formate in $CFCl_3$ after exposure to ^{60}Co γ-rays: a, at 77 K; b, at *ca.* 140 K, showing features assigned to the π radical-cation

We therefore tentatively invoke a theory similar to one that we originally proposed for the acetaldehyde cation,[15] but which we later showed to be incorrect.[9] The concept involves some 'through-space' interaction with the *p* (π) orbital or the carbonyl oxygen, as in (VI). We also need to explain why there is a barrier to complete rotation of the methyl group of >4 kcal mol^{-1} when that for interconverting two hydrogens is only *ca.* 2 kcal mol^{-1}. It seems to us that the tentative formulation shown in (VI) can explain both results. The preferred conformation places one hydrogen above the carbonyl oxygen, possibly forming a weak hydrogen bond thereto, and acquiring considerable spin density. On warming, H(2) can swing around and interact with the lower lobe of the *p* (π) orbital (dashed lines) so that H(1) and H(2) become equivalent. However if this interaction is significant, neither hydrogen can readily move past the oxygen atom, so that H(3) cannot participate, at least up to *ca.* 160 K. We make this proposal tentatively, and hope to check the possibility with theoretical calculations.

Results for the acetate were similar, except that the two β-protons were no longer equivalent in the low-temperature spectra (Table 1). Also, two γ-proton couplings were observed, one large and one small. It seems that the extra methyl group has distorted the structure adopted by the formate. The resulting asymmetric structure is more rigid since no clear averaging was observed up to 160 K. Other formates and acetates gave broad spectra, some of which can be well analysed in terms of intramolecular hydrogen-atom transfer. However, for isopropyl and t-butyl acetates well resolved spectra were obtained which suggest other modes of breakdown.

t-Butyl Acetate.—The results in this case are clear. A well defined nine-line spectrum was obtained (Figure 4). which can be assigned to the π-olefin cation, $(\mathrm{H_2C{=}CMe_2})^+$, first studied by Shida and his co-worker.[22] The process envisaged for this break-down is given in reaction (5), the driving force for the process coming from the stability of the other product, acetic acid.

Isopropyl Acetate.—In this case, two break-down products were obtained at 77 K. The more stable of the two gave the well defined septet shown in Figure 5a. This is almost certainly due to the radical $\mathrm{Me_2\dot{C}OC(\overset{+}{O}H)Me}$. This rearrangement may also occur, on annealing, for the ethyl ester, giving $\mathrm{Me\dot{C}HOC(\overset{+}{O}H)^+Me}$, but the features were too poorly defined for positive identification. The parameters for these radicals are normal, the remote positive charge having no discernible effect.

Table 1. Experimental e.s.r. parameters for π-cations of esters

Esters	Hyperfine coupling (G)[a,b] $A_{\mathrm{acyl}}^{\mathrm{H}}$	A_{β}^{H}	A_{γ}^{H}
$\mathrm{HCO_2CH_3}$[c]	5.5	23 (2 H), 4 (1 H)	
$\mathrm{CH_3CO_2CH_3}$	5 (3 H)	22 (2 H)	
$\mathrm{CH_3CO_2CD_3}$	5	3.5 (2 ^{2}H)	
$\mathrm{CH_3CH_2CO_2CH_3}$[d]	7 (1 H)	25 (2 H)	
$\mathrm{HCO_2CH_2CH_3}$	≤4	22 (2 H)	10 (2 H) (160 K) 16 (1 H) (77 K)
$\mathrm{CH_3CO_2CH_2CH_3}$		22 (1 H), 31 (1 H)	8 (1 H) 17 (1 H)

[a] G 10^{-4} T. [b] g_{av} *ca.* 2.0026. [c] Formed at *ca.* 140 K from the original adduct. [d] D. Becker, K. Plante, and M. D. Sevilla, personal communication.

Table 2. E.s.r. parameters for species formed from ester cation-radicals.

Esters	Radicals	Nucleus	Hyperfine coupling (G)
$\mathrm{HCO_2CH_3}$	$\mathrm{HC(OCH_3)O^+}$ | $\mathrm{ClCCl_2F}$	^{1}H ^{35}Cl(∥)	(1H) 17 84.5
$\mathrm{CH_3CO_2CH(CH_3)_2}$	$\mathrm{(CH_3)_2\dot{C}OC(OH)\overset{+}{C}H_3}$	^{1}H	(6 H) 22
$\mathrm{CH_3CO_2C(CH_3)_3}$	$\mathrm{H_2C{=}\overset{\bullet +}{C}(CH_3)_2}$	^{1}H	(8 H) 14.6

However, at 77 K there are clearly two species formed, one being the $\mathrm{Me_2\dot{C}OC(\overset{+}{O}H)Me}$ radical. We tentatively suggest that the other is the cation $[\mathrm{H_2C{=}CH(Me)}]^+$ formed by the process proposed above for the $(\mathrm{H_2C{=}CMe_2})^+$ radical-cation, (5). Unfortunately, two quite different e.s.r. spectra have been assigned to this cation, one species being formed from certain saturated alkane cations on annealing, the other being formed directly from propylene.[3] Our spectra, so far as we can judge, quite closely resemble that obtained from propylene, but we will need better spectra for conclusive identification. We obtained no clear evidence for the parent cations for either of these esters.

In view of our firm identification of the $\mathrm{(CH_3)_2\dot{C}O(OH)\text{-}CH_3^+}$ radical, we need to explore the possibility that similar intramolecular hydrogen transfers occurred for the other esters. For methyl formate and acetate this was indeed our original interpretation since the radicals $\mathrm{H_2\dot{C}CO(OH)R^+}$ should give a major triplet. However, the splitting of 22—23 G is greater than that expected, and the $M_I = \pm 1$ features are narrow and more isotropic than is possible for a $\mathrm{\dot{C}H_2}$ group. In our experience, well defined anisotropic features are expected for such a group and indeed are found for $\mathrm{H_2\dot{C}OH}$ radicals formed in this medium. Even more compelling is the spectrum for ethyl formate. The radical $\mathrm{Me\dot{C}HCO(OH)H^+}$ is expected to give a

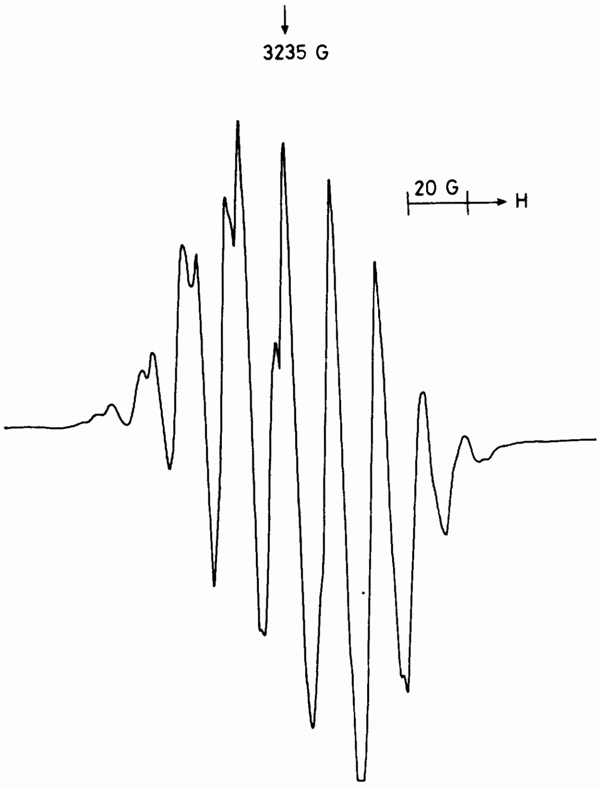
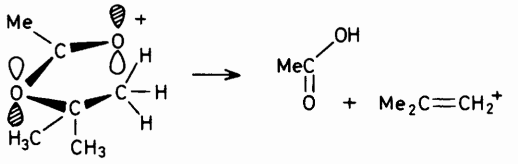


Figure 4. First-derivative X-band e.s.r. spectrum obtained from a dilute solution of t-butyl acetate in $\mathrm{CFCl_3}$ after exposure to ^{60}Co γ-rays at 77 K and annealing to *ca.* 120 K, showing features assigned to the cation, $[\mathrm{H_2C{=}CMe_2}]^{+\bullet}$



(5)

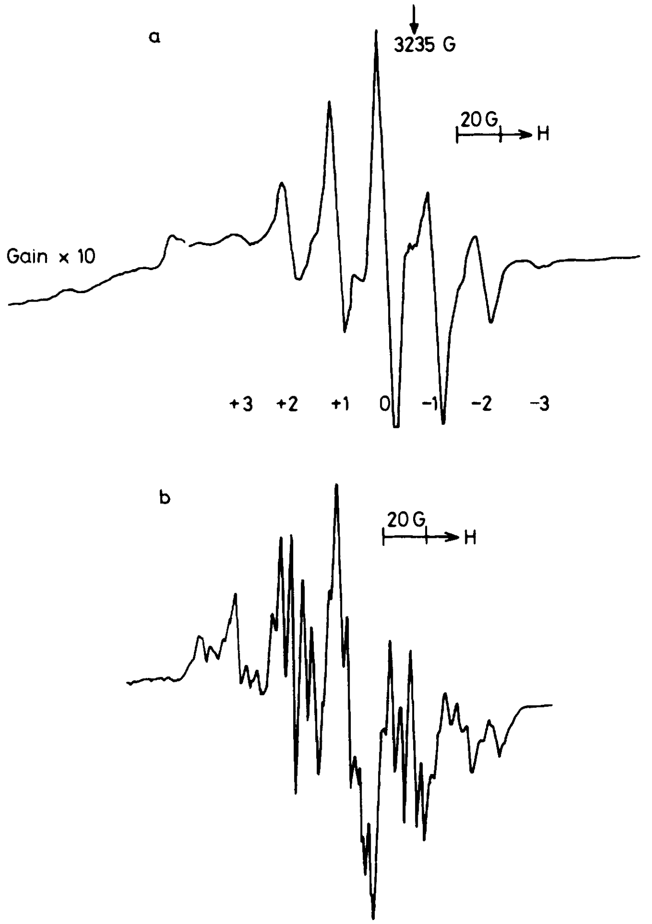


Figure 5. First-derivative X-band e.s.r. spectrum obtained from a dilute solution of isopropyl acetate in $CFCl_3$ after exposure to ^{60}Co γ-rays at 77 K; a, after annealing to *ca.* 140 K showing features assigned to $Me_2CO{-}C(OH)CH_3$ radicals, and b, before annealing, showing extra lines tentatively assigned to $(H_2C{=}CHMe)^+$ cations

broad quintet with $A(^1H)$ *ca.* 20 G, similar to that for the $Me_2\dot{C}HOH$ radical. It seems to us very difficult to assign the detected spectra (Figure 5) to this rearranged radical. We therefore strongly favour the above assignments.

Acknowledgements

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