

Radical-cations of Aldehydes and Ketones generated by Ionizing Radiation: an Electron Spin Resonance Study

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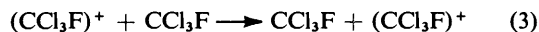
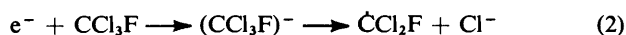
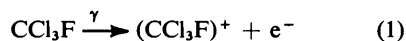
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Exposure of dilute solutions of various aldehydes and ketones in trichlorofluoromethane to ^{60}Co γ -rays at 77 K gave, in most cases, the corresponding cations, identified by e.s.r. spectroscopy. The acetaldehyde cation is characterized by a very large proton hyperfine coupling, the SOMO being the in-plane, formally non-bonding, p -orbital on oxygen. At 77 K there was a weak interaction with one chlorine atom of a solvent molecule, but this was lost reversibly on annealing to *ca.* 120 K. That the quartet splitting was due to chlorine rather than to the methyl protons as had been previously supposed was established by studying the $(\text{CD}_3\text{CDO})^+$ cation. The acetone cation spectrum comprised a single asymmetric feature with no evidence of solvent interaction or hyperfine coupling to the γ -protons. In contrast, aldehyde and ketone cations with δ -protons showed hyperfine coupling in the 10–30 G range to conformationally selected protons. For methyl groups, one proton only is selected, the coupling being lost reversibly on annealing. These findings are semi-quantitatively supported by INDO calculations.

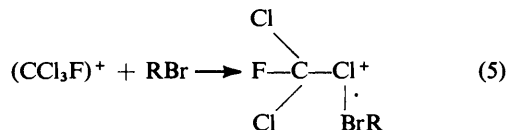
It is commonly supposed that radiation chemistry comprises a multitude of indiscriminate reactions brought about by the very large energies available in X -rays, γ -rays, or high-energy electrons. This is not the case. Instead, by careful control of the systems involved it is possible to study specific electron-addition and electron-loss.^{1,2} When low-temperature solids are used, the primary electron-gain or electron-loss centres are frequently trapped and can be studied at leisure. We have used e.s.r. spectroscopy for this purpose since the spectra are generally able to provide unequivocal identification together with very detailed structural information.

One method for the specific preparation of matrix-isolated radical cations that has been used most successfully during the past few years, initiated by one of us,^{3,4} involves irradiating dilute solutions of neutral substrates in CCl_3F and related solvents.⁵

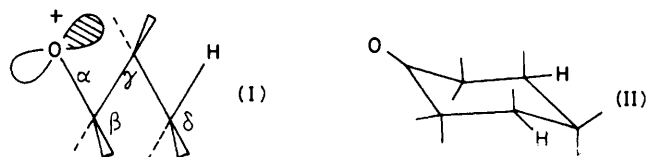
These solvents react so rapidly with ejected electrons that there is no evidence for electron-capture by solute molecules. However, the electron-loss centres $(\text{CCl}_3\text{F})^+$ migrate by electron transfer until they react with a solute molecule (S) as in reactions (1)–(4). The cations $\text{S}^{+\bullet}$ are either trapped as such,



or undergo unimolecular rearrangements or dissociation. Sometimes reaction (4) is incomplete in the sense that a weak σ^* bond is formed between one atom of S and one chlorine ligand of CCl_3F . Thus, for example, RBr reacts as in (5).⁶ Such complexing seems to occur for radical-cations

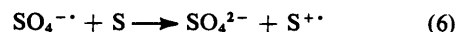


whose SOMO is strongly confined to a single atom, and whose



ionization potential is relatively close to that of CCl_3F (*ca.* 11.8 eV).⁷

The first example of a carbonyl cation, $(\text{R}_2\text{CO})^+$, to be studied by e.s.r. spectroscopy was H_2CO^+ , formed in a sulphuric acid glass.⁸ We have found that this is often a good medium for preparing radical-cations for substrates that are water soluble, or that are protonated,⁹ the key reaction being thought to be (6) or (7). Unfortunately we have not yet been



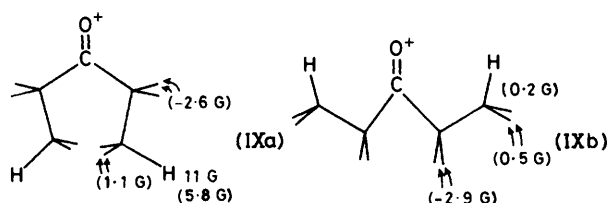
able to form $(\text{H}_2\text{CO})^+$ in Freon, so this work remains unsupported. However, we have been successful in preparing several radical-cations of other aldehydes and ketones.^{10,11}

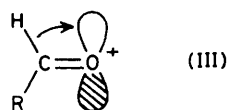
As with $(\text{H}_2\text{CO})^+$,⁹ the aldehydes exhibit a very large hyperfine coupling to the aldehydic proton (120–130 G). We initially supposed that the extra quartet splitting observed at 77 K for $(\text{CH}_3\text{CHO})^+$ was due to coupling to the methyl protons, but later realized that this is actually caused by reversible complex formation with a solvent molecule, the quartet being due to hyperfine coupling to chlorine nuclei.⁷ This was confirmed by studying deuteriated cations.^{7,12} The real coupling to the methyl protons must be small, as is also the case for acetone cations at 77 K.^{10–12} When this study was essentially complete, Snow and Williams published their results for a variety of aldehyde and ketone cations.¹³ In particular, they have shown that, although the coupling to γ -protons is small, the more remote δ -protons can give well resolved splitting when in the optimum in-plane W -plan structure (I), although the average splitting remains small. This is exemplified by the remarkably large coupling of 27.5 G to two δ -protons for the cation of cyclohexanone depicted in (II). Our own results agree well with these assign-

Table. Observed and calculated e.s.r. parameters for various aldehyde and ketone radical cations

No.	Radical	T/K	Hyperfine coupling constants (G) ^{a,b}		
			β-Protons	γ-Protons	δ-Protons
1		77	136(63.7) ^d	(-3.9, -3.9, -0.4)	
2		120	135(61.9)	(-4.0, -4.0)	12.5 (1 H) ^e (4.9, 0.4, 0.4) ^f
3		77	138(68.2)	(1.3)	20 (2 H) (3.1, 1.4, 0.9) × 2
4		77		(-2.3, -2.3, -1.6) × 2	
5		77		(-2.6) × 4	11 (2 H) ^g (5.8, 1.1, 1.1) × 2 ^h
6		77		(-0.6) × 2	15 (4 H) (3.0, 1.6, 0.9) × 4
7		77			15 (4 H) (5.7, 1.0, 1.0) × 4 (2.9, 1.5, 0.9) × 2
8		77		(-1.6, -1.5) × 2	13 (2 H) (2.2, 0.0) × 2
9		77		(-1.9, -1.4) × 2	27.5 (2 H) (5.5, 0.4) × 2
10		77		(-1.8, -1.7) × 2	19.5 (2 H) (4.1, 0.3) × 2

^a $G = 10^{-4} T$. ^b Average g -values *ca.* 2.0035 ± 0.001 . ^c $A_{\parallel}(^{35}\text{Cl})$ 19.0 G; $A_{\perp}(^{35}\text{Cl})$ *ca.* 6 G(CH_3CHO^+); *ca.* 4 G(CD_3CHO^+). ^d The numbers in parentheses are the results of INDO calculations. ^e Lost reversibly on annealing. ^f Calculated for the conformation of structure (Vb). ^g Changes to 3 (4 H) reversibly on annealing. ^h Calculated for the conformation of structure (IXa).





ments, and it seems to be a general rule for these carbonyl cations that, whilst γ -proton coupling has not yet been resolved, that to the δ -protons can be relatively large for the optimum conformation.

Experimental

The carbonyl derivatives were all of the highest grade available and their purities were checked by n.m.r. spectroscopy. Solutions were in the region of 0.1% mole fraction except when the effect of concentration was being studied. Solutions were either frozen as small beads or in quartz tubes and exposed to ^{60}Co γ -rays to doses up to *ca.* 1 MRad. The products, as judged by the e.s.r. spectra, were independent of dose in this range. Spectra were measured on Varian E 109 or JEOL JES-FE-3X spectrometers. They were annealed using a variable-temperature Dewar, or by warming in an insert Dewar after decanting the liquid nitrogen, the samples being recooled to 77 K whenever significant spectral changes were observed.

Results and Discussion

Dilute Freon solutions of all the simple aldehydes and ketones except formaldehyde gave e.s.r. features clearly assignable to radical cations (Table). However, when more concentrated solutions were used, and on annealing to near the softening point of the solids, reactions were observed which resulted in hydrogen atom transfer. Internal hydrogen atom transfer occurred for several of the longer chain species, including *n*-propyl and *n*- or iso-butyl derivatives. The four-membered ring cations gave ring opening, but the five- and six-membered ring derivatives gave the parent cations (see later). The aldehyde cations are all characterized by a 120–130 G doublet splitting, but the ketone cations only exhibit resolved proton coupling to δ -protons if present. Otherwise, they are characterized by asymmetric singlet features with slight *g*-value variation. We now consider the results in detail:

Formaldehyde.—This was prepared in the gas phase from paraformaldehyde, and should have been free of the hydrate. Using a SF_6 matrix, high yields of $\text{H}\dot{\text{C}}\text{O}$ were detected after irradiation at 4 K, but this was not formed in a Freon matrix at 77 K. No features of the type expected for H_2CO^+ could be found for either system. We are not able to explain these results, particularly in the light of our success with other aldehyde cations.

Acetaldehyde.—The cation in this case was stable (Figure 1). The large doublet splitting was expected by analogy with that for the isoelectronic radical $\text{MeHC}=\text{N}\cdot$ (85 G).¹⁴ The large increase of 85–130 G accords with the concept of hyperconjugative delocalization involving electron-donation into the SOMO from the C–H orbital [structure (III)]. The SOMO for these radicals is, formally, a non-bonding in-plane orbital on nitrogen or oxygen. However, because of the short C=N and C=O bonds, σ – π overlap is strong, encouraging extensive delocalization.

The extra quartet splitting shown in Figure 1 is due to hyperfine coupling to chlorine (^{35}Cl and ^{37}Cl have $I = 3/2$). As

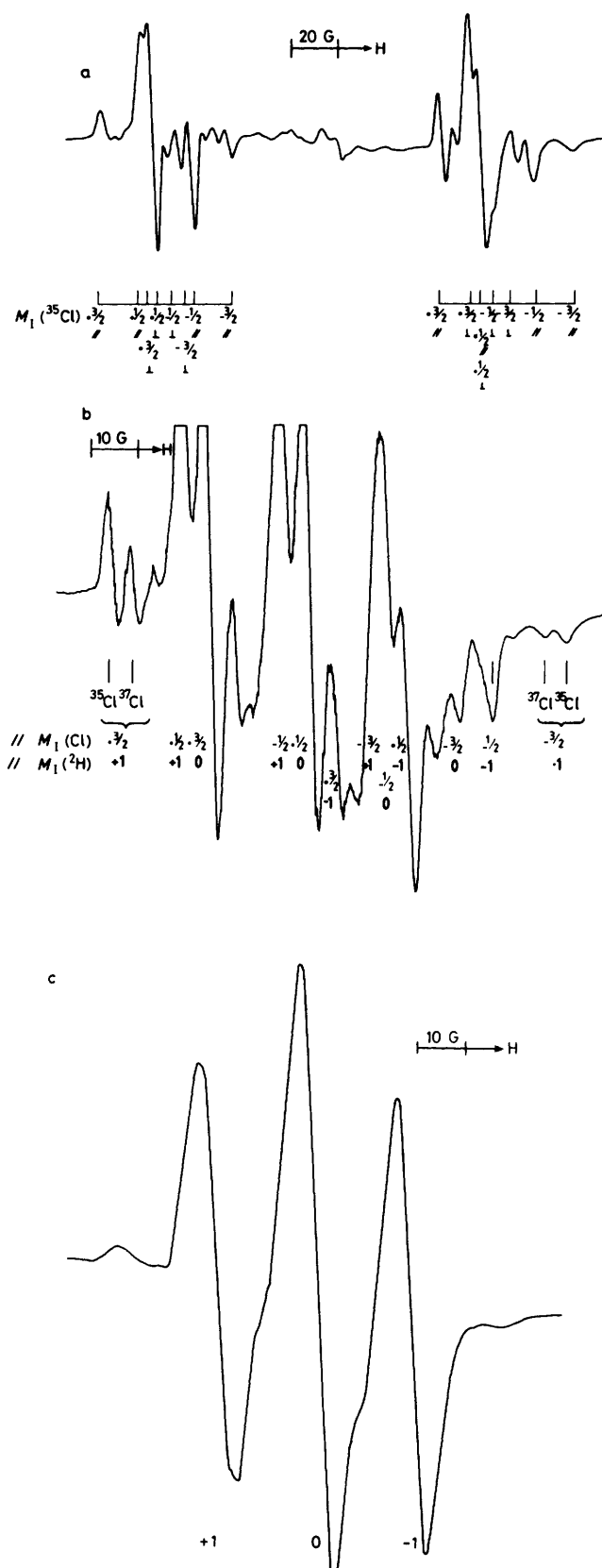
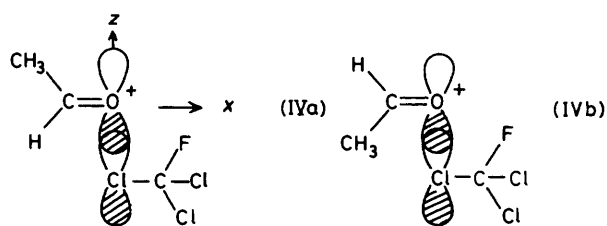


Figure 1. First-derivative X-band e.s.r. spectra for a dilute solution of acetaldehyde in Freon after exposure to ^{60}Co γ -rays at 77 K, showing features assigned to its radical-cation: a, for $(\text{CH}_3\text{CHO})^+ \cdots \text{Cl}_3\text{CF}$ adduct at 77 K; b, for $(\text{CD}_3\text{CDO})^+ \cdots \text{Cl}_3\text{CF}$ adduct at 77 K; c, for $(\text{CD}_3\text{CDO})^+$ at *ca.* 140 K



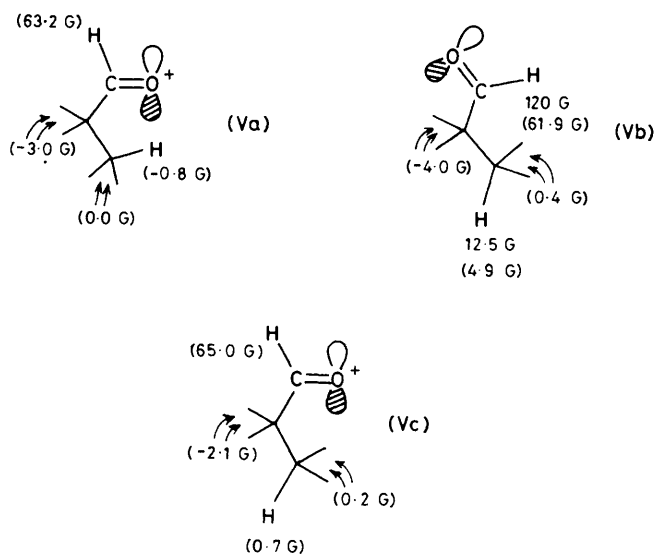
usual with halogen hyperfine interactions in the solid state, the parallel (z) features are well defined, but the 'perpendicular' features are very poorly resolved, and there is no clear evidence for our tentative assignment, especially since there is probably a small x - y splitting. Nevertheless, our estimated value for the 'perpendicular' splitting is close to that given by Snow and Williams¹² (Table). The spectrum for the corresponding adduct of $(\text{CD}_3\text{CDO})^+$ is shown in Figure 1b at 77 K, and in 1c at *ca.* 140 K, showing the reversible loss of the chlorine hyperfine coupling. The $\text{Cl}(\perp)$ result derived from Figure 1b differs somewhat from that for the protonated cation (Table). Derivation for the former is more difficult because of the anisotropy of the large ^1H coupling. Since that for ^2H is trivial, the spectrum is dominated by the g and $A(\text{Cl})$ anisotropies, which are therefore more accurately determined.

We have suggested that the structure for this species is the σ^* from (IV), but Snow and Williams¹² favour a less well defined structure similar to that postulated for alkyl-halide ion adducts.^{15,16} This led them to suggest that $A_{\parallel}(\text{Cl})$ is negative, as we found for the alkyl-halide ion adducts.¹⁷ The σ^* structure (IVa or b) requires that $A_{\perp}(\text{Cl})$ lies along the direction of the $2p$ orbital on oxygen (z), for which g is expected to be close to the free spin value (2.0023). If our analysis of the e.s.r. spectrum is correct, this is indeed the case. As the temperature is gradually increased above 77 K, both $A_{\parallel}(\text{Cl})$ and $A_{\perp}(\text{Cl})$ decrease in magnitude. This shows that $A_{\perp}(\text{Cl})$ must be negative.¹⁸ Hence the extent of delocalization estimated from the $2B$ value of *ca.* 16.7 G is *ca.* 17%. This value of $2B$, although small, is far too large to be accounted for by purely dipolar coupling.

On warming, the chlorine coupling is lost reversibly. In our view, this occurs because of a thermal dissociation of the oxygen-chlorine bond. The fact that the large proton coupling is hardly changed is then good evidence for the weakness of the bond. However, Snow and Williams point out that if $A_{\perp}(\text{Cl})$ is negative, $A_{\text{iso}}(\text{Cl})$ would be unresolvably small (*ca.* 3 G), and hence they postulate a motional averaging of the hyperfine anisotropy as the reason for the loss of resolved coupling. We find this suggestion less acceptable since, if there is a weak bond, the whole complex (IV) would need to rotate to remove this anisotropy. Since the doublet features remain slightly anisotropic in shape, we feel that this is not occurring. If bonding is not significant, and a weak charge-transfer interaction is involved, it is hard to understand why one unique chlorine atom should be involved, rather than two or three equivalent chlorine atoms. If all that is occurring is rotational averaging, we would not expect any change in $A(^1\text{H})$, since the weak interaction presumably remains. At present we are unable to distinguish between these alternative postulates.

The line shapes suggest a slight g -anisotropy for this cation. This is better defined for some of the other cations, especially for $[(\text{CD}_3)_2\text{CO}]^+$ discussed below. This is expected, since coupling between the SOMO and the carbonyl π and π^* orbitals should occur for the field along the $\text{C}=\text{O}$ bond (x). A study at Q -band frequencies is needed for a better estimation of the g -values for this cation.

Propionaldehyde.—The aldehydic proton coupling is



slightly reduced (*ca.* 120 G), and there is no well defined chlorine coupling in this case. Actually, features which may be due to weak complex formation were observed for $(\text{CH}_3\text{CH}_2\text{CHO})^+$ at 77 K, as shown in Figure 2a, but curiously, no such features were observed for the deuteriated derivative (Figure 2c). However, a well defined extra doublet splitting of 12.5 G is resolved at 77 K (Figure 2). This also is lost reversibly on annealing. Loss of this doublet splitting for the deuteriated cation (Figure 1c) shows that this splitting is due to ^1H not to ^{19}F .¹⁹ A clear distinction between the γ - and δ -protons comes from Snow and Williams' results for $(\text{CH}_3\text{CD}_2\text{CHO})^+$ cations, which still exhibit the 12.5 G splitting. Reversible thermal loss of this splitting shows that a rather precise conformation is required before delocalization is significant. This is expected for such long-range interactions, the rule being that a so-called **W**-structure is required.²⁰⁻²² We originally postulated a through-space interaction,¹⁰ as in (Va), whereas according to the **W**-rule (Vb), the interaction presumably occurs mainly *via* delocalization and spin-polarization in the σ -frame. One way of thinking about this is to consider that it occurs *via* delocalization into the $\text{OC}-\text{CH}_2-\sigma$ bond *via* hyperconjugation. Given such delocalization, coupling to a unique proton of the CH_3 group is then analogous to the situation for $(\text{C}_2\text{H}_6)^+$ cations which exhibit very large coupling to two unique protons (A 152 G) in a similar arrangement.⁴ This analogy shows that delocalization into the alkyl group remains small for the carbonyl cations.

The fact that, for each component of the main doublet, singlet rather than quartet features result reversibly on annealing shows that the coupling either falls to zero rapidly when the ideal **W**-structure is lost (presumably with onset of rotation of the methyl group) or that there are appreciable negative contributions to the coupling for other orientations. Thus, there is a clear fall in total hyperfine interaction with the onset of rotation. This was the situation that we envisaged in our original, but mistaken, interpretation of the methyl interaction for the cation of acetaldehyde. It is consistent with the result of Ingold and his co-workers for various alkyl radicals,²¹ and with the theoretical results of Ellinger and his co-workers.²²

The INDO calculations carried out for structures (Va—c) (see the numbers in parentheses) indicate that the **W**-plan conformation (Vb) is most compatible with the experimental result, although the absolute values are uniformly smaller than the experimental (shown without parentheses).

At 77 K there is a marked broadening of the features,

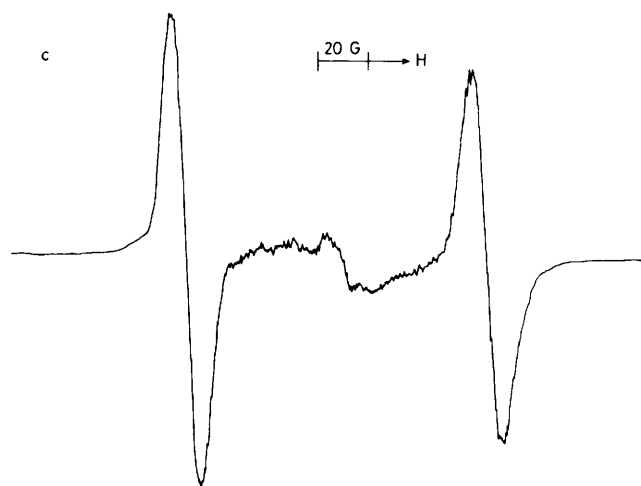
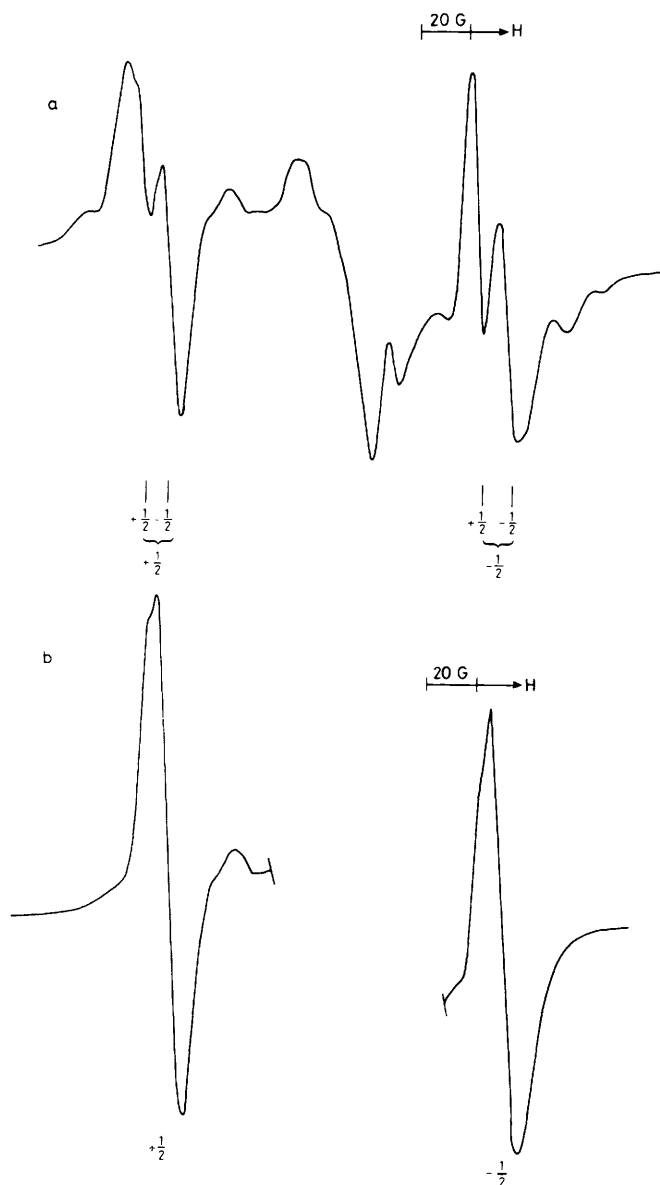


Figure 2. First-derivative X-band e.s.r. spectra for a dilute solution of $\text{CH}_3\text{CH}_2\text{CHO}$ in CFCl_3 after exposure to ^{60}Co γ -rays at 77 K, showing features assigned to the radical-cation: a, for $(\text{CH}_3\text{CH}_2\text{CHO})^+$ at 77 K, showing the doublet splitting (the central features are due to an impurity; the weak shoulders may be due to a solvent adduct); b, on annealing, showing loss of the doublet splitting; c, for $(\text{CD}_3\text{CH}_2\text{CHO})^+$ at 77 K, showing loss of the doublet splitting (note also the absence of any chlorine features in this case)

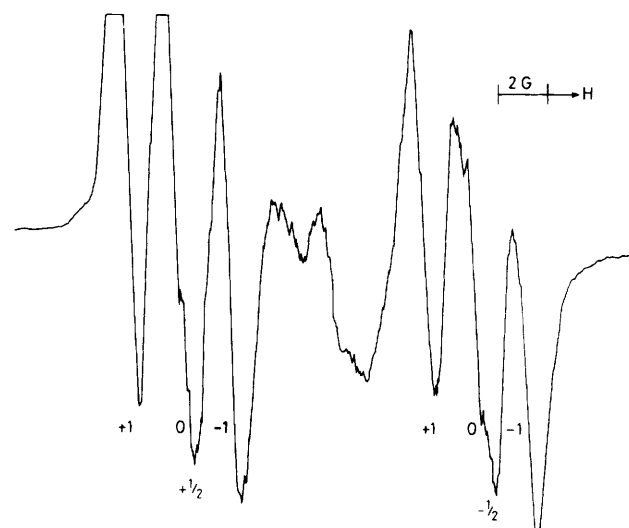
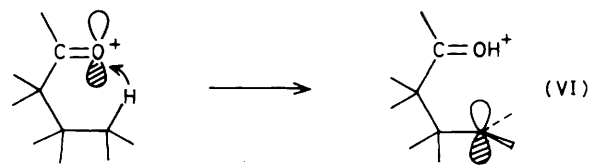


Figure 3. First-derivative X-band e.s.r. spectrum for $(\text{CH}_3)_2\text{CHCHO}$ in CCl_3F after exposure to ^{60}Co γ -rays at 77 K, showing features assigned to $[(\text{CH}_3)_2\text{CHO}]^+$ cations



suggestive of weak interaction with a solvent molecule, but no well defined splitting such as that observed for the acetaldehyde cation was resolved. This was the case for most of the cations studied in this work, and in all cases the broadening was lost rapidly on annealing.

Isobutyraldehyde.—In addition to the large doublet splitting, this cation showed a triplet (*ca.* 20 G) indicative of coupling to two equivalent protons (Figure 3) (see Discussion on INDO results). Again, on annealing, this splitting was lost reversibly. By analogy, and with reference to INDO calculations, it must arise from coupling to one proton from each of the two methyl groups which must be remarkably firmly locked close to the most favourable conformation.

Other aldehydes with larger alkyl substituents gave e.s.r. spectra typical of alkyl radicals. These may have been formed by hydrogen atom transfer as in (VI), for example.

Acetone.—No proton hyperfine coupling is resolved for the acetone cation. Comparison of the spectral width with that for $[(\text{CD}_3)_2\text{CO}]^+$ suggests an average coupling of <2 G. The

e.s.r. spectra for both these cations in CCl_3F undergo reversible changes on annealing as indicated in Figure 4. In contrast, their spectra in CCl_4 were narrower, and temperature invariant in the 77–160 K range. The reversible change observed for the CCl_3F solutions may possibly be associated

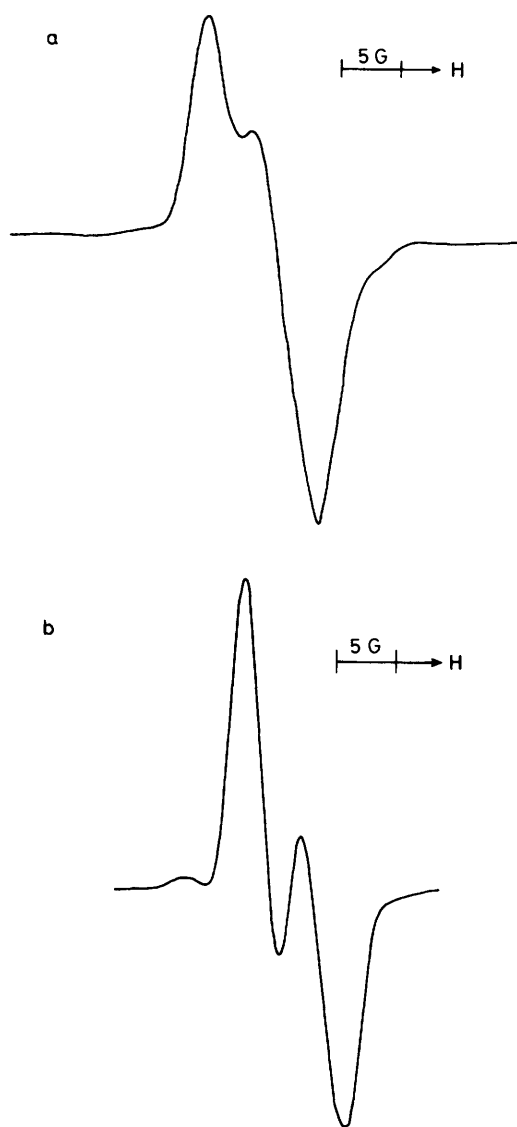


Figure 4. First-derivative X-band e.s.r. spectra for acetone in CFCl_3 or CCl_4 after exposure to ^{60}Co γ -rays at 77 K, showing features assigned to $[(\text{CH}_3)_2\text{CO}]^+$ cations: a, in CFCl_3 ; b, in CCl_4 , both at 77 K

with a slight charge delocalization to a fluorine atom of the solvent molecules. However, on cooling to *ca.* 10 K, the spectrum for the cation in CCl_4 resembled that for the Freon solution (Figure 4a). Hence both the CCl_4 spectrum (4b) and the Freon spectrum at *ca.* 129 K may be due to some type of motional averaging.

Diethyl Ketone.—The spectrum at 77 K comprised a well defined triplet, indicating hyperfine coupling (11 G) to two equivalent protons. On annealing to *ca.* 140 K this collapsed to a poorly resolved quintet of *ca.* 3 G splitting. This suggests that the preferred conformation of the cation places one hydrogen of each methyl group in the preferred W sites and that on annealing two protons for each group participate, with a clear reduction in total hyperfine interaction. We have compared two conformations in the INDO calculation, the result of which is shown in structure (IX). It shows that the W-plan structure gives a semi-quantitative agreement with the experimental result. We failed to observe a state exhibiting free rotation of the methyl groups.

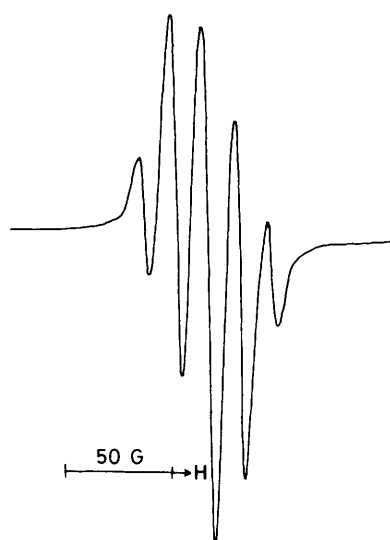


Figure 5. First-derivative X-band e.s.r. spectrum for $[(\text{CH}_3)_2\text{CH}]_2\text{CO}$ in CCl_3F after exposure to ^{60}Co γ -rays at 77 K, showing features assigned to $[(\text{Me}_2\text{CH})_2\text{CO}]^+$ cations

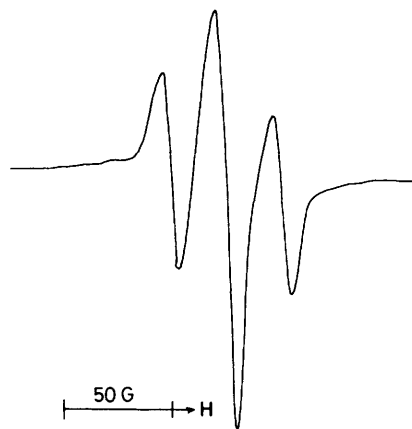


Figure 6. First-derivative X-band e.s.r. spectrum for cyclohexanone in CCl_3F after exposure to ^{60}Co γ -rays at 77 K, showing features assigned to cyclohexanone cations

Di-isopropyl Ketone.—The results were similar, with a quintet showing coupling (15.2 G) to four equivalent protons. That one proton from each of the methyl groups may be responsible for the quintet is supported by the INDO calculation (Table) (Figure 5). No marked changes were observed on annealing prior to radical loss, so the four methyl groups must be quite firmly locked in a single conformation, probably for steric reasons.

Di-*t*-butyl Ketone.—The e.s.r. spectrum for this cation closely resembled that of the isopropyl derivative with a 15 G quintet. So only four of the six available protons can couple strongly in the favourable conformation in this case. This is semi-quantitatively in agreement with the INDO calculation in the Table.

As with the aldehydes, ketones with larger alkyl chains gave spectra characteristics of alkyl radicals, presumably formed by intermolecular hydrogen transfer.

Cyclic Ketones.—The results for the five- and six-membered ring cations were normal, with strong coupling to two of the

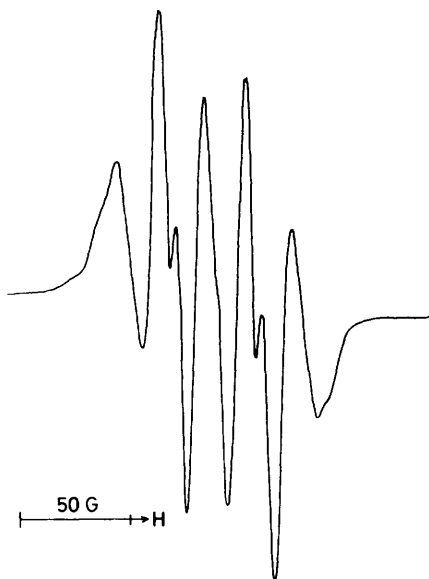
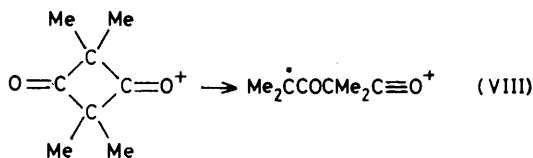


Figure 7. First-derivative X-band e.s.r. spectrum for cyclobutanone in CCl_3F after exposure to ^{60}Co γ -rays at 77 K, showing features tentatively assigned to $\text{H}_2\dot{\text{C}}\text{CH}_2\text{CH}_2\text{C}\equiv\text{O}^+$ radicals



four δ -protons (Figure 6). The coupling constants are remarkably large (Table) suggesting that the equatorial hydrogens are ideally placed for σ -delocalization especially in the cyclohexanone cation. This is supported by the INDO calculation (Table). A similar triplet, but with reduced splitting, was obtained from the 4-oxo-derivative (Table). However, for cyclobutanone the spectrum (Figure 7) is incompatible with any that we had expected for the parent cation. The clear anisotropy of the proton coupling together with the large overall width suggests an alkyl radical with two α -protons, so we postulate that ring opening has occurred to give (VII). $\text{RC}\equiv\text{O}^+$ cations are isoelectronic with cyanoalkanes, and are expected to be reasonably stable. If this is correct, the driving force is presumably associated with the release of ring strain, since this is not a general reaction for cyclic ketones under our conditions. We might mention that in current work on some dicarbonyl derivatives we have unambiguous evidence that the tetramethyl derivative gives (VIII) on electron loss.

Aspects of Mechanism.—The present study lends strong support to the basic mechanism given in equations (1)–(4), with clean production of the primary radical cations. For alkyl substituents R in R_2CO^+ cations with chains of three or more carbon atoms, cyclic hydrogen atom transfer is apparently facile. Similar hydrogen transfer reactions occur on excessive annealing. Thus, for acetone, for example, $\text{H}_2\dot{\text{C}}\text{COCH}_3$ radicals are formed.

Iminyl Radicals.—It is of interest to compare the results above with those of isoelectronic iminyl radicals, $\text{R}_2\text{C}=\text{N}^{\cdot}$,

which, as one of us stressed,²² are remarkably common and relatively stable species, of considerable importance as intermediates in certain reactions.²³

The β -proton couplings for $\text{H}_2\text{C}=\text{N}^{\cdot}$ and $\text{HRC}=\text{N}^{\cdot}$ radicals are ca. 80 G, the marked increase on going to $\text{HRC}=\text{O}^+$ being a reflection of the greater electron affinity of the positively charged oxygen relative to neutral nitrogen. However, the isotropic proton hyperfine coupling constants for the alkyl group protons are uniformly small, being ca. 2.7 G for γ - and 0.7 G for δ -protons in $\text{HRC}=\text{N}^{\cdot}$ derivatives, and ca. 1.4 and 0.4 G for γ - and δ -protons in $\text{R}_2\text{C}=\text{N}^{\cdot}$ radicals.^{23–27} No evidence for preferred conformations which confer large coupling constants on one or more δ -protons has been obtained.

These results help to explain why it was not immediately obvious that the large splittings observed for the cyclohexanone cation were due to δ -protons. They support the concept that the average δ -proton coupling must be small despite the large values obtained for structures close to the ideal W configuration.

INDO Calculations.—It is of considerable interest to see whether the observed e.s.r. features can be reasonably well reproduced by the standard INDO calculation because it provides in many cases a general guide for the interpretation of the observed spectra.²⁸ For the present systems it is particularly interesting to check whether the theory predicts correctly the prominently large hyperfine coupling constants of δ -protons in a favourable conformation. As a result of calculations which are shown in parentheses in structure (V) and the Table, it is found that the reproduction is not satisfactory in a quantitative sense. However, we notice that the multiplication of the calculated coupling constants by 2–3 times brings about a fair agreement with the observed values. Thus, semiquantitatively, the calculation gives indications that the hyperfine coupling constants of δ -protons in the favourable structure are larger than those of γ -protons (see, e.g., entries 3, 5, 6, 9, and 10 in the Table). Also, the calculation indicates that a selected proton of the methyl group possesses a relatively large coupling constant (e.g. entries 2, 3, 6, and 7). The large coupling constant of the aldehydic protons is, of course, reflected in the calculation (see entries 1–3).

The results of the calculations are found to be rather insensitive to slight changes in bond length and angle. By and large the established semi-empirical calculation may be said to be useful for the interpretation of the experimental result in the present work. For better quantitative agreements *ab initio* calculations taking into account electron correlation as well as spin correlation effects are needed.²⁹

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