

Fragmentation of $\text{CF}_3\text{C}\overset{\cdot}{\text{O}}\text{CH}_3$ Radical Cations in a Freon Matrix

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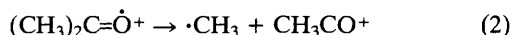
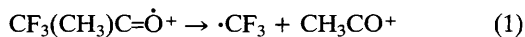
Exposure of a dilute solution of CF_3COCH_3 in CFCl_3 to ionising radiation at 77 K yields $\cdot\text{CF}_3$ radicals, formed, presumably, by fragmentation of the radical cation; on annealing, the e.s.r. signal due to $\cdot\text{CF}_3$ decreases in intensity and is replaced by a 22 G triplet (1 G = 10^{-4} T), which we assign to $\cdot\text{CH}_2\text{C}\equiv\overset{\cdot}{\text{O}}$ radicals, formed by hydrogen atom abstraction from $\text{CH}_3\text{C}\equiv\overset{\cdot}{\text{O}}$ cations by the $\cdot\text{CF}_3$ radicals.

The technique of exposing dilute freon solutions of various substrates to ionising radiation at low temperatures has been successfully used to produce the radical cations of a wide variety of compounds.¹

As part of an effort to extend this range to fluorinated

derivatives, we treated CF_3COCH_3 in this way, but instead of observing an e.s.r. spectrum assignable to the parent cation, we obtained a spectrum characteristic of randomly oriented $\cdot\text{CF}_3$ radicals.^{2,3} Under these conditions, direct radiolysis of the substrate is negligible,⁴ and the 'positive hole' transfer

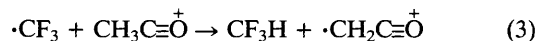
mechanism will dominate the initial chemistry, giving rise to the $\text{CF}_3\text{C}\overset{+}{\text{O}}\text{CH}_3$ radical cation. This must fragment in order to give rise to the $\cdot\text{CF}_3$ radical; the additional fragment, the $\text{CH}_3\text{C}\equiv\overset{+}{\text{O}}$ cation, being isoelectronic with cyanomethane must be relatively stable, and presumably provides part of the driving force for this process. It is curious, however, that when CH_3COCH_3 is irradiated in CFCl_3 , only the spectrum of the parent radical cation is observed.⁵ Even on annealing to the matrix softening point, we were unable to detect the formation of $\cdot\text{CH}_3$ radicals. Thus reaction (1) is complete at 77 K whilst (2) does not occur even at *ca.* 160 K.



One factor which may well be important is that the geometry of the CF_3 fragment is largely retained on bond fission, whereas the CH_3 group must change from its pyramidal structure in the acetone cation to its normal planar structure in the radical. This requirement of a major change in shape may provide an extra barrier to bond breaking.⁶ Also, delocalisation onto the three fluorine ligands, illustrated by the large ^{19}F hyperfine coupling, will help to stabilise $\cdot\text{CF}_3$ relative to $\cdot\text{CH}_3$.

On annealing, the spectrum of $\cdot\text{CF}_3$ first shows shifts of anisotropic features towards the expected isotropic positions, as a result of greater librational motion of the $\cdot\text{CF}_3$ radicals,

followed by a decrease in the intensity of the $\cdot\text{CF}_3$ signal, with the concomitant development of a 22.3 G 1 : 2 : 1 triplet (1 G = 10^{-4} T). We interpret this result as being due to a reaction within the solvent cage, in which the $\cdot\text{CF}_3$ radicals abstract hydrogen atoms from the $\text{CH}_3\text{C}\equiv\overset{+}{\text{O}}$ fragment:



The 22.3 G coupling is higher than the 21.2 G α -proton coupling reported for the isoelectronic $\cdot\text{CH}_2\text{CN}$ radical in solution.⁷ This is probably because the energy of the C–O π -bond levels is lower than that of the C–N π -levels, resulting in less electron spin delocalisation onto the $-\text{C}\equiv\overset{+}{\text{O}}$ group.

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