Fragmentation of $CF_3C\dot{O}CH_3$ Radical Cations in a Freon Matrix

Christopher J. Rhodes and Martyn C. R. Symons
Department of Chemistry, The University, Leicester LE1 7RH, U.K.

Exposure of a dilute solution of CF_3COCH_3 in $CFCl_3$ to ionising radiation at 77 K yields $\cdot CF_3$ radicals, formed, presumably, by fragmentation of the radical cation; on annealing, the e.s.r. signal due to $\cdot CF_3$ decreases in intensity and is replaced by a 22 G triplet (1 G = 10^{-4} T), which we assign to $\cdot CH_2C\equiv\overset{+}{O}$ radicals, formed by hydrogen atom abstraction from $CH_3C\equiv\overset{+}{O}$ cations by the $\cdot CF_3$ 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 $\cdot CF_3$ 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 $CF_3C\dot{O}C\overset{+}{H}_3$ radical cation. This must fragment in order to give rise to the $\cdot CF_3$ radical; the additional fragment, the $CH_3C{\equiv}\overset{+}{O}$ 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 $\cdot CH_3$ radicals. Thus reaction (1) is complete at 77 K whilst (2) does not occur even at *ca.* 160 K.

$$CF_3(CH_3)C{=}\dot{O}^+ \rightarrow \cdot CF_3 + CH_3CO^+ \qquad (1)$$

$$(CH_3)_2C{=}\dot{O}^+ \rightarrow \cdot CH_3 + CH_3CO^+ \qquad (2)$$

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 $\cdot CF_3$ relative to $\cdot CH_3$.

On annealing, the spectrum of $\cdot CF_3$ first shows shifts of anisotropic features towards the expected isotropic positions, as a result of greater librational motion of the $\cdot CF_3$ radicals, followed by a decrease in the intensity of the $\cdot CF_3$ 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 $\cdot CF_3$ radicals abstract hydrogen atoms from the $CH_3C{\equiv}\overset{+}{O}$ fragment:

$$\cdot CF_3 + CH_3C{\equiv}\overset{+}{O} \rightarrow CF_3H + \cdot CH_2C{\equiv}\overset{+}{O} \qquad (3)$$

The 22.3 G coupling is higher than the 21.2 G α-proton coupling reported for the isoelectronic $\cdot CH_2CN$ 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 $-C{\equiv}\overset{+}{O}$ group.

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