Anionic Oligomerisation of Hexafluoropropene: Fission of a Carbon–Carbon Bond by Fluoride Ion

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Summary Fluoride ion catalyses the oligomerisation of hexafluoropropene, and treatment of the individual dimers and trimers with fluoride ion leads to isomerisation and, in the case of one trimer, to fission of a carbon–carbon bond to give a dimer and the heptafluoro-isopropyl carbanion.

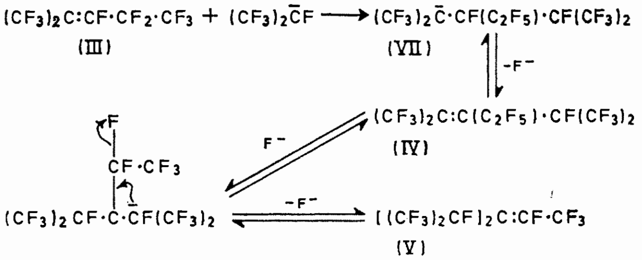
THE addition of a small amount of trimethylamine (*ca.* 2%[†]) to hexafluoropropene (I) in a dipolar aprotic solvent (tetrahydrofuran or Diglyme) initiates the carbanionic oligomerisation of (I). Thus reaction at 25° for 72 h gives the dimers (II) and (III) (49 and 9%) and the trimers (IV) and (V) (11 and 7%), along with the adduct (VI) (2%) from the reaction of (III) with hydrogen fluoride.

The dimers are isostructural; kinetic conditions (25°, 35 h) give a 64% yield of the dimers in which (II) predominates over (III) in the ratio 20 : 1, and a 7% total yield of trimers, with a 26% recovery of (I), whereas thermodynamic conditions (25°, 65 h, followed by 115°, 24 h) afford (III) as the only dimer in 67% yield, and trimers in 12% total yield, with no recovery of (I). Separate experiments show that fluoride ion catalyses the isomerisation of (II) into (III):

$$\begin{aligned}
&\text{(I)} \xrightleftharpoons{F^-} (CF_3)_2\bar{C}F \xrightarrow{\text{(I)}}\\
&(CF_3)_2CF\cdot CF_2\cdot\bar{C}F\cdot CF_3 \xrightleftharpoons{-F^-}\\
&\underset{\text{(II)}}{(CF_3)_2CF\cdot CF{:}CF\cdot CF_3} \xrightleftharpoons{F^-}\\
&(CF_3)_2CF\cdot\bar{C}F\cdot CF_2\cdot CF_3 \xrightleftharpoons{-F^-}\\
&\underset{\text{(III)}}{(CF_3)_2C{:}CF\cdot CF_2\cdot CF_3} \xrightarrow{\substack{\text{(i)}F^-\\ \text{(ii)}H^+}}\\
&\underset{\text{(VI)}}{(CF_3)_2CH\cdot CF_2\cdot CF_2\cdot CF_3}
\end{aligned}$$

The reactions here and later are presented as if they involve fluorocarbanion intermediates, but they could also involve a concerted mechanism.

The trimers are also isostructural, and arise from the attack of the isopropyl carbanion on dimer (III) to give the *tertiary* carbanion (VII); loss of fluoride ion from (VII) gives trimer (IV), which in turn affords trimer (V). Separate experiments have verified that (IV) and (V) can be interconverted and that their equilibrium mixture in presence of fluoride ion contains approximately 50% of each isomer.



When the reaction is carried out at temperatures above 100° only a third trimer (VIII) (*ca.* 10%) is obtained, not isostructural with (IV) and (V); this may arise *via* attack of the isopropyl carbanion on the terminal olefin (IX) which is isostructural with (II) and (III), but which has not been isolated from the mixture of oligomers, presumably since it is very susceptible to nucleophilic attack on the terminal CF_2.

When trimer (IV) [and similarly trimer (V)] is treated with KHF_2 in dimethylformamide at 100°, after 10 h 66% of the original trimer has been consumed to give trimer (VIII) (50%) along with small amounts (*ca.* 2%) of dimer (III) and the hydrogen fluoride adducts of (I) and (III); after 100 h only trimer (VIII) (50%) and $(CF_3)_2CHF$ (17%) result. Fluoride ion attack on the sp^2 carbon in (IV) which bears the isopropyl groups leads to ejection of the isopropyl carbanion in an analogous manner to that recently observed in the heterocyclic series.[1]

$$\begin{tikzcd}
(CF_3)_2\bar{C}F + \underset{\text{(IX)}}{CF_2{:}C(CF_3)\cdot CF_2\cdot CF_2\cdot CF_3} \arrow[r] & (CF_3)_2CF\cdot CF_2\cdot\bar{C}(CF_3)\cdot CF_2\cdot CF_2\cdot CF_3 \arrow[d, "-F^-"] \\
 & \underset{\text{(VIII)}}{(CF_3)_2CF\cdot CF{:}C(CF_3)\cdot CF_2\cdot CF_2\cdot CF_3}
\end{tikzcd}$$

$$\begin{tikzcd}
\text{(IV)} \arrow[r, shift left, "F^-"] & (CF_3)_2\bar{C}\cdot CF(C_2F_5)\cdot CF(CF_3)_2 \arrow[l, shift left] \arrow[r, shift left] & \underset{\text{(III)}}{(CF_3)_2C{:}CF\cdot C_2F_5} \arrow[l, shift left] \arrow[ddl] \arrow[ddr, "HF"] & + & (CF_3)_2\bar{C}F \arrow[d, "H^+"] \\
 & & & & (CF_3)_2CHF \\
\text{(VIII)} & \text{(IX)} \arrow[l, "(CF_3)_2CF^-"'] & & \text{(VI)} &
\end{tikzcd}$$

$$\begin{tikzcd}
\text{(III)} + Et\bar{O} \arrow[r] & (CF_3)_2\bar{C}\cdot CF(OEt)\cdot C_2F_5 \arrow[r, "-F^-"] \arrow[d, "-F^-"] & \underset{(6\%)}{(CF_3)_2C{:}C(OEt)\cdot C_2F_5} \\
 & \underset{(10\%)}{CF_2{:}C(CF_3)\cdot CF(OEt)\cdot C_2F_5\ \text{(X)}} \arrow[d, "\substack{\text{(i)}EtO^-\\ \text{(ii)}-F^-}"] & \\
 & \underset{(58\%)}{EtO\cdot CF{:}C(CF_3)\cdot CF(OEt)\cdot C_2F_5} &
\end{tikzcd}$$

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† Throughout this communication yields are reported as wt. % based upon monomer charged.

Thus the formation of trimers (IV) and (V) is reversible, and under thermodynamic conditions trimer (VIII) is favoured.

The terminal olefin (IX) presumably arises by rearrangement of dimer (III) and it is noteworthy that attack of ethoxide on (III) at −80° produces terminal olefin (X) analogous in structure to (IX).

Previous workers on the oligomerisation of (I) report the formation of three trimers,[2] all isostructural and none corresponding to the structures established by us;‡ all of them would arise *via* attack of the isopropyl carbanion on dimer (II) rather than on dimer (III), and would involve formation of a secondary carbanionic intermediate $(CF_3)_2CF\cdot\bar{C}F\cdot CF(CF_3)\cdot CF(CF_3)_2$ rather than a tertiary one (VII). Not only has this present work shown that, in the presence of fluoride ion, dimer (III) is more stable than dimer (II), but in each case where a choice between a secondary and a tertiary carbanionic intermediate has been possible, the products observed in the above and similar reactions have indicated formation of the latter.

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‡ All new compounds reported give satisfactory elemental analyses, mass and n.m.r. spectra, the details of which will be discussed in the full publication.

[1] R. D. Chambers, R. P. Corbally, J. A. Jackson, and W. K. R. Musgrave, *Chem. Comm.*, 1969, 127; C. J. Drayton, W. T. Flowers, and R. N. Haszeldine, *ibid.*, 1970, 662.

[2] J. A. Young, *Fluorine Chem. Rev.*, 1967, **1**, 359, and references therein.