THE FLUORINATION OF PROPANE OVER COBALT TRIFLUORIDE

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The main products (there are at least 20 altogether) in the fluorination of propane over CoF_3 at 150-250^{0}C are $CF_2HCFHCFH_2$ (30%), $CFH_2CFHCFH_2$ (10%), and $CF_2HCFHCH_3$ (10%). The NMR spectra of the products will be discussed.

A computor-aided simulation of the fluorination process, but one that does not allow for the formation of alkene intermediates, is, for the most part, successful.

A radical-cation mechanism is proposed and its major sequence proceeds through a succession of: (i) electron-abstraction from the substrate by Co^{3+}; (ii) proton loss; (iii) oxidation to a cation; and (iv), quenching by fluoride ion. At the very beginning of the fluorination, these steps would be:-

$$CH_3CH_2CH_3 \xrightarrow{(i)} [CH_3CH_2CH_3]^{\ddagger} \xrightarrow{(ii)} CH_3\dot{C}HCH_3 \xrightarrow{(iii)}$$

$$CH_3\overset{+}{C}HCH_3 \xrightarrow{(iv)} CH_3CHFCH_3 \longrightarrow \text{repeat}$$

$$\downarrow (ii)$$

$$CH_3CH{=}CH_2 \longrightarrow \text{fluorination}$$

The role played by alkene intermediates is not at all certain: it could be particularly significant at the beginning of the fluorination. Since small amounts of fluoropropenes have been observed amongst the products, the fluorination, at least in part, must indeed proceed through alkene intermediates, presumably formed as indicated by loss of a proton from a cation.