The Abstraction of Fluorine by Hydrogen Atoms

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ALTHOUGH it has recently been shown that methyl radicals abstract fluorine from SF_6 above 140°,[1] no case has been reported of the abstraction of a fluorine atom from a fluoroalkane. Hydrogen atoms produced by an electrical discharge do not appear to react with CH_3F,[2] and the mercury-photosensitized decomposition of hydrogen in the presence of CF_4 gives no reaction even at 300°.[3]

In a study of the mercury-photosensitized decomposition of ethyl fluoride at room temperature, we have found that the major products are $CH_3\cdot CHF\cdot CHF\cdot CH_3$ (*meso-* and DL-forms) (I) and $CH_3\cdot CHF\cdot CH_2\cdot CH_3$ (II) together with smaller quantities of n-C_4H_{10}, C_2H_6, C_2H_4, $CH_2{=}CFH$, and H_2. These suggest that the primary process is exclusively the formation of a $CH_3\cdot CFH\cdot$ radical and a hydrogen atom by a direct interaction of the $Hg(^3P_1)$ atom and the C–H bond as suggested by Gunning *et al.*[4] Simple energy-transfer is ruled out, since HF elimination would then be the major process.[5] Carbon–fluorine bonds do not quench $Hg(^3P_1)$ atoms; for example, the quenching cross-sections of CH_4, CHF_3, and CF_4 are 0·059 Å^2, 0·005 Å^2, and "very small", respectively.[6]

The hydrogen atoms from the above process then appear to react with the substrate as follows:

$$H\cdot + CH_3\cdot CH_2F \rightarrow CH_3\cdot CHF\cdot + H_2 \qquad (1)$$

$$H\cdot + CH_3\cdot CH_2F \rightarrow CH_3\cdot CH_2\cdot + HF \qquad (2)$$

Subsequent reactions of the $CH_3\cdot CHF\cdot$ and $CH_3\cdot CH_2\cdot$ radicals then lead to the observed products.

This is supported by the fact that when molecular hydrogen is added to the system so that this is the predominant quenching molecule, the yields of (II), n-C_4H_{10}, C_2H_6, and C_2H_4 are enhanced relative to (I).

A similar reaction appears to occur in the mercury-photosensitized decomposition of 1,1-difluoroethane. In the primary process, the hydrogen atom is lost predominantly from the fluorinated carbon atom to give $CH_3\cdot CF_2\cdot$ radicals which dimerize to give the major product $CH_3\cdot CF_2\cdot CF_2\cdot CH_3$ (III). Smaller quantities of $CH_3\cdot CF_2\cdot CH_2\cdot CF_2H$ (IV) were also found, indicating that a small proportion of the hydrogen atoms are lost from the nonfluorinated carbon atom. A number of minor products increased markedly when molecular hydrogen was added to the system. In this case, the yield of $CH_3\cdot CF_2\cdot CFH\cdot CH_3$ (V) became comparable with the yield of (III). Small quantities of (I), C_2H_6, C_2H_4, $CH_2{=}CHF$, and $CH_2{=}CF_2$ were obtained whereas the yield of product (IV) was negligible. It therefore appears that the only important reactions of the hydrogen atoms are:

$$H\cdot + CH_3\cdot CF_2H \rightarrow CH_3\cdot CF_2\cdot + H_2 \qquad (3)$$

$$H\cdot + CH_3\cdot CF_2H \rightarrow CH_3\cdot CFH\cdot + HF \qquad (4)$$

Both reactions (2) and (4) are approximately 20 kcal./mole exothermic. Fluorine abstraction reactions are therefore likely to be important in other systems containing fluoroalkanes and hydrogen atoms.

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