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DOES ACETYLHYPOFLUORITE REACT THROUGH A RADICAL-CATION MECHANISM?

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Recently, acetylhypofluorite (CH_3COOF) was developed as a mild fluorinating agent to overcome the problem of overreactivity of most other fluoroxy-reagents. Its first reported synthesis took place in freon at -78°C (Rozen et al., J.Chem. Soc.Chem.Commun.(1981) 443) but nowadays CH_3COOF is conveniently prepared at room temperature, either in acetic acid or by a gas-solid phase reaction and is as such a very easily handled fluorinating agent. Because of the short period that has passed since its discovery, little is known of the basic chemical properties of CH_3COOF in acetic acid. It is supposed to be a source for electrophilic fluorine. However, upon reaction with triacetylglucal we found - besides the expected cis and trans glucose and mannose derivatives - an unexpected 2-fluoro-1-methylglucose derivative, while reversed addition products were also found as byproducts (v.Rijn et al., Int.J.Appl.Radiat. Isot., 36 111 (1985)). The reaction of gaseous CH_3COOF with cyclohexene in CD_3COOD revealed us that apart from the formation of substantial amounts of 2-methyl-cyclohexylfluoride a large amount of 3-acetoxycyclohexene was formed, that was exclusively perdeuteroacetylated. The latter compound indicates the formation of an interesting non-fluorinated resonance stabilized carbocation. The same reaction carried out in CH_2Cl_2 gave 1,2-difluorocyclohexane as the main byproduct (Visser et al., Rec.Trav.Chim. Pays-Bas, 105, 214 (1986)). Upon reaction of CH_3COOF with arylmercury compounds we found apart from fluorodemercuration products, acetoxy- and methyldemercuration products, whereby the acetoxy and methyl group originated from CH_3COOF, not from the solvent (Visser et al., J.Org.Chem. 51 1886 (1986)). Finally, reaction of gaseous CH_3COOF with uracil in water mainly gave the 5F,6OH-adduct indicating an easy formation of an 'open' fluorocarbocation (Visser et al., J.Org.Chem., 51 1466 (1986)).

In order to explain the formation of all these observed products, for CH_3COOF a single-electron-transfer (SET) mechanism leading to an intermediate radical cation, a fluoride anion and an acetoxy radical is proposed as the first step. It will be shown that, depending on the solvent and the substrate, the acetoxy radical may either recombine directly, decompose into a methyl radical and carbon dioxide and then recombine, abstract a hydrogen atom or carry out a second one-electron oxidation. The fluoride anion may either recombine, act as a base or escape the intimate ion pair.

The general applicability of the SET concept with regard to the various unsaturated systems studied will be discussed. As an example, the SET concept also fits with 'electrophilic' behaviour, because in compounds that contain polarized double bonds the SET mainly occurs at the carbon that carries the highest electron density. Furthermore, with respect to the solvent and substrate dependency of the several reaction pathways the link between this concept and the earlier proposed mechanisms such as the 'tight ion' mechanism and the 'molecule assisted homolysis' will be shown.