TETRAMETHYLAMMONIUM FLUORIDE: A VERSATILE FLUORIDE ION SOURCE

James H. Clark, Craig W. Jones and Helen Smith,
Department of Chemistry, University of York, York, YO1 5DD, U.K.
and
Nubia Boechat, Fundecéo Oswaldo Cruz, Fermeuguimbar, Brazil.

The excellent solubility of quaternary ammonium fluorides makes them attractive alternatives to traditional fluoride ion sources such as potassium fluoride. Unfortunately the high hydroscopicity and low thermal stability of most of these reagents severely restricts their synthetic value. In the light of the work of Christe on the preparation of anhydrous tetramethylammonium fluoride (TMAF) we have carried out research into the use of this reagent.

TMAF forms stable hydrogen bonded complexes with a variety of protic molecules, including 4-cyanophenol. The TMAF 4CN-C_6H_4OH complex shows a number of interesting properties and in particular the tendency to decompose into the parent molecules rather than the proton transfer products as is normally the case with strongly H-bonded complexes. This observation in particular led us to believe that TMAF can be prepared and used as a soluble and reasonable stable fluoride ion source.[1] The use of anhydrous TMAF as a variety of nucleophilic fluorine transfer reactions will be reported. Very high reactivity towards chloroaromatics and nitroaromatics has been observed. The results from n.m.r. studies will also be reported so as to help explain the unusual solvation behaviour of this reagent which can be attributed to complex equilibria of the type:

$$\text{TMAF.solv} \rightleftharpoons \text{TMAF} \rightleftharpoons (\text{TMAF})_x$$

An understanding of this association behaviour can help to predict the best conditions for using this reagent in organofluorination reactions.

1. J.H. Clark and C.W. Jones, "Solvent Dependent Proton Transfer in a Strongly Hydrogen Bonded Fluoride Complex", Chemical Communications, 1990, 1786.