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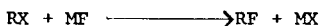
CALCIUM FLUORIDE SUPPORTED ALKALI METAL FLUORIDES – NEW REAGENTS FOR NUCLEOPHILIC FLUORINE TRANSFER REACTIONS

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Ionic fluorides and potassium and caesium fluorides in particular, are widely used as sources of nucleophilic fluorine in the preparation of organo-fluorine compounds. We have studied the effects of inert high surface area inorganic materials on the reactivity of KF and CsF as sources of fluorine in exchange reactions of the type:



Very high surface area supports such as alumina and silica generally have a detrimental effect on the rate of fluorination although KF-alumina, for example, is a powerful basic reagent. Surface hydroxyl-F⁻ hydrogen bonding is believed to be responsible for the reduction in F⁻ nucleophilicity. In an attempt to overcome this problem, we have turned our attention to the use of moderate surface area, non-surface hydroxylated supports such as group IIA metal fluorides which do not themselves act as sources of fluorine under normal reaction conditions. Calcium fluoride is a good example of such a support and in the presence of CaF₂, the reactivity of KF and CsF are significantly improved. We have observed a useful improvement in the rate of a variety of nucleophilic fluorine transfer reactions. The CaF₂ acts as a catalyst and is unchanged during the course of reaction. Both high resolution solids n.m.r. spectroscopy and X-ray diffraction have been used to study the KF-CaF₂ interaction and the techniques reveal that there is no chemical interaction between the salts.

We believe that the use of an inexpensive, inert solid to accelerate nucleophilic fluorine transfer reactions provides a viable alternative to the use of thermally sensitive phase transfer catalysts.

- 1 'Calcium Fluoride Supported Alkali Metal Fluorides', J.H. Clark et al. Chem. Commun., 1986.
- 2 'The Combination of Potassium Fluoride and Calcium Fluoride : A Useful Fluorinating Reagent', J. Ichihara et al. Chem. Commun., 1986.
- 3 'High Resolution Solids ¹⁹F n.m.r. Spectroscopy as a Tool for the Study of Ionic Fluorides', J.H. Clark et al. Chem. Commun., 1986.