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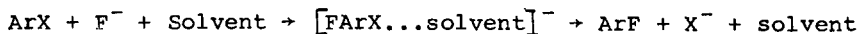
SOLVENT EFFECTS ON NUCLEOPHILIC FLUORINE TRANSFER REACTIONS

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Nucleophilic fluorine transfer reactions using alkali metal fluorides are usually carried out in polar aprotic solvents where it is assumed that the fluoride ion is effectively unsolvated and able to act as a powerful nucleophile. We have observed that the nature of the solvent, even when it is aprotic, can have a profound effect on reactions of this type in terms of the rate of fluorination and, on some occasions, the course of reaction. By studying a wide variety of polar aprotic solvents (including sulphones, sulphoxides and amides) and reaction types (including halogen exchange reactions of aliphatic and aromatic substrates, fluorodenitration reactions of aromatic substrates and both catalysed and non-catalysed reactions) we are able to analyse the role of the solvent.

Our results show that the effect of the solvent on the rate of fluorination is substrate dependent. The rate of reaction of simple aliphatic substrates is largely influenced by the solubility of the ionic fluoride but this need not be the case for aromatic substrates. We believe that the interaction of intermediate anionic complexes (Meisenheimer complexes) with the solvent can play a major role in determining the rate of reaction:



Both the structure and the polarisability of the solvent are important factors.

We believe that our results have important consequences for system design in nucleophilic fluorine transfer reactions.