Xenon Fluoride Solutions Effective as Fluorinating Agents

The problem:
To develop a mild fluorinating agent to use with materials which normally must be fluorinated with fluorine alone at high temperatures. Halogen fluoride compounds in liquid-phase reactions are often too vigorous and tend to disrupt the organic molecules during the substitution reaction, while other mild fluorinating agents (such as CoF₃ and SbF₃) leave a nonvolatile residue which is hard to separate from the reaction product.

The solution:
Solutions of xenon fluorides in anhydrous hydrogen fluoride (HF) have shown promise as effective mild fluorinating agents. They have fewer disruptive effects than halogen fluorides and leave a residue consisting solely of gaseous xenon, which can be recovered and refluorinated.

How it's done:
Halogen fluorides have never been widely used due to their extremely corrosive nature. The high cost of xenon might raise problems in commercial applications of this method. Preliminary research at Argonne National Laboratory has indicated that these problems might be overcome in some applications by the use of solutions of xenon fluorides in anhydrous HF.

Each of the xenon fluorides (XeF₂, XeF₄, and XeF₆) is quite soluble in anhydrous HF, and the resulting solution can be safely retained in polychloro trifluoroethylene or synthetic sapphire for use in laboratory scale reactions. For larger scale reactions ceramic liners of alumina could be used if corrosion of fluoride protected base metals became excessive.

Solutions of XeF₂ and XeF₄ are effective as mild fluorinating agents, and a solution of XeF₆ is a powerful fluorinating mixture which is also a highly electrically conducting system with both fluoride donor and fluoride acceptor properties. In use, one could select the compound having the required fluorine content and dissolve this in anhydrous hydrogen fluoride to obtain the fluorinating solution. During the reaction, the gaseous xenon residue could be recovered, refluorinated, and recycled to partially offset the economic disadvantages of xenon’s high cost.

Although no complete and systematic fluorination studies have been carried out yet, research which has been completed has demonstrated promise for these fluorinating solutions. As an example, researchers at Argonne have successfully used a solution of XeF₄ in HF as the fluorinating agent in a room temperature synthesis of fluorobenzene.

Notes:
1. Additional details are contained in the following publications:
2. Inquiries concerning this innovation may be directed to:
   Office of Industrial Cooperation
   Argonne National Laboratory
   9700 South Cass Avenue
   Argonne, Illinois 60439
   Reference: B67-10133
   Source: H. H. Hyman, I. Sheft, and L. A. Quarterman
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Patent status:
Inquiries about obtaining rights for commercial use of this innovation may be made to:
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