

PYRIDINIUM POLY(HYDROGEN FLUORIDE). A VERSATILE FLUORINATING REAGENT
PREPARATION AND CHARACTERIZATION OF NONMETAL AND METAL COMPLEX
FLUORO SALTS

D. K. Padma

Department of Inorganic and Physical Chemistry, Indian Institute of Science,
Bangalore 560 012 (India)

Pyridinium poly(hydrogen fluoride), PPHF, [Olah's reagent], has been found to be a versatile fluorinating reagent for the preparation of several complex fluoro salts of metals and nonmetals, such as phosphorus, boron, silicon, titanium, aluminium, iron, silver, copper, zirconium, vanadium, cobalt and nickel. These salts have been prepared by a one step procedure. Addition of the corresponding chloride/oxide/acid of the nonmetal or metal to pyridinium poly(hydrogen fluoride) at room temperature precipitates out near quantitative yields of the corresponding pyridinium salt [PyH PF₆, PyH BF₄, (PyH)₂SiF₆, (PyH)₂TiF₆ etc.]. Making use of a pure recrystallised salt as the precursor, pure alkali metal (Na, K, Rb, Cs, and NH₄) salts can be obtained by metathetic reactions with the corresponding alkali metal halides (Cl, Br) or their hydroxides. High purity alkyl ammonium salts can be prepared by reacting at room temperature a solution of pyridinium complex fluoro salt in ether or directly with the corresponding primary, secondary, tertiary, amines. All amines whose pK_a value is more than that of pyridine can be exchanged for the pyridinium ion. By adopting the same procedure tetra alkyl ammonium salts can be isolated. The isolated salts are pure and are obtained in near quantitative yields. All the salts have been characterized by IR, NMR [¹³C, ¹⁹F, ³¹P, ¹H], X-ray diffraction and chemical analysis.

Details of this novel method of preparation and characterisation by chemical analysis and spectra data for hexafluorotitanates(IV) (TiF₆⁻), hexafluorophosphates (PF₆⁻), hexafluorosilicates (SiF₆⁻), tetrafluoroborates (BF₄⁻) and hydrazinium hexafluorophosphate (N₂H₅⁺PF₆⁻) will be presented in detail.

Thermal decomposition studies on N₂H₅⁺PF₆⁻ will also be presented.