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STABILITY OF HOMOPOLYATOMIC NON-METAL CATIONS IN ANHYDROUS HYDROGEN FLUORIDE

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Around 1970, R.J. Gillespie and co-workers identified several homopolyatomic cations of the halogens and of the chalcogens by selective oxidation of the elements with $S_2O_6F_2$ in HSO_3F, a medium of very high acidity. Subsequently they obtained solids for structure determination by isolating compounds of these and other cations with very weakly basic anions, such as $Sb_2F_{11}^-$ and AsF_6^-, from solvents of low basicity, such as SO_2, SO_2ClF and AsF_3. Fairly recently at Melbourne we generated many of these cations in anhydrous HF using increasing amounts of the chemically simpler oxidant F_2 to produce in turn, I_5^+, I_3^+ and I_2^+ as well as S_8^{2+} and S_4^{2+}. However, subsequently we have placed much more emphasis on controlling the acidity of the HF in order to determine the thresholds of acidity at which cations of progressively greater charge-to-element ratio can be stabilized, even in the presence of excess oxidant and reductant. Regardless of the chemical nature of the medium, cations which are stable at particular acidities disproportionate on addition of the base of the solvent system. This disproportionation has been shown to be reversible. Thus stoichiometric mixtures of I_2 and IF_5 and of S_8 and SF_4 have given the cations I_5^+, I_3^+, I_2^+. S_4^{2+} and S_8^{2+} when the acidity of the HF has been adjusted by means of appropriate concentrations of suitable Lewis acids. The possibility of formation of homopolyatomic cations of phosphorus is currently under investigation by studying the oxidation of P_4 by PF_3 in highly acidic HF. Concurrently homopolyatomic metal cations of the type M_m^{n+} (for M = Ag, Hg, Au, Cd, Sn, Bi, etc) are being sought from the interaction of stoichiometric amounts of metals and their stable fluorides in HF of appropriate acidities.