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FLUORINE: OXIDIZER *PAR EXCELLENCE*

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This is a largely historical review on the employment of fluorides and fluorine to bring about unusual oxidations. It is based on the perspective of Bartlett and his coworkers. The discovery of $O_2^+PtF_6^-$ led to the realization that PtF_6 is an oxidizer of extraordinary power. PtF_6 was used in the first oxidation of xenon. Study of a similar interaction between RuF_6 and Xe at The Argonne National Laboratory led to the preparation of XeF_4 (Claasen, Selig & Malm, 1962). Independently, XeF_2 was synthesized (Hoppe, 1962). Subsequently the relative ease of Xe oxidation was shown by the photochemical generation of XeF_2 in Pyrex glass (Streng & Streng, 1965). The known noble-gas compounds involve the three heaviest elements (Kr, Xe, Rn) in combination with small highly electronegative atoms. The most effective ligand for noble-gas compound formation is the F atom, followed by O atom. The N ligand (with appended SO_2F groups, DesMarteau, 1981; Schrobiligen, 1982) is known in some Xe compounds. There is still doubt concerning the existence of a true Xe-C band. Thermochemical data show a striking direct dependence of total bond energy in the difluorides upon the ionization potential of the noble-gas atom. This and more direct charge assessment point to the bonding in these and related compounds being semi-ionic. Although ArF_2 is seen to be an unbonded ground state species, the cation ArF^+ is known to be bound (Berkowitz et al. 1970). Stabilization of such a cation requires that the ionization potential of the counter MF_6^- must be $\gg$ 193 kcal mole^{-1} (for which AuF_6^- would be a candidate). In addition the enthalpy, ΔH ($MF_6^- \rightarrow MF_5 + F^-$), should exceed 113 kcal mole^{-1} (in this regard AuF_6^- is inadequate).

The third transition series hexafluorides exhibit a steady increase in electron affinity with increasing atomic number E (kcal mole^{-1}) being: WF_3 (81), ReF_6 (∿110), OsF_6 (∿135), IrF_6 (∿160), PtF_6 (188). The spontaneous intercalation of the last three by graphite gave the first indication that the electron affinity of the oxidizing guest species needs to exceed ∿120 kcal mole^{-1}. This has been shown to be general for hexafluoroanion forming species. $C_x^+PF_6^-$ (second or higher stage) prepared from x C + PF_5 + 1/2 F_2 is reduced spontaneously by PF_3 to yield PF_5. This is consistent with $\Delta H(3/2\ PF_5 + e \rightarrow PF_6^- + 1/2\ PF_3)$ = -86 kcal mole$^-$.

When high charges are developed in the carbon sheets (e.g. $C_8^+MF_6^-$) extensive F^- transfer from anion to the positive carbon takes place. This has a dramatic impact on the electrical-conducting properties of the graphite sheets.