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The oxidizing properties of cationic high oxidation state transition-element fluoro species

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The substraction of F^- from thermodynamically stable salts such as those of NiF_6^{2-} or AgF_4^-, using fluoride ion acceptors (e.g. BF_3 or AsF_5) in anhydrous hydrogen fluoride (AHF), gives access to fluorides such as NiF_4, NiF_3 and AgF_3, which are thermodynamically unstable towards loss of fluorine. The neutral binary fluorides are stronger oxidizers than their anionic relatives and the cationic species are better oxidizers than the neutral or less positively charged species of the same oxidation state. In anhydrous HF (AHF) at −60 °C, AgF_3 oxidizes oxygen quantitatively according to the equation:

$$O_2(g) + AgF_3(c) + 2AsF_5(solv) \longrightarrow O_2^+\ AsF_6^-(c) + AgF^+\ AsF_6^-(c)$$

even though the loss of translational entropy for reactants to products is high. In strongly acid AHF solution, AgF_3 will oxidize either PtF_6^- or RuF_6^- to the neutral molecule:

$$MF_6^- + AgF_3 + 3AsF_5 \longrightarrow Ag^{2+}(solv) + 3AsF_6^-(solv) + MF_6$$

When used as the fluoride ion acceptor, BiF_5 promotes high yields of hexafluoride (72% for PtF_6) by enhancing the solubility of Ag^{II} and alkali cations. Even at −78 °C, interaction of AgF_3 with AsF_5 in AHF yields AgF^+ AsF_6^- and $1/2F_2$.

$AgF^+MF_6^-$ salts, where M = Sb, Bi, Ir, can be prepared by the action of F_2 on $AgMF_6$ at −20 °C in AHF, but $AgOsF_6 + F_2$ yields AgF_2 and OsF_6. The AgF^+ MF_6^- salts all contain the one-dimensional chain cation $(AgF)_n^{n+}$ which is characterized by its temperature-independent paramagnetism from 50 K upwards. In contrast, salts containing the tetragonally elongated octahedral Ag^{II} species such as $Ag(MF_6)_2$, M = Bi, Sb, or $Ag(M^1F_4)_2$, M^1 = Ag or Au, obey the Curie–Weiss law from 50 K upwards and have magnetic moments of ~2 BM.

Solvated Ag^{2+} in AHF is a more powerful oxidizer than the $(AgF)_n^{n+}$ species and liberates IrF_6 from its anion and $S_2O_6F_2$ from SO_3F^-, and at −78 °C generates $C_6F_6^+$ salts from C_6F_6 and oxidizes $CF_3CF{=}CF_2$ to $CF_3CF_2CF_3$ quantitatively. At −78 °C Ag^{2+}(solv) will also oxidize O_2:

$$Ag^{2+}(solv) + O_2(g) + 2AsF_5(solv) \longrightarrow O_2^+\ AsF_6^-(c) + AgAsF_6(c)$$

but even at −60 °C these products re-establish the reactants because of their high translational entropy. In contrast, basic AHF favors the formation of Ag^{III} from Ag^{II}:

$$AgF_2 + O_2AsF_6 + 2KF \longrightarrow KAgF_4 + KAsF_6 + O_2$$

the $KAgF_4$ being obtained in 42% yield based on O_2AsF_6 consumption.

The disproportionation of AgF^+ AsF_6^- in AHF:

$$4AgF^+\ AsF_6^- \longrightarrow AgAsF_6 + (AgF)_2AsF_6AgF_4 + 2AsF_5$$

indicates the marginal stability of Ag^{II} in AHF with respect to Ag^I and Ag^{III}. The compound $(AgF)_2AsF_6AgF_4$ contains $(AgF)_n^{n+}$ chains, AsF_6^- and AgF_4^-, and is conveniently prepared in AHF from AgF_2:

$$3AgF_2 + O_2AsF_6 \longrightarrow (AgF)_2AsF_6AgF_4 + O_2$$

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It is a temperature-independent paramagnet from 50 K upwards.

CuF_3 is formed as a red solid at −78 °C by solvolysis of K_3CuF_6 in AHF. It loses F_2 at −40 °C in KHF_2-rich AHF and oxidizes Xe to XeF_6 at −78 °C. NiF_4, a brown solid, yields RuF_6 or PtF_6 from their MF_6^- salts in AHF at −65 °C when BF_3 or AsF_5 is used to acidify the AHF. A similar release of these powerfully oxidizing hexafluorides occurs when rhombohedral NiF_3 is used in place of NiF_4, but BF_3 is not then an effective acid. This is attributed to the release of Ni^{IV} from the $R-NiF_3$ by strong acid (e.g. AsF_5). Acidified AHF solutions of Ni^{IV} like those of Ag^{III} may be the strongest electron oxidizers known to date.

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