

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

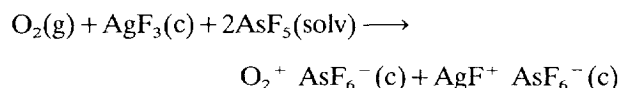
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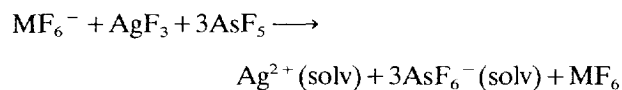
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The subtraction of  $F^-$  from thermodynamically stable salts such as those of  $NiF_6^{2-}$  or  $AgF_4^-$ , using fluoride ion acceptors (e.g.  $BF_3$  or  $AsF_5$ ) in anhydrous hydrogen fluoride (AHF), gives access to fluorides such as  $NiF_4$ ,  $NiF_3$  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  $-60^\circ C$ ,  $AgF_3$  oxidizes oxygen quantitatively according to the equation:



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:

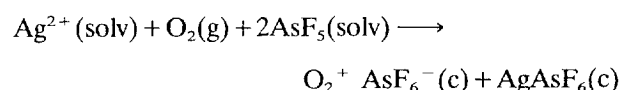


When used as the fluoride ion acceptor,  $BiF_5$  promotes high yields of hexafluoride (72% for  $PtF_6$ ) by enhancing the solubility of  $Ag^{II}$  and alkali cations. Even at  $-78^\circ C$ , interaction of  $AgF_3$  with  $AsF_5$  in AHF yields  $AgF^+ AsF_6^-$  and  $1/2F_2$ .

$AgF^+ MF_6^-$  salts, where  $M = Sb, Bi, Ir$ , can be prepared by the action of  $F_2$  on  $AgMF_6$  at  $-20^\circ C$  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  $Ag(M^I F_4)_2$ ,  $M^I = Ag$  or  $Au$ , obey the Curie-Weiss law from 50 K upwards and have magnetic moments of  $\sim 2$  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  $-78^\circ C$  generates  $C_6F_6^+$  salts from  $C_6F_6$  and oxidizes  $CF_3CF=CF_2$  to  $CF_3CF_2CF_3$  quantitatively. At  $-78^\circ C$   $Ag^{2+}(solv)$  will also oxidize  $O_2$ :

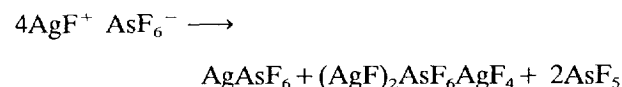


but even at  $-60^\circ C$  these products re-establish the reactants because of their high translational entropy. In contrast, basic AHF favors the formation of  $Ag^{III}$  from  $Ag^{II}$ :

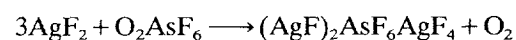


the  $KAgF_4$  being obtained in 42% yield based on  $O_2AsF_6$  consumption.

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



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  $AgF_2$ :



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

$\text{CuF}_3$  is formed as a red solid at  $-78\text{ }^\circ\text{C}$  by solvolysis of  $\text{K}_3\text{CuF}_6$  in AHF. It loses  $\text{F}_2$  at  $-40\text{ }^\circ\text{C}$  in  $\text{KHF}_2$ -rich AHF and oxidizes Xe to  $\text{XeF}_6$  at  $-78\text{ }^\circ\text{C}$ .  $\text{NiF}_4$ , a brown solid, yields  $\text{RuF}_6$  or  $\text{PtF}_6$  from their  $\text{MF}_6^-$  salts in AHF at  $-65\text{ }^\circ\text{C}$  when  $\text{BF}_3$  or  $\text{AsF}_5$  is used to acidify the AHF. A similar release of these powerfully oxidizing hexafluorides occurs when rhombohedral  $\text{NiF}_3$  is used in place of  $\text{NiF}_4$ , but  $\text{BF}_3$  is not then an effective acid. This is attributed to the release of  $\text{Ni}^{\text{IV}}$  from the  $\text{R-NiF}_3$  by strong acid (e.g.  $\text{AsF}_5$ ). Acidified AHF solutions of  $\text{Ni}^{\text{IV}}$  like those of  $\text{Ag}^{\text{III}}$  may be the strongest electron oxidizers known to date.

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