

Some chemistry of high oxidation state transition metal fluorides in anhydrous HF

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Received 27 July 1994; accepted 1 September 1994

Abstract

The salt AgFIrF_6 ($\text{AgIrF}_6 + 1/2\text{F}_2$ in AHF) is isostructural with AgFAsF_6 . Failure to prepare AgFOsF_6 ($\text{AgOsF}_6 + \text{F}_2 \rightarrow \text{AgF}_2 + \text{OsF}_6$) indicates that the one-dimensional chain cation $(\text{AgF})_n^{n+}$ takes the electron from OsF_6^- . The $\text{Ag}_{(\text{solv})}^{2+}$ ion oxidizes IrF_6^- to IrF_6 and at -78°C in AHF, O_2 to O_2^+ ($\text{O}_2 + \text{Ag}^{2+} + 2\text{AsF}_6^- \rightarrow \text{O}_2^+ \text{AsF}_6^- + \text{AgAsF}_6$). This reaction is negligible at $\sim 20^\circ\text{C}$ because of the loss of translational entropy that accompanies the formation of the crystalline products. Dissolution of AgF_3 in AHF with A ($\text{A} = \text{AsF}_5, \text{SbF}_5$ or BiF_5) gives a solution $\{\text{Ag}_{(\text{solv})}^{\text{III}}\}$ which oxidizes PtF_6^- or RuF_6^- to MF_6 and O_2 to O_2^+ . K_2NiF_6 in AHF below -60°C with greater than threefold molar excess of BF_3 yields yellow-brown solutions $\{\text{Ni}_{(\text{solv})}^{\text{IV}}\}$ which also oxidize PtF_6^- or RuF_6^- to MF_6 . The species $\text{Ag}_{(\text{solv})}^{\text{III}}$ and $\text{Ni}_{(\text{solv})}^{\text{IV}}$ in AHF are oxidizers of unsurpassed power.

Keywords: Anhydrous hydrogen fluoride; Nickel hexafluoride salts; Silver tetrafluoride salts; Oxidizing power; Reactivity

1. Introduction

Salts of NiF_6^{2-} were first prepared by Klemm and Huss [1] and those of AgF_4^- by Hoppe [2]. Although AgF_3 had been claimed as a product of the action of KrF_2 in AHF on silver or other silver fluorides [3], the X-ray powder diffraction data and magnetic properties of that material indicated [4] that it is the more thermally-stable mixed-valence solid $\text{Ag}^{\text{II}}\text{Ag}^{\text{III}}\text{F}_8$ (Ag_3F_8). X-Ray powder diffraction data for the solid prepared by the interaction of O_2F_2 with AgF_2 in ClF_3 , also claimed to be AgF_3 [5], are more consistent with the data for Ag_3F_8 , and do not resemble the pattern of authentic AgF_3 . To date, NiF_4 and authentic AgF_3 have only been preparable [6] from salts of NiF_6^{2-} and AgF_4^- , respectively, by fluoride abstraction using good F^- acceptors in AHF. Each of these binary fluorides loses F_2 spontaneously in AHF, NiF_4 converting eventually [6] to NiF_3 at temperatures above -60°C and AgF_3 giving [4] Ag_3F_8 slowly at $\sim 20^\circ\text{C}$.

The instability of NiF_4 and AgF_3 with respect to loss of F_2 in AHF was itself evidence of the greater elec-

tronegativity of each of these high-oxidation states in the neutral compounds, compared with those same states in the anions. It raised the possibility of even higher oxidative potency in cationic Ni^{IV} and Ag^{III} species, themselves derived from NiF_4 and AgF_3 , using strong F^- acceptors in AHF. Such an investigation into cationic Ag^{III} led to the discovery [7] that even cationic Ag^{II} was capable of oxidizing xenon at ordinary temperatures and pressures. Such high oxidizing power presaged extraordinary potency for cationic Ag^{III} and Ni^{IV} . This paper gives a short report of these investigations, with emphasis on the chemistry of both cationic Ag^{III} and Ag^{II} , and a brief comparison of Ag^{III} and Ni^{IV} .

The relative oxidizing power of the various Ni^{IV} , Ag^{III} and Ag^{II} species have been assessed by applying them to the oxidation of a range of hexafluoro anions, MF_6^- ($\text{M} = \text{Os}, \text{Ir}, \text{Pt}, \text{Ru}$), the first ionization potential of each being known from a combination of physical [8,9] and chemical [10,11] studies. Each of the cationic Ni^{IV} and Ag^{III} is capable of oxidizing either PtF_6^- or RuF_6^- to yield the neutral hexafluoride. Since the compound $\text{KrF}^+\text{PtF}_6^-$ is preparable [12], this suggests that these Ni^{IV} and Ag^{III} species may be the most potent oxidizers known so far.

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2. Experimental details

2.1. Materials

K_2NiF_6 (Ozark-Mahoning Pennwalt, Tulsa, OK) was dissolved in AHF (Matheson), itself distilled from K_2NiF_6 (to destroy water), in one arm of a T-shaped translucent fluorocarbon polymer tubing (FEP) assembly, closed by a Teflon valve (previously described [7]). The solution was decanted to the arm at right angles, and most of the AHF was removed under vacuum. When the bulk of the K_2NiF_6 had crystallized, the remaining solution (containing KF impurity) was decanted to the other arm. $KAgF_4$ was prepared by the method of Hoppe [2] and AgF_3 was obtained from it as described previously [4]. AgF and AgF_2 were prepared as before [4,7]. KMF_6 salts ($M=Ru, Os, Ir$) were prepared by the methods of Casteel and Horowitz [13] and $KPtF_6$ by addition of KF to O_2PtF_6 in AHF, the O_2PtF_6 being prepared as previously described [14]. The pentafluorides of Ru and Ir were prepared by heating the metals in F_2 (5–10 atm, 20 °C) to 300 °C in a nickel can with a Teflon gasket (water-cooled) and an SS-KS4 Whitey valve. $LiRuF_6$ and $LiIrF_6$ were made from equimolar mixtures of LiF and MF_5 in AHF at ~20 °C and were shown to be of high purity by X-ray powder photography [15]. $LiPtF_6$ was prepared from a 1:1 molar ratio mixture of LiF and O_2PtF_6 [14] in AHF at ~20 °C. $AgOsF_6$ and $AgIrF_6$ were precipitated from solutions of $KOsF_6$ or $KIrF_6$ in AHF with AgF in FEP T-reactors, and separated from the more soluble potassium hydrofluoride solution by decantation. The $AgMF_6$ salts were washed by back-distillation of AHF and decantation. BF_3 (Matheson, Newark, CA) and AsF_5 (Ozark-Mahoning Pennwalt) were checked by IR spectroscopy to ensure absence of major impurities, then used as supplied.

2.2. Apparatus and technique

A metal vacuum line, fluorine-handling equipment and valves were as described previously [7,16]. In the experimental work involving AHF, the apparatus was constructed from FEP tubing (CHEMPLAST, Inc., Wayne, NJ). The commonly used reactor was constructed from a 3/8 in o.d. FEP tube sealed at one end and with a Teflon valve (previously described [7]) at the other, a similar tube being joined mid-way by a Teflon Swagelok T compression fitting. This entire T-shaped assembly was connected to the gas handling and vacuum system via ~1 ft length of 1/4 in o.d. FEP tubing. This facilitated the decanting of the AHF solutions from one tube to that at right angles to it in the T-assembly. The T-reactors were passivated with ~2 atm F_2 for several hours, then evacuated before use. All solid starting materials and products were

handled in the dry argon atmosphere of a Vacuum Atmospheres DRILAB. X-Ray powder photographs and IR and Raman spectra were obtained as described previously [4,16].

2.3. Preparation of $AgF^+IrF_6^-$

An FEP T-reactor was loaded with $AgIrF_6$ (0.244 g, 0.589 mmol) and AHF (~1 ml) was condensed on to the insoluble, orange reagent. The reactor was pressurized to 1500 Torr with F_2 gas at room temperature and agitated. The bright orange solid (which darkened within 3 min) was agitated for 6 h, 3 h beyond the point when all the orange solid had been replaced by a black powder beneath a slightly yellow AHF solution. With the mixture cooled to -196 °C, any remaining F_2 was removed under dynamic vacuum. Once again, the AHF was brought to room temperature and then pressurized to 1500 Torr with BF_3 gas. The formation of $AgFBF_4$ converted the AHF solution from pale yellow to pale green. The black sediment was washed six times with AHF. X-Ray powder photographs of material prepared in this manner showed a pattern similar to that of $AgFAsF_6$ [17] and single crystals of the same material prepared by low-pressure F_2 modification of this procedure without agitation gave a unit cell ($Pnma$; $a=7.627$, $b=7.067$, $c=10.253$ Å) and structure close to that of $AgFAsF_6$ [18]. Temperature-dependent magnetic susceptibility measurements at both 5 and 40 kG revealed the presence of only a minute amount of AgF_2 impurity [19].

2.4. Attempted preparation of $AgFOsF_6$

One arm of an FEP T-reactor was loaded with $AgOsF_6$ (0.118 g, 0.286 mmol), AHF (~1.8 ml) condensed on to it and the mixture warmed to ~20 °C. The $AgOsF_6$ did not dissolve. The reactor was pressurized to 1500 Torr with F_2 gas and agitated continuously over the next 16 h, after which a dark brown sediment remained in a clear solution of AHF. The AHF was condensed into the other arm of the reactor along with OsF_6 , which condensed at -196 °C as a yellow solid. SF_4 was introduced and reacted slowly [20] with the melting OsF_6 /HF solution. When the yellow OsF_6 was no longer evident, the reactor was evacuated to leave a pale lavender solid. X-Ray photographs of this solid showed it to be SF_3OsF_6 (cubic, $a=5.58$ Å [20,21]). The yield of SF_3OsF_6 was 0.070 g (62%). X-Ray powder patterns demonstrated that the dark brown solid was a mixture of AgF_2 [22] and the starting material, $AgOsF_6$ [23].

2.5. Interaction of $Ag(SbF_6)_2$ with $LiIrF_6$ in AHF

One arm of an FEP T-reactor was loaded with $LiIrF_6$ (0.104 g, 0.332 mmol) and $Ag(SbF_6)_2$ (0.332 g, 0.574

mmol), and AHF (~2.0 ml) condensed on to the mixed solids. On warming to ~20 °C, the mixture first became royal blue in color and then dark green as a yellow solid precipitated out of solution. The AHF and the volatile, yellow IrF₆ were condensed into the other arm of the reactor. SF₄ was introduced into the reactor and produced SF₃IrF₆ (cubic, $a=5.58 \text{ \AA}$ [20,21]) as the IrF₆/AHF mixture melted, resulting in a colorless solution. The yield of SF₃IrF₆ was 0.0654 g (0.165 mmol), i.e., 50% of the Ir in LiIrF₆.

2.6. Interaction of $\text{Ag}_{(\text{sol})}^{2+}$ with O₂ in AsF₅-rich AHF

AgFAsF₆ (0.68 g, 2.2 mmol) was loaded into one arm of an FEP T-reactor, AsF₅ (2.0 g, 11.8 mmol) and AHF (5 ml) condensed on to the solid at -196 °C, and the system evacuated under dynamic vacuum. The resulting royal blue solution was allowed to equilibrate at -70 °C for 15 min. No sediment appeared during this time. The vacuum line was pressurized with 1600 Torr of dry O₂. When opened to the reactor, there was an immediate drop in pressure due to expansion into the reactor volume. This was followed by a further steady, slow decrease in pressure accompanied by the formation of a colorless solid and near disappearance of the blue solution color. Within 15 min, O₂ uptake had ceased and a copious colorless precipitate had formed. Warming the reaction mixture slightly to -60 °C resulted in an increase in line pressure, an increase in the intensity of the blue color in the solution and a decrease in the quantity of colorless solid. At -40 °C, no solid remained in the royal blue solution and the line pressure had returned to the level observed immediately after opening the line to the reactor. Warming to room temperature and removing the AsF₅/AHF solution under vacuum left only AgFAsF₆ which was identified by X-ray powder photography [17,24]. Restoring the AsF₅/AHF solution and cooling to -70 °C again resulted in O₂ uptake and again produced the colorless solid. To facilitate removal of the AsF₅/AHF solution under vacuum, the mixture was warmed to -60 °C and as a consequence the colorless solid diminished in quantity. On drying under dynamic vacuum, 0.80 g of light blue solid product remained corresponding to a yield of 0.16 g (0.79 mmol; 37%) of O₂AsF₆ based on the anticipated formation of 2.2 mmol of AgAsF₆. X-Ray powder photographs of the solid indicated that it contained O₂⁺AsF₆⁻ [25] and AgAsF₆ [26]. The faint blue tint indicated that some AgFAsF₆ was also present, but this was not revealed by the X-ray powder photographs.

2.7. Interaction of cationic Ag^{II} with C₆F₆ in AsF₅-rich AHF

A solution of cationic Ag^{II} was prepared by dissolving AgF₂ (0.19 g, 1.3 mmol) in AHF (~3 ml) containing

AsF₅ (~3 mmol). With the solution at -196 °C, residual fluorine was removed under vacuum and C₆F₆ (1.0 ml, 8.6 mmol) was condensed on to the frozen solution. As soon as the AHF began to melt a bright yellow solid began to form, the reaction being complete in less than 1 min as judged by the disappearance of the blue color characteristic of Ag^{II} at temperatures below -50 °C. The yellow solid appeared to have significant solubility in AHF even at -60 °C, and it was washed by several decantations into the free arm of the reactor. Ultimately, a colorless solid in colorless AHF was left in the original reaction arm, with bright yellow solid remaining in the second. AHF and excess C₆F₆ were removed under vacuum through a soda lime scrubber while holding the arm containing the yellow solid at 0 °C. The total weight of products in both arms of the reactor was 0.43 g. Assuming product formation as C₆F₆ + Ag²⁺ + 2AsF₆⁻ → C₆F₆AsF₆ + AgAsF₆, the anticipated yield of AgAsF₆ in 0.39 g and of C₆F₆AsF₆ is 0.49 g. It is probable that much of the C₆F₆AsF₆ formed [27] decomposed to C₆F₆ and 1,4-C₆F₈ (2C₆F₆AsF₆ → C₆F₆ + C₆F₈ + 2AsF₅). The yield of C₆F₆AsF₆, assuming 1.3 mmol of the product is AgAsF₆, is 0.09 mol (7%). X-Ray powder photographs showed that the yellow product was rhombohedral C₆F₆⁺AsF₆⁻ $a_0=6.60(1) \text{ \AA}$, $\alpha=106.0(1)^\circ$ contaminated with some AgAsF₆ [26]. The colorless solid in the other arm was AgAsF₆.

2.8. Interaction of cationic Ag^{II} with C₃F₆ in AsF₅-rich AHF

Using a one-armed Teflon tube reactor, AgFAsF₆ was synthesized in situ from AgAsF₆ (0.24 g, 0.80 mmol) and a greater than twofold molar excess of AsF₅. An overpressure of 2 atm of fluorine was maintained until all solids had dissolved to yield a royal blue solution. With the solution cooled to -196 °C, fluorine was removed in a dynamic vacuum and then C₃F₆ (0.36 mmol, 220 Torr × 30 ml) was added to the frozen mixture in three separate aliquots of 0.2, 0.1 and 0.06 mmol, respectively. The reaction mixture was allowed to warm to -70 °C after the addition of each aliquot. A colorless precipitate formed at the first signs of AHF melting. Each successive aliquot resulted in a paler blue supernatant solution over larger quantities of colorless solid. Ultimately (the entire reaction took ~5 min), a pale blue supernatant solution and a copious colorless solid remained. Volatiles were condensed at -196 °C under static vacuum into a tube filled with NaF, which was then warmed to ~20 °C for 15 min. This took up AHF (as NaHF₂) and AsF₅ (as NaAsF₆). Remaining volatiles were condensed at -196 °C into a 5 ml stainless-steel tube reactor, sealed at one end and equipped with an SS-KS4 Whitey valve at the other. Infrared spectroscopy of the collected volatiles [28] showed only the spectrum of C₃F₈. No traces of CF₄, C₂F₆ or residual

C_3F_6 were observed. The weight of volatiles was 70 mg, corresponding to 0.35 mmol of C_3F_8 .

2.9. Oxidation of PtF_6^- to PtF_6 by $Ag_{(solv)}^{III}$ in AHF

One arm of an FEP T-reactor was loaded with $LiPtF_6$ (0.0997 g, 0.316 mmol), AgF_3 (0.103 g, 0.625 mmol) and BiF_5 (0.791 g, 2.60 mmol), and AHF (~2.1 ml) was condensed on to the mixed solids. As the AHF melted and approached room temperature, it first became orange in color and then turned a very dark red. Intermittent agitation of the reaction mixture was maintained for 15 min before the AHF and the volatile, red PtF_6 were condensed into the other arm of the reactor. Oxygen gas was introduced and reacted with the dark red PtF_6 as it melted, to give a deep red precipitate in a yellow-tinted AHF solution. The AHF was removed at room temperature leaving a dark red solid. An X-ray powder photograph of the solid showed it to be O_2PtF_6 (cubic, $a = 10.032 \text{ \AA}$) [14] (0.0775 g, 0.227 mmol; 72% yield).

2.10. Oxidation of RuF_6^- to RuF_6 by $Ag_{(solv)}^{III}$ in AHF

One arm of an FEP T-reactor was loaded with $LiRuF_6$ (0.141 g, 0.633 mmol), AgF_3 (0.219 g, 1.33 mmol) and BiF_5 (1.19 g, 3.90 mmol), and AHF (~2.0 ml) was condensed on to the mixed solids and warmed to $-25 \text{ }^\circ\text{C}$. At this temperature the AHF was colored orange–yellow, but there was no sign that the AgF_3 was involved in any reaction. As the solution warmed to room temperature it became very dark red in color. Intermittent agitation of the reaction mixture was maintained for 15 min before the AHF and the volatile, red RuF_6 were condensed into the other arm of the reactor. Oxygen gas was introduced and reacted with the RuF_6 as it melted, to give a deep red precipitate in a yellow-tinted AHF solution. The AHF was removed at $\sim 0 \text{ }^\circ\text{C}$ leaving a dark red solid. An X-ray powder photograph of the solid showed it to be O_2RuF_6 [29] (cubic, $a = 10.004 \text{ \AA}$) (0.0909 g, 0.368 mmol; 58% yield).

2.11. Interaction of $Ag_{(solv)}^{III}$ with O_2 in AsF_5 -rich AHF

One arm of an FEP T-reactor was loaded with AgF_3 (0.147 g, 0.893 mmol) and AHF (3 ml) as AsF_5 (1.5 g, 8.8 mmol) condensed on to it at $-196 \text{ }^\circ\text{C}$. As the tube was warmed to $-70 \text{ }^\circ\text{C}$, the entire vacuum system and reactor were pressurized to 1500 Torr (10 mmol) with dry O_2 . The pressure of the system increased slightly until the AsF_5 /AHF mixture began to melt. The pressure in the line then began to drop, and a colorless solid and pale blue solution began to form.

The reaction arm was allowed to warm to $-60 \text{ }^\circ\text{C}$ and was held at that temperature for 20 min with intermittent agitation until all traces of the red solid, AgF_3 , had disappeared. A voluminous colorless solid and a blue solution remained, the latter becoming more intensely colored as the solution was warmed. The O_2 uptake during the reaction was ~ 1.0 mmol. With the colorless solid held at $-60 \text{ }^\circ\text{C}$, the blue solution was decanted into the free arm of the reactor and the volatiles then removed as the solution warmed to room temperature. The colorless solid was identified from its X-ray powder pattern [25] as $O_2^+AsF_6^-$ (0.13 g, 0.64 mmol; 72% yield based on AgF_3) and by its characteristic O_2^+ Raman stretch [25] at 1857 cm^{-1} . The dark blue solid retrieved from the decanted blue solution was shown by X-ray powder photography to be $AgFAsF_6$ (loc. cit.).

2.12. Oxidation of RuF_6^- to RuF_6 by $Ni_{(solv)}^{IV}$ in AHF

One arm of a T-reactor was loaded with K_2NiF_6 (0.294, 1.17 mmol) and $KRuF_6$ (0.0997 g, 0.392 mmol), and then AHF (~2 ml) was condensed on to the solids at $-196 \text{ }^\circ\text{C}$ and the mixture warmed to $-65 \text{ }^\circ\text{C}$. The active $Ni_{(solv)}^{IV}$ species was prepared in situ by adding BF_3 (4.74 mmol). [N.B. Upon addition of BF_3 to K_2NiF_6 , a tan precipitate (NiF_4) was formed as the red color of NiF_6^{2-} disappeared. Addition of a stoichiometric amount of BF_3 led to a colorless solution. With addition of excess BF_3 , a yellow species appeared in solution. If a very large excess of BF_3 was added, the color of the solution became very intense and appeared dark brown.] Once the solution had achieved a dark brown color (indicative of the presence of $Ni_{(solv)}^{IV}$), the reaction mixture was allowed to warm to $-35 \text{ }^\circ\text{C}$ at which temperature it was agitated for 1.5 h to mix the reactants. During this time the brown color of the solution was replaced by the intense red color of RuF_6 in solution. The deep red gaseous RuF_6 , along with AHF, was then condensed to the other arm of the T-reactor at $-196 \text{ }^\circ\text{C}$. Once the transfer was complete, dry O_2 (3.63 mmol) was admitted into the reactor where, as it warmed, it combined with the RuF_6 in AHF, to produce red crystalline material under a yellow AHF solution. The AHF was removed at temperatures below $-20 \text{ }^\circ\text{C}$ to yield O_2RuF_6 (0.092 mmol, 23.4%). In a separate reaction, it was found that repeating the process of acidifying the solution with BF_3 (i.e., regenerating the oxidizing Ni^{IV} species), agitating and then condensing RuF_6 to the side-arm a second time, increased the yield of O_2RuF_6 twofold (49.8%). Presumably at the low temperatures necessary to maintain the $Ni_{(solv)}^{IV}$ the solubility of the KMF_6 salts is low. An X-ray powder photograph of O_2RuF_6 showed the product to have the same unit cell (cubic, $a = 10.004 \text{ \AA}$) as reported previously [29].

2.13. Oxidation of PtF_6^- to PtF_6 by $Ni_{(solv)}^{IV}$ in AHF

One arm of an FEP T-reactor was loaded with K_2NiF_6 (0.152 g, 0.607 mmol) and $KPtF_6$ (0.104 g, 0.299 mmol), AHF (~2.5 ml) condensed on to the solids at -196°C and the mixture warmed to -61°C . Then BF_3 (12.7 mmol) was added to produce a deeply colored brown solution. The reaction mixture was warmed to -35°C and agitated for 1 h. During this time, the brown color of the $Ni_{(solv)}^{IV}$ was replaced by the intense red color of PtF_6 in solution. The red gaseous PtF_6 was then condensed, along with AHF, to the other arm of the reactor at -196°C . Once transfer was complete, dry O_2 (1.76 mmol) was admitted to the reactor forming orange-red crystals in a clear yellow solution. After removal of the AHF at temperatures below -20°C , this solid darkened to yield deep red crystalline O_2PtF_6 (0.0231 g, 0.0673 mmol; 22.5%). An X-ray powder photograph of this material showed the same unit cell (cubic, $a = 10.032 \text{ \AA}$) as reported previously [14].

3. Results and discussion

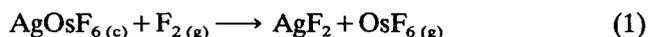
Since the hexafluorides of the third transition series are approximately of the same size [30,31] (as are their mono anions [13]), differences in their oxidizing power are determined mainly by differences in the electron affinity of MF_6 , i.e., the ionization potential of MF_6^- , $I(MF_6^-)$. This energy term increases [10] by $\sim 1 \text{ eV}$ for each unit increase in atomic number, z , of M, from W to Pt. This is in accord with the steady lowering of the energy of the t_{2g} frontier orbitals as z increases. The liberation of particular third transition series MF_6 from MF_6^- in AHF shows that the various nickel and silver species studied here can be ranged in order of increasing oxidizing power as follows: $(AgF)_n^{n+} < Ag_{(solv)}^{2+} < Ag_{(solv)}^{III} \approx Ni_{(solv)}^{IV}$.

The $Ag_{(solv)}^{III}$ and $Ni_{(solv)}^{IV}$ are the Ag^{III} and Ni^{IV} species which are present in AHF solutions prepared by dissolving the binary fluoride (AgF_3 or NiF_4) using a good fluoride-ion acceptor. These species are most probably cationic and possess great oxidizing power – perhaps the greatest available in a chemical reagent so far. The implications of the experimental findings for each of the silver and nickel oxidizers will be considered in order of the hierarchy just mentioned.

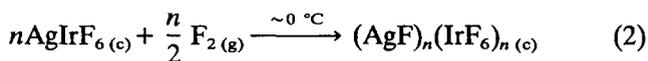
3.1. The $(AgF)_n^{n+}$ oxidizer

These salts, the first example of which ($AgFAsF_6$) was prepared [17] and characterized structurally by Gantar et al. [18], are of low solubility in AHF as befits the one-dimensional nature of their polymeric cation. The immediate release of OsF_6 when $AgOsF_6$

(which is of very low solubility in AHF) is treated with elemental fluorine can be interpreted as signifying electron capture by AgF^+ from OsF_6^- :



Certainly, $(AgF)_n^{n+}(IrF_6^-)_n$ is formed quantitatively under comparable conditions:



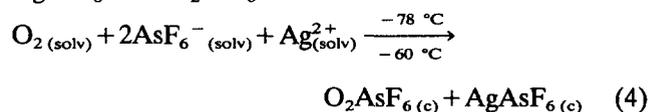
The solubilities of $AgIrF_6$ and F_2 are sufficiently low that the reaction proceeds at a rate which is slow enough to yield crystals suitable for a structure determination (the structure is very like that of $AgFAsF_6$ [18]). In addition, elemental F_2 in AHF, under conditions comparable to those used for the attempted synthesis of $AgFOsF_6$, liberates neither OsF_6 nor IrF_6 from alkali salt solutions of their MF_6^- anions. The $(AgF)_n^{n+}$ species therefore has an oxidizing potential [10,11] in AHF which is greater than that of OsF_6 , $I(MF_6^-) \approx 5.7 \text{ eV}$, but less than that of IrF_6 , $I(MF_6^-) \approx 6.7 \text{ eV}$.

3.2. The $Ag_{(solv)}^{2+}$ species in AHF

When $AgFAsF_6$ is treated with an equimolar quantity of AsF_5 , or when $AgAsF_6$ is oxidized [32] by an equivalent of O_2AsF_6 , a clear light blue solution of $Ag_{(solv)}^{2+}$ is obtained. The exact nature of this cation is not known. The Ag^{2+} ion may be coordinated (through F) to four HF molecules (as in the coordination of Ag^{2+} to four F ligands in $Ag(SbF_6)_2$ [33]). There is no doubt that this species is a more potent oxidizer than $(AgF)_n^{n+}$. This is shown by the rapid evolution of IrF_6 when an AHF solution of $LiIrF_6$ is mixed with an $Ag(SbF_6)_2$ solution:



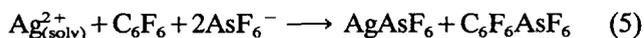
The greater potency of the $Ag_{(solv)}^{2+}$ oxidizer is also demonstrated by its ability to oxidize xenon as described previously [7]. Since the ionization potential of xenon is the same as that of O_2 [34], it seemed likely that $Ag_{(solv)}^{2+}$ would also oxidize oxygen. The failure to achieve that result at the time that the xenon oxidation by $Ag_{(solv)}^{2+}$ was discovered was a consequence of carrying out the experiments at or near room temperature. When O_2 is passed into a solution of $Ag_{(solv)}^{2+}$ at -78°C or below, there is a rapid uptake of the gas and a fast fading of the blue color of the solution, simultaneously accompanied by precipitation of colorless $AgAsF_6$ and O_2AsF_6 :



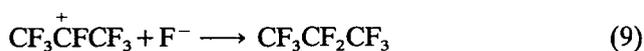
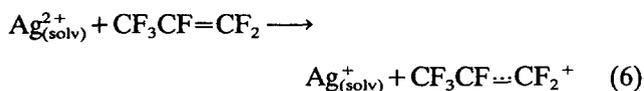
The reverse reaction is already extensive at -60°C as indicated by the stronger blue color at that tem-

perature. This large effect of temperature on the equilibrium is simply a consequence of the large change in translational entropy in going from reactants to products. The lower solubility of O₂ in AHF relative to xenon must also be to the detriment of O₂ oxidation, but it is in any case clear from these experiments that O₂ is effectively oxidized by Ag_(solv)²⁺ at low temperatures.

Since the O₂⁺ salts are effective oxidizers for the preparation of C₆F₆⁺ and other perfluoroaromatic cation salts [27], it was anticipated that Ag_(solv)²⁺ would also serve for such oxidations. This proved to be the case:

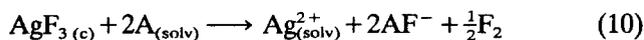


Since the ionization potentials of perfluoro-olefins such as perfluoropropene, C₃F₆ (*I* = 10.62 eV) [32], are much lower than those of Xe or O₂, this also suggests that they can be electron-oxidized by Ag_(solv)²⁺. The observed quantitative oxidation of C₃F₆ to C₃F₈ therefore probably involves two sequences of electron oxidation followed by F⁻ attack on the radical cations, as follows:

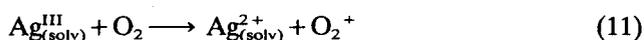


3.3. The Ag_(solv)^{III} species in AHF

Although BF₃ is not a sufficiently good F⁻ acceptor to cause AgF₃ to enter into solution in AHF, the stronger acids AsF₅, SbF₅ and BiF₅ [A in Eq. (10)] do so quickly with liberation of F₂:



It appears that there is a relatively long-lived Ag^{III} species present in the AHF under these conditions, since both PtF₆⁻ and RuF₆⁻ are oxidized to their neutral relatives in high yield (~60% or better). Neither hexafluoride is generated by the action of F₂ on solutions of PtF₆⁻ or RuF₆⁻. This dissolved Ag^{III} species is probably cationic in view of the strongly acid conditions that prevail. Since it effectively removes the electron from each of PtF₆⁻ and RuF₆⁻, it is superior in that regard to KrF⁺ since the KrF⁺PtF₆⁻ salt is known and is thermally stable at ordinary temperatures [12]. As anticipated, the dissolved Ag^{III} species oxidizes oxygen in AHF at ordinary temperatures (unlike Ag_(solv)²⁺):



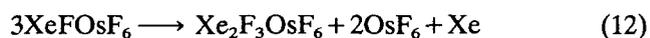
and the O₂⁺ salt is obtained in high yield. In combination with the reaction depicted in Eq. (4), this means that 1 mol of AgF₃ in acid (A) AHF will fix nearly 2 mol of O₂ as O₂⁺ at -78 °C.

3.4. The Ni_(solv)^{IV} species in AHF

Although NiF₄ has even lower kinetic stability than AgF₃, both the solid and its solution species in acid AHF can be maintained at -60 °C or lower. Unlike AgF₃, the relatively weaker acid [35] BF₃ will bring about dissolution of NiF₄ to yield deep yellow-brown solutions, which probably contain cationic NiF_{4-x}^{x+}(solv) species, here labelled Ni_(solv)^{IV}. Such solutions oxidize RuF₆⁻ and PtF₆⁻ to their neutral MF₆. Thus in one assembly, using BF₃ to convert K₂NiF₆ to Ni_(solv)^{IV}, a readily available NiF₆²⁻ salt may be converted to an oxidizer of unsurpassed power.

3.5. The hierarchy of powerful oxidizers

The liberation of PtF₆ and RuF₆ by cationic Ag_(solv)^{III} and Ni_(solv)^{IV} indicates that these oxidizers are perhaps the most potent found to date. Hitherto KrF⁺ had been assessed as the most powerful oxidizing species [36]. Since KrFPtF₆ is reported by Gillespie and Schrobilgen [12] to decompose in solution with the formation of PtF₅, it appears that KrF⁺ does not capture the electron from PtF₆⁻ but rather the F⁻ ion. Bartlett [37] had estimated from a Hess' law cycle that the electron affinity of KrF⁺ must be at least 12 eV, which is in harmony with the observation of Gillespie and Schrobilgen [12] that KrF⁺ salts oxidize oxygen to O₂⁺. Stein showed [38] that O₂⁺ salts oxidize Xe to yield XeF⁺ salts. In addition, the work of Sladky et al. [39] demonstrated that XeF⁺OsF₆⁻ underwent decomposition according to the equation:



as a consequence of electron loss from OsF₆⁻ to XeF⁺. The liberation of OsF₆ in attempts to prepare AgFOsF₆ suggests that the (AgF)_nⁿ⁺ cation has a comparable electron affinity to XeF⁺.

For the more potent electron oxidizers encompassed in these studies, the sequence in oxidizing power therefore appears to be AgF⁺ ≈ XeF⁺ < O₂⁺ ≈ Ag_(solv)²⁺ < KrF⁺ < RuF₆ ≈ PtF₆ < Ni_(solv)^{IV} ≈ Ag_(solv)^{III}

Acknowledgments

The work carried out at Berkeley was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the US Department of Energy under Contract Number DE-AC-03-76F00098. Additional support was provided by

the US–Slovene Joint Fund for Scientific and Technological Cooperation, in association with the National Science Foundation under grant number JF947. One of us (L.C.) is grateful to NPSC for a fellowship.

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