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Novel Synthesis of ClF_6^+ and BrF_6^+ Salts[†]

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For a compound in a given oxidation state, its oxidizing strength increases from its anion to the neutral parent molecule to its cation. Similarly, an anion is more easily oxidized than its neutral parent molecule, which in turn is more easily oxidized than its cation. This concept was systematically exploited in our search for new superoxidizers. Transition metal fluoride anions were prepared in their highest known oxidation states by high temperature/high pressure fluorinations with elemental fluorine and subsequently converted to their more strongly oxidizing cations by a displacement reaction with a strong Lewis acid. The application of this principle resulted in new syntheses for $ClF_6^+AsF_6^-$ and $BrF_6^+AsF_6^-$ using the highly reactive and thermally unstable NiF_3^+ cation that was prepared from the reaction of the NiF_6^{2-} anion with AsF_5 in anhydrous HF. Attempts to prepare the known KrF^+ and $ClO_2F_2^+$ cations and the yet unknown XeF_7^+ cation by the same method were unsuccessful. The results from this and previous studies show that NiF_3^+ is a stronger oxidative fluorinator than PtF_6, but whether its oxidizing strength exceeds that of KrF^+ remains unclear. Its failure to oxidize Kr to KrF^+ might have been due to unfavorable reaction conditions. Its failure to oxidize ClO_2F to $ClO_2F_2^+$, in spite of its favorable oxidizer strength, is attributed to the high Lewis basicity of ClO_2F which results in a rapid displacement reaction of NiF_3^+ by ClO_2F, thus generating the weaker oxidizer NiF_4 and the more difficult to oxidize substrate ClO_2^+. Therefore, the general applicability of this approach appears to be limited to substrates that exhibit a weaker Lewis basicity than the neutral transition metal parent molecule. Compared to KrF^+- or PtF_6-based oxidations, the NiF_3^+ system offers the advantages of commercially available starting materials and higher yields, but product purification can be more difficult and tedious than for KrF^+.

Introduction

In complex fluorides, the removal of a fluoride ion from the central atom increases its effective electronegativity. Consequently, the oxidizing power of a compound in a given oxidation state increases in the order anion < neutral molecule < cation, and high oxidation state anions are more stable and can be prepared more easily than the corresponding cations.[1−4]

The increased accessibility of the anions is well-known and has been exploited for the syntheses of the highest oxidation states of transition metal fluorides.[5] It is also well-known that the addition of strong Lewis acids to these complex transition metal fluoride anion salts liberates the free parent molecules[1] which, in turn, can form with an excess of Lewis acid the corresponding complex transition metal fluoride cations.

The combination of these two principles, i.e., the ready synthesis of anions at the limits of oxidation by high pressure/high temperature fluorinations and their subsequent conversion into cations of even higher oxidizing power by acidification, offers the potential for new superoxidizers of unprecedented power.[1−4] Their power might rival or surpass that of the strongest presently known oxidizer, the KrF^+ cation.[6]

This approach, however, exhibits a general problem. It arises from the fact that frequently the corresponding neutral parent molecule and cation are thermodynamically unstable tending to decompose rapidly to a lower oxidation state fluoride and elemental fluorine. This property has previously been exploited for the first chemical synthesis of elemental fluorine[2] and for solid propellant fluorine gas generators.[3] Although the principle of generating very powerful new oxidizers by acidification of high oxidation state transition metal fluoride anions had been known for many years,[1−3] only few studies have been carried out on the oxidizer strengths of these species. Thus, Bartlett and Žemva were able to oxidize xenon to XeF_6, RuF_6^- to RuF_6, and PtF_6^- to PtF_6 by using mixtures of NiF_6^{2-} salts and BF_3 or AsF_5 in aHF.[4,7] Furthermore, mixtures of K_2NiF_6 and BF_3 in aHF were used as a fluorinating reagent in organic chemistry. For example, CH_3CN reacts under these conditions with formation of CF_3CN and $CF_3CF_2NF_2$.[8]

[†] This paper is dedicated to the memory of Dr. Donald Pilipovich, a dear friend and former colleague.

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The goal of this study was the exploration of the oxidizing strength of NiF_3^+ and its comparison with that of KrF^+ and PtF_6. Suitable substrates for these studies were ClF_5, BrF_5, XeF_6, ClO_2F, and Kr.[6] Until now, ClF_6^+ salts were only obtainable from the reactions of ClF_5 with KrF^+ salts[9] and PtF_6,[10] and BrF_6^+ salts only from the reaction of BrF_5 with KrF^+ salts.[11]

Experimental Section

CAUTION! *All substances used in this investigation are strong oxidizers, and contact with moisture, water, or organic materials must be avoided. HF is toxic and can cause severe burns. Protective gear and a face shield must be worn while working with these substances.*

Materials and Apparatus. All volatile materials were handled in a stainless steel−Teflon FEP vacuum line.[12] This line and all reaction vessels were passivated with ClF_3 prior to use. All nonvolatile materials were handled in the dry argon atmosphere of a glovebox.

Infrared spectra were recorded in the range 4000−400 cm^{-1} on a Midac FT-IR model 1720 at a resolution of 1 cm^{-1}. Spectra of solids were obtained by using dry powders pressed between AgCl windows in an Econo press (Barnes Engineering Co.). Raman spectra were recorded in the range 4000−10 cm^{-1} on a Bruker Equinox 55 FT-RA spectrophotometer using a Nd:YAG laser at 1064 nm. Pyrex melting point tubes that were baked out at 300 °C for 48 h at 10 mTorr vacuum were used as sample containers. ^{19}F NMR spectra were recorded on a Bruker AM-360 instrument at 339 MHz using neat CCl_3F at room temperature as an external standard. Samples were measured in heat-sealed 3 mm i.d. Teflon FEP tubes (Wilmad Glass Co.).

Literature methods were used for the preparation of Cs_2NiF_6[5e], ClF_5,[13] ClO_2F,[12] and XeF_6.[14] BrF_5 (Matheson) and AsF_5 (Ozark Mahoning) were purified by fractional condensation prior to use. Kr (Matheson) was used without further purification. HF was dried[15] over BiF_5 (Ozark Mahoning) and treated with K_2NiF_6 (Ozark Mahoning) prior to its use.

Reaction of Cs_2NiF_6 with AsF_5 and ClF_5. The reaction was carried out in the apparatus depicted in Figure 1. It consisted of a $^{3}/_{4}$ in. FEP trap and two $^{1}/_{2}$ in. FEP U-traps that were interconnected by Teflon PFA unions containing Teflon filters (Pall Corp.). The apparatus was closed on both sides by PFA valves that were connected to the stainless steel vacuum line through 1 ft long $^{1}/_{4}$ in. FEP tubes.

Cs_2NiF_6 (1.32 mmol) was placed into the $^{3}/_{4}$ in. FEP trap and suspended at −60 °C in ClF_5 (8.32 mmol). Approximately 5 mL of liquid anhydrous HF (aHF) was condensed into the trap at −60 °C. A two-phase system was obtained consisting of a colorless lower phase (ClF_5) and a dark red upper phase of Cs_2NiF_6 dissolved in aHF. AsF_5 (1.32 mmol) was added to the mixture in four equal increments. After the first addition under vigorous stirring at −60 °C, tan-colored NiF_4 was formed. After the second addition and a reaction time of $^{1}/_{2}$ h at −60 to −40 °C, the formation of brown violet $Ni(NiF_6)$ was observed, while the aHF layer was still dark red colored. After the addition of the third and fourth increments of AsF_5 and a total reaction time of 14 h at −60 to −10 °C, the aHF layer turned pale yellow and the NiF_4 had disappeared. All volatile compounds were removed in a dynamic vacuum at 25 °C. The dark violet brown residue was suspended in 5 mL of aHF at 25 °C, and the yellow mother liquor was filtered into U-trap I using 1.5 atm of argon pressure. The aHF was distilled back into the $^{3}/_{4}$ in. trap cooled to −196 °C under a dynamic vacuum. The residue was stirred with the aHF at 25 °C, and the HF solution was filtered again into U-trap I. This washing procedure was repeated twice. U-trap I containing the aHF solution and U-trap II were cooled with dry ice until a white solid precipitated from the solution in U-trap I. The yellow mother liquor was filtered at −78 °C into U-trap II using 1.5 atm of argon pressure. Using the above-mentioned method, the white precipitate was washed twice with aHF at −78 °C until the washing solution was only pale yellow in color. The aHF solvent in U-trap II was pumped off, and the solids in the three traps were dried in a dynamic vacuum for 12 h at 25 °C.

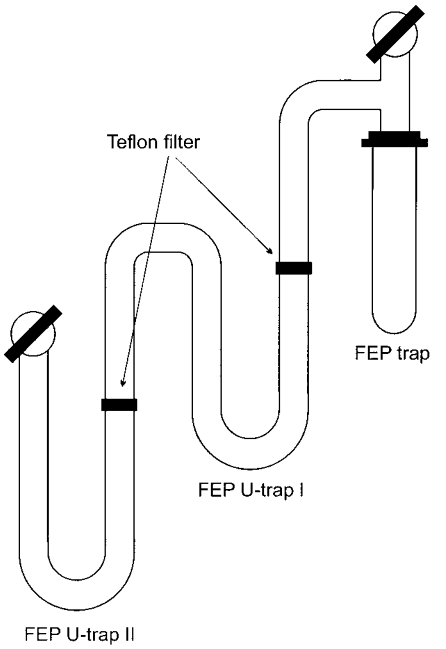

Figure 1. FEP/PFA reaction vessel.

Based on its color and Raman spectrum, the brown violet residue (800 mg) in the $^{3}/_{4}$ in. FEP trap consisted of mainly $CsAsF_6$ (Raman, cm^{-1} (int): $\nu_1(AsF_6^-) = 682$ (100); $\nu_2(AsF_6^-) = 584$ (27); $\nu_5(AsF_6^-) = 373$ (44)) and some $Ni(NiF_6)$.

The pale yellow solid (200 mg) in U-trap I was mainly ClF_6AsF_6[10b] with ClF_4AsF_6[16] as an impurity (^{19}F NMR, $^{35}ClF_6^+ = 385.4$ ppm (6 F, q (1:1:1:1), $^1J_{^{19}F,^{35}Cl} = 338$ Hz); $^{37}ClF_6^+ = 385.3$ ppm (6 F, q (1:1:1:1), $^1J_{^{19}F,^{37}Cl} = 284$ Hz); $ClF_4^+ = 273.3$ ppm (4F, m); Raman, cm^{-1} (int): $\nu_1(ClF_4^+) = 817$ (6); $\nu_1(ClF_6^+) + \nu_1(AsF_6^-) = 688.2$ (100); $\nu_2(ClF_6^+) = 635$ (11); $\nu_2(AsF_6^-) = 575$ (15); $\nu_2(ClF_4^+) = 569$ (4); $\nu_5(ClF_6^+) = 519$ (25); $\nu_5(AsF_6^-) = 372$ (35)). According to the ^{19}F NMR data the composition of the product was ClF_6AsF_6 (0.52 mmol) and ClF_4AsF_6 (0.07 mmol).

The yellow residue (228 mg) in U-trap II consisted mainly of $Ni(AsF_6)_2$ (vibrations for C_{4v} distorted AsF_6^- in $Ni(AsF_6)_2$[17] Raman, cm^{-1} (int), $\nu_1 = 706$ (41.2); $\nu_5 = 370$ (10); IR, cm^{-1} (int), $\nu_8 = 767$ (vs); $\nu_1 = 706$ (m); $\nu_2 = 613$ (vs); the presence of Ni^{2+} was supported by the formation of a red-colored complex with an aqueous solution of dimethylglyoxime).

The reaction was repeated with $Cs_2NiF_6 = 2.367$ mmol, $AsF_5 = 11.836$ mmol, and $ClF_5 = 35.508$ mmol at room temperature. After the suspension was stirred for 2 days at room temperature, all the NiF_6^{2-} salt was reduced to $Ni(AsF_6)_2$. However, on the outer wall of the FEP reaction trap a yellow film was noted that probably resulted from the plasticization of the Teflon by the reagents and their subsequent hydrolysis. After removing all volatiles at 25 °C, the yellow solid residue was worked up as described above. In contrast to the reaction carried out at −10 °C, the main product isolated was ClF_2OAsF_6.[18]

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ClF_2OAsF_6: ${}^{19}F$ NMR, $ClF_2O^+ = 278.4$ ppm (2 F, s); Raman, cm^{-1} (int): $\nu_1(ClF_2O^+) = 1330$ (24); $\nu_2(ClF_2O^+) = 759$ (40); $\nu_1(AsF_6^-) = 675$ (100); $\nu_2(AsF_6^-) = 563$ (13); $\nu_3(ClF_2O^+) = 510$ (29); $\nu_5(AsF_6^-) = 370$ (57).

Reaction of Cs_2NiF_6 with AsF_5 and BrF_5. The reaction was carried out in a $^3/_4$ in. FEP tube, which was heat sealed at one end and connected to a PFA T-piece at the other end. The leg of the T-piece, which formed a 90° angle to the FEP trap, was closed by a PFA valve, while the third leg was closed by a PFA stopper.

Cs_2NiF_6 (1.482 mmol) was suspended in BrF_5 (35.529 mmol) at 25 °C. The suspension was frozen at −196 °C, and AsF_5 (8.894 mmol) was added. The mixture was warmed to 25 °C, and colorless BrF_4AsF_6 formed at the wall of the FEP tube. After the suspension was stirred for 5 min, it was frozen again at −196 °C and aHF (39.180 mmol) was condensed into the reaction vessel. Thawing the mixture and stirring vigorously at 25 °C resulted in the formation of a brown violet solid. The suspension was stirred for 12 h at 25 °C. After this time it consisted of yellow mother liquor and a white solid. All volatiles were removed in a dynamic vacuum (12 h at 25 °C), leaving behind 2049 mg of a pale yellow residue.

This residue was suspended in approximately 3 mL of aHF at −20 °C. The yellow mother liquor was siphoned off into a $^1/_2$ in. FEP tube that also contained a PFA T-piece, as described above. For the siphoning step, the PFA stoppers on both reactors were replaced by PFA stoppers, which contained two small holes. Through one of the holes in each Teflon stopper, a small FEP tube (1 mm o.d.) had been pulled, creating a leak-tight connection between the two vessels. During the whole operation a slow nitrogen flow was passed through the FEP reactors. The mother liquor was then pneumatically transferred from one tube into the other by closing the second hole of the Teflon stopper of the reactor that contained the undissolved solid and the mother liquor. After the transfer of the mother liquor both reactors were immediately evacuated and all volatile material was pumped off. This extraction process was repeated two more times until the color of the mother liquor was only pale yellow. According to its Raman and ${}^{19}F$ NMR spectra, this residue (1103 mg) consisted of mainly $CsAsF_6$ and some BrF_6AsF_6.

The yellow solid obtained from the evaporation of the mother liquor was washed three times with aHF at −78 °C, using the above-described technique. The washings were collected in a second $^1/_2$ in. FEP tube. The reaction product (180 mg), insoluble in aHF at −78 °C, consisted of BrF_6AsF_6, containing a very small amount of $Ni(AsF_6)_2$ as impurity. The yellow product (394 mg) obtained from the evaporation of the washing solutions was $Ni(AsF_6)_2$.

BrF_6AsF_6:[11] ${}^{19}F$ NMR, $BrF_6^+ = 337.2$ ppm (6 F, 2 q (1:1:1:1), ${}^1J_{^{19}F,^{79}Br} = 1578$ Hz; ${}^1J_{^{19}F,^{81}Br} = 1700$ Hz); Raman, cm^{-1} (int), $\nu_1(AsF_6^-) = 686$ (100); $\nu_2(BrF_6^+) = 673$ (14); $\nu_1(BrF_6^+) = 662$ (37); $\nu_2(AsF_6^-) = 574$ (29); $\nu_5(BrF_6^+) = 408$ (22); $\nu_5(AsF_6^-) = 371$ (45).

Reaction of Cs_2NiF_6 with AsF_5 and Kr. In a 3 mm i.d. FEP NMR tube, Cs_2NiF_6 (0.08 mmol) was dissolved in ca. 0.3 mL of aHF at −40 °C. The solution was frozen at −196 °C, and AsF_5 (0.241 mmol) was condensed into the tube. The mixture was warmed to −78 °C and pressurized with 2 atm of Kr, and the tube was heat sealed under vacuum at −196 °C. Warming the sample to above −20 °C resulted in the formation of $Ni(NiF_6)$, but there was no ${}^{19}F$ NMR evidence for the formation of $KrFAsF_6$.

The reaction was repeated in a stainless steel cylinder, using 15 atm of Kr pressure. Again, no evidence for the formation of $KrFAsF_6$ could be obtained.

Reaction of Cs_2NiF_6 with AsF_5 and XeF_6. In the reaction vessel depicted in Figure 1, Cs_2NiF_6 (0.287 mmol) was dissolved in aHF at −78 °C, and then AsF_5 (0.862 mmol) was added at −196 °C. Warming the mixture to −60 °C resulted in the formation of solid tan-colored NiF_4 and the disappearance of the NiF_6^{2-} anion color from the aHF mother liquor. This suspension was frozen at −196 °C, and XeF_6 (0.862 mmol) was added. The mixture was thawed at −60 °C. At this point, NiF_4 dissolved in the aHF under formation of red-colored $(XeF_5)_2NiF_6$. This result confirms the observations of Žemva et al.[7] No evidence for the oxidation of XeF_6 to the XeF_7^+ cation was obtained.

Reaction of Cs_2NiF_6 with AsF_5 and ClO_2F. In a 3 mm i.d. FEP tube, Cs_2NiF_6 (0.128 mmol) was suspended in liquid ClO_2F (5.700 mmol) at −40 °C. The suspension was frozen at −196 °C, and AsF_5 (0.640 mmol) was added. Warming the mixture to −40 °C resulted in the formation of colorless ClO_2AsF_6,[19] but in no apparent reaction of Cs_2NiF_6. At −50 °C, a small amount of aHF was added to this mixture. Immediately, the formation of dark violet $Ni(NiF_6)$ was observed. The sample was warmed to 25 °C, and all volatiles were removed in a dynamic vacuum. The ${}^{19}F$ NMR spectrum of the residue in 0.3 mL of aHF at 25 °C gave no evidence for the formation of $ClO_2F_2AsF_6$.[20]

Results and Discussion

Synthesis of ClF_6AsF_6. The ClF_7 and BrF_7 molecules, the parents of the coordinately saturated complex cations ClF_6^+ and BrF_6^+, respectively, do not exist. Therefore, the normally facile cation formation by a simple F^- abstraction from the parent molecule using a Lewis acid is not possible. Moreover, ClF_5 and BrF_5 are strong oxidizers, and very strong oxidative fluorinators are needed to prepare the corresponding cations. In view of this, it is not surprising that, until now, the formation of the ClF_6^+ cation had only been achieved by using either KrF^+ salts[9] or PtF_6.[10] The oxidation of BrF_5 had only been attained by using the strongest known oxidizer, the KrF^+ cation. We have now found that ClF_6AsF_6 and BrF_6AsF_6 can be prepared in 40% and 32% yield, respectively, from the corresponding halogen pentafluorides and $NiF_3^+AsF_6^-$ in anhydrous HF solution, as shown in eq 1 where X can be Cl or Br.

$$Cs_2NiF_6 + 5AsF_5 + XF_5 \xrightarrow[-60\text{ to }-10\ °C]{aHF} XF_6AsF_6 + Ni(AsF_6)_2 + 2CsAsF_6\downarrow \tag{1}$$

This rather complex reaction involves several steps. A suspension of Cs_2NiF_6 in ClF_5 forms a two-phase system with aHF at −60 °C. The colorless lower phase consists of ClF_5, while the dark red upper phase contains the Cs_2NiF_6 dissolved in aHF. The addition of AsF_5 at −60 °C produces at first precipitates of tan-colored NiF_4 and colorless $CsAsF_6$ and is accompanied by the decolorization of the aHF phase (eq 2).

$$Cs_2NiF_6 + 2AsF_5 \xrightarrow[-60\ °C]{aHF} NiF_4\downarrow + 2CsAsF_6\downarrow \tag{2}$$

Raising the temperature to −10 °C and subsequent addition of more AsF_5 result in a very fast reduction of NiF_4 to brown violet, HF-insoluble NiF_3. The observed oxidation products are ClF_6AsF_6 and possibly some fluorine. Most likely, NiF_4 forms with AsF_5 an HF-soluble NiF_3^+ salt (eq 3).[4] This very powerful oxidizer can act as a one-electron oxidizer and removes an electron from the substrate with formation of NiF_3 and the ClF_5^+ radical cation (eq 4). The latter can react with either NiF_4 or NiF_3 to give the final product ClF_6AsF_6 (eq 5a or 5b).

$$NiF_4 + AsF_5 \xrightarrow[-60\ °C]{aHF} NiF_3^+ + AsF_6^- \tag{3}$$

$$NiF_3^+ + AsF_6^- + ClF_5 \xrightarrow{aHF} {}^{\bullet}ClF_5^+ + AsF_6^- + NiF_3\downarrow \tag{4}$$

$${}^{\bullet}ClF_5^+ + AsF_6^- + NiF_4 \xrightarrow{aHF} ClF_6AsF_6 + NiF_3\downarrow \tag{5a}$$

$${}^{\bullet}ClF_5^+ + AsF_6^- + NiF_3 \xrightarrow{aHF} ClF_6AsF_6 + NiF_2\downarrow \tag{5b}$$

This one electron oxidation mechanism is most plausible because it can explain the formation of NiF_3. In addition, it is supported by the known reaction of K_2NiF_6/BF_3 with PtF_6^- salts

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under formation of PtF_6,[4] the decomposition of NiF_4 to NiF_3 and F_2,[7] and the formation mechanism of NF_4^+ salts,[21] all of which are best described as one electron transfer reactions.

After the fast depletion of free NiF_4, the formed NiF_3, which is only sparingly soluble in aHF, reacts slowly under the formation of $Ni(AsF_6)_2$ and additional ClF_6AsF_6 at −10 °C. This observation can be rationalized by the known tendency of nickel(III) fluoride to disproportionate into Ni(II) and Ni(IV), forming $Ni(NiF_6)$ (eq 6).[1b,7] In the presence of AsF_5, the latter forms aHF-soluble $Ni(AsF_6)_2$ and more NiF_4 (eq 7) that can reenter the oxidation cycle (eqs 3−5). Since, in each cycle, only half of the NiF_4 is consumed, many such cycles are required until essentially all of the NiF_6^{2-} salt is reduced to Ni(II), thus explaining the slowness of this reaction. The low solubilities of NiF_3 and $Ni(NiF_6)$ in aHF[7,22] contribute further to the slowness of the reduction reaction.

$$2NiF_3 \xrightarrow{aHF} Ni(NiF_6) \quad (6)$$

$$Ni(NiF_6) + 2AsF_5 \xrightarrow[-10\ °C]{aHF} NiF_4\downarrow + Ni(AsF_6)_2 \quad (7)$$

Due to the ability of ClF_5 to plasticize the FEP material of the reactor,[23] the reaction should not be performed at higher temperatures or for a longer reaction time. For example, products derived from chlorine oxides and chlorine oxofluorides were detected on the outer wall of the FEP reaction vessel after the reaction of Cs_2NiF_6 with AsF_5 and ClF_5 had been carried out at room temperature for 2 days. The only nonvolatile product in the reactor which was identified was $ClOF_2AsF_6$,[18] which might have arisen from hydrolysis with a small amount of adventitious water.[24]

The use of a stainless steel cylinder instead of a FEP reactor seems to inhibit the formation of ClF_6AsF_6. This is not surprising because the combination of HF with a strong oxidizer is known to rapidly attack metal. This attack results in the formation of $FeNiF_6$ as the major product, which is only sparingly soluble in aHF. In contrast to $Ni(NiF_6)$, $Fe(NiF_6)$ is completely stable at room temperature in aHF and exhibits no pronounced fluorinating abilities.[22]

The separation of ClF_6AsF_6 from the coproducts $CsAsF_6$ and $Ni(AsF_6)_2$ can be achieved by suspending the product mixture in HF at 25 °C. At this temperature, $CsAsF_6$ is the most insoluble component and can be filtered off. At −78 °C, ClF_6AsF_6 precipitates out from the mother liquor and is filtered off. The filtrate contains $Ni(AsF_6)_2$, the most HF-soluble reaction product at this temperature. The isolated yield of ClF_6AsF_6, 40% based on the limiting reagent $Cs_2[NiF_6]$, is higher than that of 11% previously obtained using $KrFAsF_6$ as the oxidizer.[9] The observed ^{19}F NMR and Raman spectra were in good agreement with previous reports.[10b,18b]

Synthesis of BrF_6AsF_6. The oxidizing power of the system Cs_2NiF_6/AsF_5/aHF is also strong enough to oxidize BrF_5 to BrF_6^+. In the absence of HF, the only reaction observed at room temperature was the well-known formation of BrF_4AsF_6.[16] However, the addition of an equimolar amount of HF relative to BrF_5 resulted in an immediate formation of NiF_4 at −78 °C. The solvent HF seems to be essential for this reaction to proceed. Its main function is most likely to solubilize the Cs_2NiF_6. As in the case of ClF_5, raising the temperature to 25 °C resulted in the initial reduction of NiF_4 to NiF_3. Due to the much lower vapor pressure of BrF_5 relative to ClF_5 at room temperature, the plasticizing effect of BrF_5 on the FEP material of the reaction vessel is less pronounced. Therefore, the reaction could be performed at 25 °C and a complete reduction of the NiF_6^{2-} anion to Ni(II) was attained within 12 h. The observed products were BrF_6AsF_6, $CsAsF_6$, and $Ni(AsF_6)_2$, as expected for reaction 8.

$$Cs_2[NiF_6] + 5AsF_5 + BrF_5 \xrightarrow[25\ °C]{aHF} [BrF_6][AsF_6] + Ni[AsF_6]_2 + 2CsAsF_6\downarrow \quad (8)$$

As in the case of $[ClF_6][AsF_6]$, $[BrF_6][AsF_6]$ can be isolated by suspending the reaction products in aHF at 25 °C. Most of the $[BrF_6][AsF_6]$ and all of the $Ni[AsF_6]_2$ can be removed from the less HF soluble $CsAsF_6$ by siphoning off the mother liquor at 25 °C. At −78 °C $[BrF_6][AsF_6]$ precipitates from the mother liquor, which now contains only $Ni[AsF_6]_2$. The yield of $[BrF_6][AsF_6]$ based on the limiting reagent $Cs_2[NiF_6]$ was 32%, which compares favorably with that of less than 20% previously reported for the KrF^+ reaction.[11b] The observed NMR and Raman spectra were in good agreement with the previous reports.[11]

Reactions of Cs_2NiF_6/AsF_5 with Kr, XeF_6, and ClO_2F. The successful syntheses of ClF_6AsF_6 and BrF_6AsF_6 from Cs_2NiF_6 and AsF_5 in aHF suggested the further investigation of the oxidizing strength and preparative scope of this system. For this purpose, Kr, XeF_6, and $ClOF_2$ were chosen as the substrates. Based on the F^+ detachment energies of KrF^+ and XeF_7^+ (115.9 and 116.7 kcal mol^{-1}, respectively),[6] the oxidation of Kr and XeF_6 should be more difficult than that of BrF_5 (F^+ detachment energy of BrF_6^+: 140.8 kcal mol^{-1}).[6] However, ClO_2F (F^+ detachment energy of $ClO_2F_2^+$: 161.0 kcal mol^{-1})[6] should be oxidized more easily than BrF_5.

KrF^+ salts are the most powerful oxidative fluorinators known today. However, KrF^+ salts are rarely used, because KrF_2 is difficult to prepare. The three most widely used methods are (1) electrical discharge of gaseous mixtures of krypton and fluorine at low temperatures and pressures;[25] (2) irradiation of fluorine/krypton mixtures by UV or sunlight;[26,27] and (3) the hot wire method.[28] The successful oxidation of Kr, using the system Cs_2NiF_6/AsF_5/HF, would provide a convenient and safe synthesis for KrF^+ and would reveal whether this system surpasses the oxidizing strength of KrF^+. However, so far KrF^+ could not be prepared from Cs_2NiF_6 and AsF_5 in aHF. Reasons for this failure might be either an insufficient oxidizing power of this system or the poor solubility of Kr in HF. An increase of the Kr concentration in aHF can be attained by increasing the Kr pressure. However, the maximum Kr pressure which can be used in the FEP reactors was 5 atm. Working under a higher Kr pressure made it necessary to carry out the reaction in stainless steel cylinders. This was not practical, due to the attack of the metal cylinder by the HF/strong oxidizer mixture with formation of transition metal hexafluoronickelates(IV) and $Fe(AsF_6)_2$.

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Also, it was not possible to oxidize XeF_6 to XeF_7^+ using Cs_2NiF_6/AsF_5 as the oxidizer in aHF. The reason that XeF_6 is not oxidized might be either its high Lewis basicity or an insufficient oxidizer strength of NiF_3^+. Even if NiF_3^+ is a strong enough reagent to oxidize XeF_6 to XeF_7^+, the high Lewis basicity of XeF_6 could prevent the desired reaction by rapidly converting the strong oxidizer NiF_4 back to the more weakly oxidizing NiF_6^{2-} anion, while forming the harder to oxidize XeF_5^+ cation. This interpretation is experimentally supported by the observation that, when XeF_6 is added to a freshly prepared suspension of NiF_4 in aHF at −60 °C, the tan-colored NiF_4 vanishes and the aHF-soluble, red-colored $(XeF_5)_2NiF_6$ salt is formed (eq 9). Reaction 9 was previously used by Žemva

$$NiF_4 + 2XeF_6 \xrightarrow[-60\ ^\circ C]{aHF} (XeF_5)_2NiF_6 \qquad (9)$$

et al. to verify the formation of NiF_4.[7] Although excess AsF_5 could be used to regenerate NiF_4 or the NiF_3^+ cation, the simultaneous formation of XeF_5AsF_6 would convert XeF_6 into the more difficult to oxidize XeF_5^+ cation. Therefore, the observed reaction products of our reaction are best described by the following equations:

$$Cs_2NiF_6 + 2AsF_5 \xrightarrow{aHF} NiF_4 + 2CsAsF_6\downarrow \xrightarrow[-2CsAsF_6]{+AsF_5} NiF_3^+AsF_6^- \xrightarrow{+XeF_6} NiF_4 + XeF_5AsF_6 \xrightarrow[-XeF_5AsF_6]{+2XeF_6} (XeF_5)_2NiF_6 \qquad (10)$$

The problems associated with strongly basic substrates were confirmed by the reaction of ClO_2F with Cs_2NiF_6 and AsF_5 in aHF. Although the oxidation of ClO_2F to the $ClO_2F_2^+$ cation (F^+ detachment energy of $ClO_2F_2^+$: 161.0 kcal mol^{-1})[6] should be easier than that of ClF_5 to the ClF_6^+ cation (F^+ detachment energy of ClF_6^+: 147.3 kcal mol^{-1}),[6] the formation of the $ClO_2F_2^+$ cation was not observed in this reaction. By analogy with XeF_6, the strongly basic ClO_2F substrate forms with AsF_5 a stable ClO_2AsF_6 salt that has no dissociation pressure at room temperature.[19] Under the described reaction conditions, all of the ClO_2F is rapidly transformed to ClO_2AsF_6, which is much harder to oxidize than ClO_2F. Contrary to the reaction of ClO_2F with PtF_6,[10b,c] the formation of small amounts of the ClF_6^+ cation as a side product was not observed. This indicates that under these conditions the ClO_2^+ cation neither is oxidized nor undergoes significant oxygen fluorine exchange.

Relative Oxidizing Strength of NiF_3^+. Until now ClF_6^+ salts were only obtainable from the reaction of ClF_5 with KrF^+ salts[9] or PtF_6,[10] and BrF_6^+ salts only from the reaction of BrF_5 with KrF^+ salts.[11] Both ClF_6AsF_6 and BrF_6AsF_6 can be synthesized using NiF_3^+ salts in aHF. According to these results, the NiF_3^+ system is a stronger oxidizer than PtF_6, because PtF_6 is capable of oxidizing only ClF_5 but not BrF_5.[21] This conclusion agrees with the observation that an aHF solution of K_2NiF_6, acidified with BF_3, oxidizes the PtF_6^- anion to PtF_6.[4]

A comparison of the oxidizing strengths of NiF_3^+ and KrF^+ is more complicated. Both compounds can oxidize ClF_5 *and* BrF_5 and, hence, are stronger than PtF_6, which can oxidize only ClF_5. Although both NiF_3^+ and KrF^+ are expected to oxidize the PtF_6^- anion to PtF_6, the observed reactions are quite different. Whereas NiF_3^+ can act as a one-electron oxidizer toward PtF_6, resulting in stable NiF_3 or $Ni(NiF_6)$ and PtF_6 (eq 11), KrF^+ behaves as an oxidative fluorinator, oxidizing a δ^- polarized fluoride ligand of PtF_6^- to F_2 (eq 12).

$$2NiF_3^+ + 2PtF_6^- \xrightarrow{aHF} Ni(NiF_6) + 2PtF_6 \qquad (11)$$

$$KrF^+ + PtF_6^- \xrightarrow{aHF} Kr + PtF_5 + F_2 \qquad (12)$$

Contrary to NiF_3^+, which requires only one electron to form stable NiF_3 or $Ni(NiF_6)$ and, therefore, can act also as a good one-electron oxidizer, KrF^+ is not a good one-electron oxidizer, because the resulting reduction product, the KrF radical, is unstable and its likely decomposition product, the F radical, is equally unstable. KrF^+ tends either to act as a positive-fluorine transfer reagent or to attack a negatively polarized fluorine ligand under F_2 elimination. Therefore, the chemical characteristics of NiF_3^+ and KrF^+ can be quite different and, in this case, do not permit a direct comparison of their relative oxidizer strengths. Consequently, it cannot be decided, on the basis of the available information, whether NiF_3^+ or KrF^+ is the stronger oxidizer. The failure to oxidize Kr with NiF_3^+ to KrF^+ may have been due entirely to unfavorable reaction conditions and does not necessarily imply that KrF^+ is a stronger oxidizer than NiF_3^+.

Advantages and Disadvantages of NiF_3^+. Compared to PtF_6, the NiF_3^+-based system offers advantages and disadvantages. On the one hand, the required $K_2(NiF_6)$, AsF_5, and HF starting materials are commercially available, and the reaction products are easier to separate than the 1:1 mixture of $ClF_6^+PtF_6^-$ and $ClF_4^+PtF_6^-$, obtained from the ClF_5/PtF_6 reaction.[21] On the other hand, PtF_6 can also oxidize strongly basic substrates, such as ClO_2F,[29] which NiF_3^+ cannot.

Compared to KrF^+, the NiF_3^+-based system again offers the advantages of commercially available starting materials and higher yields, 40% for ClF_6^+ and 32% for BrF_6^+, compared to 11%[10c] and <20%[11b] with KrF^+. However, product isolation and purification is more cumbersome and the final product purity is inferior.

Conclusions

According to these results, the system $Cs_2NiF_6/AsF_5/HF$ should be capable of oxidizing all compounds that have a higher F^+ attachment energy than BrF_5, provided that the substrate exhibits a lower Lewis basicity than NiF_4. Therefore, a successful oxidation is a function not only of the oxidizing strength but also of the relative Lewis acidities/basicities of all components, because the oxidizing strengths vary significantly from the cation to the neutral parent molecule to the anion.

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