Journal of Fluorine Chemistry, 23 (1983) 267–282

Received: December 14, 1982; accepted: February 4, 1983

THE REACTION OF URANIUM HEXAFLUORIDE WITH SILVER FLUORIDE IN ANHYDROUS HYDROGEN FLUORIDE AND THE CHEMICAL PROPERTIES OF THE PRODUCT Ag_2UF_8 [*†]

JOHN G. MALM[**]

Argonne National Laboratory, Argonne, Illinois 60439 (USA)

SUMMARY

UF_6 reacts with AgF dissolved in anhydrous hydrogen fluoride to precipitate Ag_2UF_8. Ag_2UF_8 has some unexpected properties: On reaction with water it produces O_2 and reduced uranium. No adequate explanation could be found of why UF_6 and AgF combined in this manner should produce a powerful oxidant. Raman spectra and chemical properties of the solid products are given.

INTRODUCTION

Liquid anhydrous hydrogen fluoride (AHF) is a good solvent and reaction medium for many inorganic compounds [1]. In this solvent, solvation of cation and fluoride complexing can occur but one can avoid the oxo-complexes that occur in aqueous solution and, in principle at least, one can observe new species and carry out reactions not otherwise possible.

---

[*] Work supported by the U.S. Department of Energy, Division of Chemical Sciences, under Contract W-31-109-Eng-38.

[†] This paper was presented at the 10th International Fluorine Symposium at Vancouver, British Columbia, August 1982.

[**] Present address: Los Alamos National Laboratory
INC-4 - MS C346
Los Alamos, New Mexico 87545 (USA)

0022-1139/83/$3.00

These advantages are especially marked with the actinide elements, where lower valence states react with water and the +5 and +6 states always occur in aqueous solution as the oxy-complexes MO_2^+ and MO_2^{++}. Recent examples of the utilization of this solvent with the actinides are the spectral studies of the valence states (III-VI) of neptunium and uranium fluorides [2], the formation of NpF_5 [3] and UOF_4 [4], and the preparation of AmF_6 [5] species unattainable by other means.

We report here the preparation of Ag_2UF_8 by the reaction of AgF and UF_6 in AHF and some of the unexpected properties of this compound. Martin et al [6], reported the solid-gas reaction of UF_6 with AgF along with their discovery of the complexes of UF_6 with alkali metal fluorides (but gave no properties). With the alkali metal fluorides they reported the stoichiometry, M_3UF_9, which was later shown to be M_2UF_8, and studied extensively [8].

EXPERIMENTAL

Materials Liquid hydrogen fluoride (99% purity, minimum) was obtained from Matheson Gas Products Company. It was further purified by treating 600 g batches in a Monel metal container with 2 atm of fluorine for several days. The excess fluorine was removed by pumping at -78°C. When purified in this manner, the liquid HF had a specific conductivity of $4 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$ which would correspond to a water content of <0.01% [9]. In addition, this treated HF gave no reaction with UF_6 which is extremely sensitive to traces of moisture or reducing impurities. Silver fluoride, typically greater than 99.8% purity was obtained from CERAC, Inc. Spectrographic analysis showed only traces of metal impurities. Silver and fluoride analyses gave a formula of $AgF_{1.004}$. Sodium fluoride, Mallinckrodt analytical reagent grade, was dried at 150°C before use. Uranium hexafluoride of high purity was purchased from Union Carbide Corp. $AgUF_6$ was prepared by addition of AgF to a solution of $Na^+UF_6^-$ in AHF as described previously [10]. AgF_2 was formed by addition of excess fluorine to a solution of AgF in AHF. The very insoluble AgF_2 precipitates rapidly. The supernatant is poured off, the precipitate washed twice with fresh anhydrous hydrogen fluoride and dried under vacuum.

Preparation Procedure The reactions were carried out in all Kel-F systems consisting of 30 cc molded tubes (with 3/4 inch flared fittings) fitted with valves and connected by 1/4 inch OD tubing and fittings. Weighed quantities of AgF (with NaF in some studies) were transferred to the Kel-F tubes in a dry box, the tubes sealed and attached to a high vacuum system. Once the apparatus was in place, the reactions and the subsequent manipulations could be carried out without exposing these very hygroscopic materials to the atmosphere. Weighed quantities of UF_6 and appropriate amounts of HF were distilled on the AgF through Kel-F Y-type connections and then the mixture warmed to room temperature. Alternatively, HF solutions of the reagents could be made up and then mixed by pouring from one vessel to the other. Usually, the reaction mixture was allowed to stand for several hours; at low fluoride concentration (with slow reaction), for 24 hours. After reaction the supernatant solution was poured to another tube and some HF distilled back for washing; this was poured off and the product pumped to a good vacuum and weighed. It was convenient to prepare up to 3-4 g of Ag_2UF_8 using 30 cc capacity tubes. Larger preparations, 30 g, were carried out in 125 cc Kel-F tubes. Excess reagents, of course, are easily recovered and, made up to appropriate concentrations, they can be used in subsequent preparations.

Analyses Weighed samples of the product were analyzed for uranium, silver, and fluoride. The uranium was determined colorimetrically, the silver by atomic absorption. The estimated error in both cases is less than 2%. After pyrohydrolysis of a sample, the fluoride was collected and determined by potentiometric titration with thorium solution. When NaF was used in the reacting solutions, the sodium incorporated in the product was determined by atomic absorption.

The amount of oxidized species in the product was determined by hydrolyzing weighed samples of the product in 0.5 M $HClO_4$ and collecting and measuring the oxygen evolved. On hydrolysis the reduced uranium present is precipitated as UF_4 and was determined separately. Reduced uranium in the products was also determined by dissolving small amounts in concentrated H_3PO_4 and determining the U(VI) and U(IV) present spectrophotometrically. Solutions of UF_5 and $AgUF_6$ in H_3PO_4 were used as standards.

TABLE 1

Analyses of the product from reaction of AgF and UF_6 in AHF

Run No.	Conditions		Product Weight, Grams	Yield Percent of UF_6	Analyses of Product on Hydrolysis		
	AgF	UF_6			Ag/U	O_2 evolved, equiv/mole U	Uranium V, equiv/mole U
#37	3.59 M	0.70 M	3.0666 g	100%	2.04	0.46	0.56
#121	3.0 M	0.7 M	3.8310 g	100%	2.03	0.50	0.52
#116	1.57 M	0.29 M	1.9200 g	68%	1.90	0.22	0.51
#288	1.09 M	0.19 M	0.9533 g	53%	1.86	0.25	0.35
#54	0.91 M	0.36 M	0.5630	26%	1.88	0.27	0.45
#113	0.82	0.21 M	0.1983	10%	1.32	0.00	0.50

TABLE 2

Analyses of product of reaction AgF and UF_6 in AHF containing NaF

Run No.	Conditions			Product Weight Grams	Yield Percent of UF_6	Analyses of Product on Hydrolysis				
	NaF	AgF	UF_6			Ag/U	Na/U	Total M/U	O_2 evolved equiv/mole U	Uranium V equiv/mole U
#281	2.18 M	0.70 M	0.36 M	1.4610 g	69%	1.92	0.27	2.19	0.34	0.48
#70	1.71 M	0.55 M	0.25 M	1.7760 g	<70%	1.80	0.16	1.96	0.22	0.50
#128	1.17 M	0.65 M	0.28 M	0.9211 g	43%	1.88	0.23	2.11	0.46	0.59
#223	0.86 M	0.62 M	0.33 M	0.6970 g	33%	1.88	0.17	2.05	0.17	0.54
#256	0.58 M	0.63 M	0.30 M	0.2254	11%	1.55	0.19	1.74	0.08	0.55
#93	0.44 M	0.46 M	0.24 M	0.1012	5%	1.30	0.38	1.68	0.00	0.87

Raman Spectra Raman spectra of the solid products were obtained using a Spex Ramalog Double Spectrometer Model No. 1403 using the Krypton 6471 Å line. The samples were sealed in 3 mm thin walled Pyrex tubes.

Visible Spectra Visible and near infrared spectra were obtained on solid samples of Ag_2UF_8 by mixing with a dried fluorocarbon grease and mounting the mixture in a thin film between two quartz disks. Data were obtained using a Cary spectrophotometer Model 14. Samples of UF_4, UF_5, and $AgUF_6$ were run for comparison.

RESULTS

Reaction with AgF Uranium hexafluoride is precipitated quantitatively from anhydrous hydrogen fluoride (AHF) solutions as the compound Ag_2UF_8, when the AgF concentration is greater than 2 M. The reaction $2AgF + UF_6 \rightleftarrows Ag_2UF_8$ is rapid and complete under these conditions, and a finely divided brown product is formed. The product is very insoluble in AHF but prolonged washing with fresh AHF should be avoided because back reaction (discussed later) at lower AgF concentrations can occur with loss of product. We have assigned the formula Ag_2UF_8 to this product at complete precipitation, although the fluoride by analysis was 5-10% low. The loss of fluoride can be explained by the difficulty of complete recovery of fluoride from actinide fluoride salts by pyrohydrolysis prior to fluoride determination.

Table 1 shows the results of a series of experiments with varying AgF concentrations. As the fluoride concentration is lowered, a smaller fraction of UF_6 is precipitated from solution. Below 0.8 M AgF, little or no reaction occurs. At the lower concentrations the reaction is very slow, taking 24 hours for completion. The product here is lighter in color. The Ag to U ratio in the product also decreases as the AgF concentration is lowered. All the products obtained gave the same x-ray powder patterns, which were indistinguishable from the powder patterns of $AgUF_6$ and $AgUOF_5$ [10,11].

Reaction with AgF in the Presence of NaF As mentioned in the previous section, little or no reaction between AgF and UF_6 in AHF occurs if the AgF concentration is below 0.8 M. The reaction, however, can be induced by raising the fluoride concentration by addition of NaF. Table 2 shows the results of a series of experiments in which the NaF concentration was varied and the AgF concentration kept relatively low. At 2 M NaF, the reaction is rapid and 70% of the UF_6 (and 70% of the AgF) is precipitated as Ag_2UF_8 with perhaps 10% of the Ag^+ replaced by Na^+ in the lattice. The product is brown and finely divided.

At lower fluoride concentration the reaction is completed only after 24 hours. The product of the slow reaction is light grey in color and forms hard crystalline-like masses on the bottom and the sides of the Kel-F vessel. As in the reaction with AgF alone the metal to uranium ratio in the product is less than 2 when precipitation is carried out at low F^- concentration.

The product formed with NaF present appears to be the same as that formed with AgF alone with some Na^+ in place of Ag^+. The x-ray powder patterns were identical.

Reaction of UF_6 with AgF in the Absence of HF No reaction was observed when AgF and excess UF_6 were mixed and allowed to stand for 7 days at 25°. No reaction was observed at 70° in the presence of liquid UF_6 after 4 days (Martin et al [6] found reaction at 67°). In a sealed Monel metal reactor, 4.23 mmoles of AgF were reacted with liquid UF_6 at 110° for 4 days to give the same product that is precipitated from anhydrous HF. The x-ray powder pattern and behavior on hydrolysis were identical to Ag_2UF_8. The product analyzed as $Ag_{2.35}UF_x$, suggesting that the reaction product is Ag_2UF_8 along with some unreacted AgF.

Properties of Ag_2UF_8 Ag_2UF_8 is a rust brown free-flowing powder. It is hygroscopic, turning green on exposure to moist air. At 25°, the product can be stored indefinitely.

X-ray powder patterns of Ag_2UF_8 were indistinguishable from those obtained from $AgUF_6$ and $AgUOF_5$ [10,11].

The solid showed no ESR signal.

When Ag_2UF_8 is heated under vacuum at 225°, UF_6 is evolved. 3.4025 g (5.64 mmoles) of Ag_2UF_8 was placed in a platinum container inside a nickel tube and heated at 225° under vacuum for 20 hours. The UF_6 given off was collected in a U-tube cooled in a liquid nitrogen. The sample lost 0.8761 g (2.49 mmoles) which corresponded to the weight of UF_6 collected. The UF_6 was identified and shown to be pure by the infra-red spectra of its vapor. After 20 hours additional heating at 325° a total of 70% of the UF_6 in the original sample evolved. There was no evidence of the evolution of a permanent gas, fluorine, during heating. This behavior is quite different from the behavior of the double salts of UF_6 with alkali fluorides which decompose evolving fluorine and UF_6 [8].

The reaction of Ag_2UF_8 with water is also quite different and will be discussed in detail in the next section.

Raman Spectra The Raman spectra (Fig. 1) of the product, Ag_2UF_8, which is precipitated rapidly and completely from AHF at high AgF concentrations showed only a broad band centered about 550 cm^{-1}. Raman spectra (Figs. 2 and 3) were also obtained on the products obtained by partial precipitation (50% of the UF_6) at lower fluoride concentrations. With these products two strong sharp peaks are observed at 592 cm^{-1} and 611 cm^{-1} along with a broad weak band at 550 cm^{-1}.

Partial washing with AHF gives a product with bands at 592 cm^{-1} and 611 cm^{-1} (Fig. 4) along with the 550 cm^{-1} band.

Thorough washing with AHF leaves an insoluble yellow product in which only the 592 cm^{-1} Raman band is predominant (Fig. 5).

Figure 6 shows the Raman spectra of pure $AgUF_6$ with its strong band at 592 cm^{-1}.

Visible Spectra Visible and near infrared spectra were obtained on solid sample of Ag_2UF_8. Samples of UF_4, UF_5, and $AgUF_6$ were run for comparison. Ag_2UF_8 showed bands in the region 800-1500 nm in the region where UF_5 and $AgUF_6$ absorb, suggesting the presence of uranium(V) in the solid. No bands were seen in the UF_4 region, 400-700 nm.

Oxidizing and Reducing Properties of Ag_2UF_8 on Hydrolysis The most interesting property of these salts is their ability to oxidize water, liberating O_2, and precipitating the insoluble lower fluoride, UF_4. (UF_6 alone, on hydrosis, gives UO_2^{++} and F^-; AgF on hydrolysis gives Ag^+ and F^-.) The results of these hydrolyses are shown in Tables 1 and 2. The hydrolyses were carried out in a closed system, the O_2 collected with a Toeppler pump, measured, and analyzed mass spectrometrically. The insoluble UF_4 was separated from the supernatant and both were analyzed. The reduced uranium is tabulated as U(V), i.e., twice the UF_4 found. The fraction of reduced uranium was also determined by dissolving a small amount of Ag_2UF_8 in conc. H_3PO_4 and then comparing the intensities of the U(IV) and UO_2^{++} bands spectrophotometrically. In general, the two methods have good agreement.

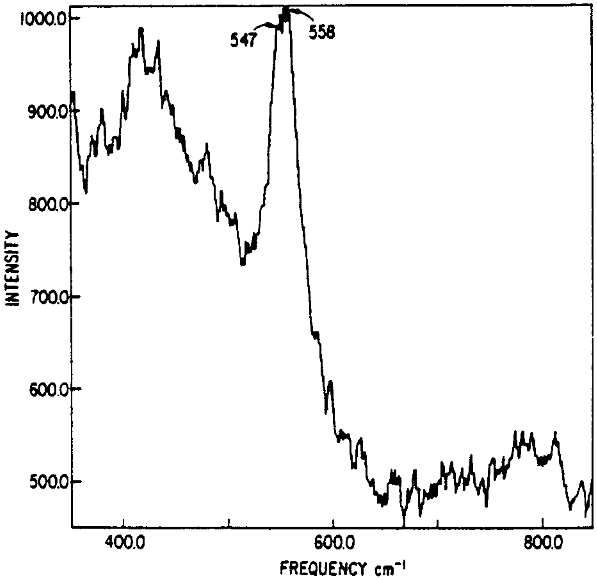

Fig. 1. Raman spectra of product, Ag_2UF_8, precipitated from 3 M AgF solution.

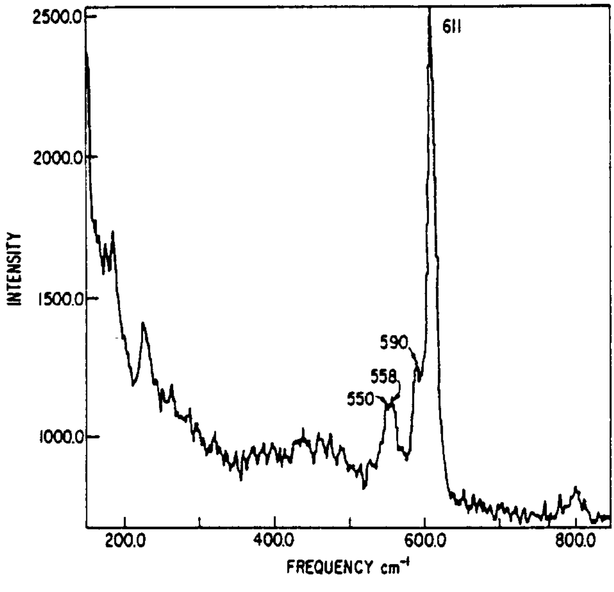

Fig. 2. Raman spectra of product, $Ag_{1.9}UF_x$, precipitated from 1.1 M AgF solution (50% yield).

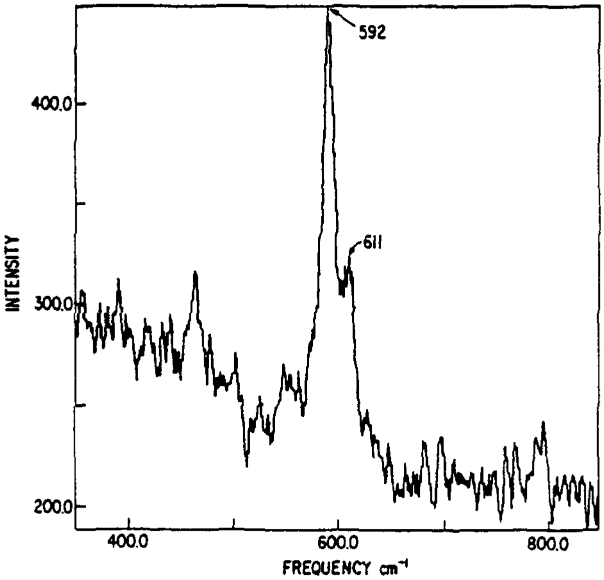

Fig. 3. Raman spectra of product, $Ag_{1.9}Na_{0.2}UF_x$, precipitated from 1.2 M NaF solution (50% yield).

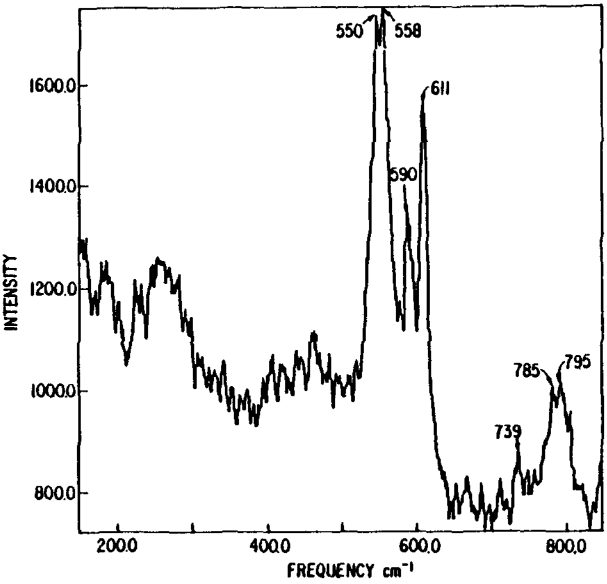

Fig. 4. Raman spectra of product obtained by treating Ag_2UF_8 twice with AHF.

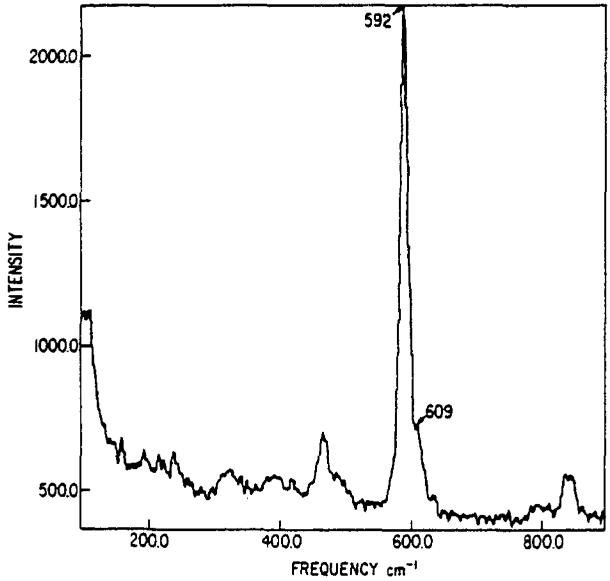

Fig. 5. Raman spectra of product obtained by treating Ag_2UF_8 six times with AHF.

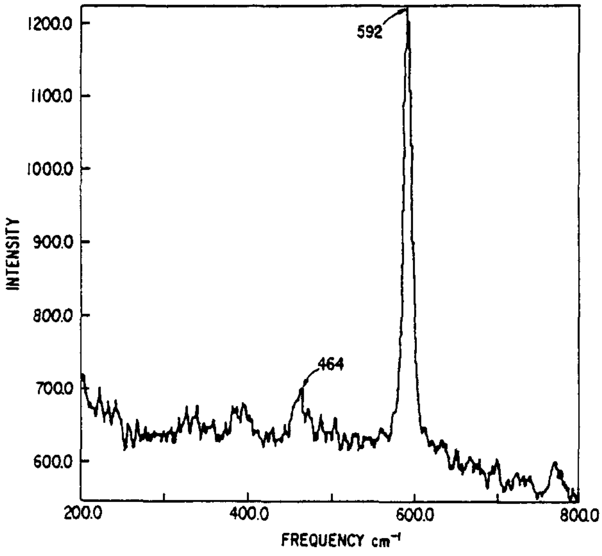

Fig. 6. Raman spectra of $AgUF_6$.

In Table 1 it can be seen that when sufficient AgF is present to give complete precipitation of the UF_6, the O_2 evolved is in good agreement with the reduced uranium produced on hydrolysis. However, at lower AgF concentrations where the UF_6 precipitation is incomplete, some of the oxidized species is lost and at low yields is completely absent from the precipitate. The product obtained with incomplete precipitation of UF_6 with NaF present (Table 2) is also deficient in the oxidized species.

Loss of Oxidized Product on Treating Ag_2UF_8 with AHF As described above, the product obtained by the partial precipitation of UF_6 with AgF at low fluoride ion concentration is depleted in the oxidized species that is capable of oxidizing water and releasing O_2. A similar product, rich in reduced uranium and deficient in the oxidized product, can be obtained when Ag_2UF_8 is treated with fresh AHF. Apparently, the reaction is partially reversed freeing AgF and UF_6

$$Ag_2UF_8 \rightleftarrows 2AgF + UF_6$$

However, a substantial fraction of reduced uranium remains behind as an insoluble silver salt and free of the oxidized species.

Samples of Ag_2UF_8 were shaken with fresh AFH for several hours and the supernatant poured to a connecting Kel-F vessel. The HF was distilled back and the washing cycle continued. The amount of Ag_2UF_8 is diminished in this procedure and the color changes from a dark brown to a yellow-orange solid. In addition, an orange colored solid appears in the receiver, in an amount roughly equal to the yellow product remaining in the original tube after washing. The orange product is rather soluble in AHF and is therefore difficult to isolate pure. A complete analysis of this product gave a formula $Ag_{1.5}UF_{7.5}$ suggesting that it is $AgUF_7$ (with some excess AgF) with the uranium in the hexavalent state. The x-ray powder pattern was the same as Ag_2UF_8. No Raman spectra could be obtained. The orange product does not oxidize water or precipitate reduced uranium.

A number of experiments were carried out in an effort to find the oxidized species in washings or solid fractions separated from the reduced $AgUF_6$ solid.

In one experiment, 3.66 mmoles of Ag_2UF_8 were treated with 11 cc of HF three times over a period of 20 hours. The supernatants were poured off and the precipitate washed once more with 9 cc of fresh HF for 3 hours. The light colored residue remaining contained 0.6 mmoles of U(V) as $AgUF_6$

and did not liberate O_2 on hydrolysis. The orange precipitate that formed in the receiver did not liberate O_2 and contained some additional U(V). The HF supernatants containing the AgF that was released were hydrolyzed but gave no O_2 evolution.

After hydrolysis the solution from orange precipitate and HF solutions were treated with KI and the I_2 released was titrated with thiosulfate. These released 0.06 meq, 0.08 meq, and 0.07 meq of I_2, respectively. The total, 0.21 meq, was only about one-third of the U(V) that remained.

The oxidizing species found in these experiments was a very sluggish oxidant only slowly oxidizing I^- over a period of 15-30 minutes.

Similar experiments were carried out with supernatants from preparations where incomplete precipitation occurred, i.e., at lower F^- concentrations (Tables 1 and 2). Again, no O_2 was liberated on hydrolysis and little or no oxidant found on subsequent I^- titration of the supernatant separated from the UF_4 precipitate. No oxidant was found in the AHF supernatant from the preparation.

Reaction with Kel-F Experiments were carried out to determine whethe any of the products formed reacted with the Kel-F equipment. There was no physical evidence that the oxidized species when released from the solid Ag_2UF_8 attacked the Kel-F containers. There was no evidence of fluorocarbons from infrared spectra of the HF vapor above these solutions.

In one experiment, 2.115 g of Ag_2UF_8 was treated with 16 cc of HF for 24 hours, the dark solid was converted to 0.15 g of yellow product. Mass spectrometric analysis of the HF vapor above this mixture showed some SiF_4 and trace amounts of fluorocarbons. However, analysis of the vapor above a sample of AgF dissolved in HF showed SiF_4 and the same fluorocarbons in the same abundance; again, showing no evidence for Kel-F attack.

Fluorination of $AgUF_6$ and AgF A few experiments were carried out in an effort to determine the ease of fluorinating $AgUF_6$ with AgF_2 to release UF_6. AgF_2 and $AgUF_6$, both insoluble, were agitated, as a slurry, in 15 cc AHF for 3 days, 0.88 mmoles of $AgUF_6$ were reacted with 0.77 mmoles of AgF_2, forming 0.71 mmoles of UF_6. In another experiment with pure UF_5, 1.95 mmoles of UF_5 reacted with 1.16 mmoles of AgF_2 in 15 cc AHF to form 1.02 mmoles of UF_6. The concentration of AgF released is low enough so that little or no reaction with UF_6 occurs.

Fluorination of AgF Some experiments were carried out to determine if AgF could be easily converted to AgF_2 by strong fluorinating agents other than fluorine itself. A solution of XeF_2 (0.5 M) in AgF (0.6 M) in AHF showed no evidence of reaction on standing at 25° for 7 days. Similarly, no reaction was observed with AgF dissolved in ClF_3 on standing at 25°. Others [12] have shown that AgF dissolves in BrF_3 and on evaporation leaves only the salt $AgBrF_4$, with no evidence of oxidation of the silver.

DISCUSSION

Complex salts of UF_6 with the alkali metal fluorides, M_2UF_8 (M = Na, K, Rb, Cs), have been studied extensively [8], and it is interesting to compare the preparation and properties of Ag_2UF_8 with those of analogous salts of the alkali metals.

The alkali metal fluorides react readily with UF_6 at 25° to form the stable double salts, M_2UF_8. The silver compound, Ag_2UF_8, is formed rapidly only at 100° under pressure.

At high fluoride ion concentration, UF_6 can be quantitatively precipitated from AHF as the insoluble product, assigned formula Ag_2UF_8. The high fluoride ion concentration needed suggests that anions such as UF_7^- or $UF_8^=$ must be produced for the reaction to proceed.

In liquid hydrogen fluoride the alkali metal salts rapidly dissolve releasing UF_6 and the metal fluoride. At very high alkali fluoride concentrations (2 M and 6 M CsF) there is spectral evidence for the presence of UF_7^- and $UF_8^=$ ions in AHF solutions [8].

When Ag_2UF_8 is heated at 300°, UF_6 is evolved; there was no evidence of fluorine evolution. Although we only carried this to 70% completion, the reaction seems to be reversible.

$$Ag_2UF_8 \xrightleftharpoons{300°} 2AgF + UF_6$$

If there is a pentavalent uranium present in the solid Ag_2UF_8 as the spectral studies suggest, then reoxidation must occur to form UF_6.

The alkali metal salts decompose above 300°C to release F_2 and UF_6 [8]. This class of compound is quite unique in its ability to generate fluorine gas on heating.

The alkali metal complexes hydrolyze to give UO_2^{+2}, F^-, and alkali metal ions. Pure UF_6 reacts with water to give UO_2^{+2} and F^- ions; AgF dissolves to give Ag^+ and F^- ion. However, the salt formed by the reaction of UF_6 and AgF, Ag_2UF_8, oxidizes water and produces reduced uranium

$$4Ag_2UF_8 + 7H_2O \rightarrow 8Ag^+ + 3UO_2^{++} + UF_4 + 1/2\ O_2 + 14H^+ + 28F^-$$

The oxidation-reduction data obtained on hydrolysis of Ag_2UF_8 may be interpreted to indicate that half the uranium is present in the pentavalent state and, if silver is being oxidized, one quarter of the silver in the salt is divalent. Visible and near infrared spectra of the solid indicate that pentavalent uranium is present in the salt; however, ESR studies gave no evidence for the presence of divalent silver.

From the data available it is difficult to rationalize the oxidation of AgF to AgF_2 by reaction with UF_6. AgF_2 is produced only by reaction of AgF with fluorine gas and a few other very reactive unstable fluorides. Clifford's studies [13] in AHF give a value of -2.27 V for the AgF(HF)-AgF_2(S) couple in this medium; he measured the F^-(HF)-F_2(g) couple in this medium; he measured the F^-(HF)-F_2(g) couple as -2.708 V. It is highly unlkikely that UF_6 or the anions produced at high fluoride ion concentration could oxidize AgF, but oxidation in the solid state cannot be ruled out.

In this work we have shown that even the very reactive fluorinating agents ClF_3, BrF_3, and XeF_2, each of which will oxidize lower uranium fluorides to uranium hexafluoride, all of which oxidize H_2O, will not convert AgF to AgF_2.

We have also shown here the reverse action, i.e. that UF_5 and $AgUF_6$ are rapidly converted to UF_6 when slurried with AgF_2 in AHF at 25°C

$$AgF_2 + AgUF_6 \rightarrow 2AgF + UF_6$$

From the results tabulated in Tables 1 and 2 it can be seen that at lower fluoride concentrations a smaller yield of product is obtained. In addition, this product is deficient in the oxidized component. This suggests that under these conditions the reaction is considerably more complex; that perhaps two or more products are formed. The treatment of Ag_2UF_8 with fresh AHF also suggests that the oxidized species is more soluble and is removed preferentially from the more insoluble species containing the reduced uranium.

The Raman studies of the solids produced also suggest this. At high fluoride concentrations the product formed Ag_2UF_8 shows only the broad band centered around 550 cm^{-1} (Fig. 1). At lower fluoride concentration the product formed shows two new bands at 592 cm^{-1} and 611 cm^{-1} (Figs.

2,3). The insoluble product obtained by washing Ag_2UF_8 with fresh AHF show the bands at 592 cm^{-1} and 611 cm^{-1} (Fig. 4).

After further treatment with AHF only the 592 cm^{-1} band remains (Fig. 5).

The band at 592 cm^{-1} can almost certainly be assigned to $AgUF_6$.

We cannot assign the 611 cm^{-1} band to any known uranium species with any certainty. The alkali metal complexes, M_2UF_8 (where M = Na, K, Rb and Cs), the strong $UF_8^=$ vibrational frequency is seen at 607 cm^{-1}, 598 cm^{-1}, 590 cm^{-1}, and 583 cm^{-1}, respectively. With the alkali complexes, MUF_7 (where M = Na, K, Rb, and Cs), the UF_7^- band is observed at 633 cm^{-1}, 626 cm^{-1}, 625 cm^{-1}, and 622 cm^{-1}, respectively.

The bands at 550 cm^{-1} cannot be assigned but they are in the region that one might expect for the species Ag_3UF_8.

The strong oxidant then is lost or missing from the product produced at low fluoride ion concentrations. The oxidant is also missing from the product obtained by treating Ag_2UF_8 with fresh HF. Hydrolyses of HF supernatants from these treatments revealed no oxidant capable of oxidizing water. However, a species capable of oxidizing I^- was detected in some cases. This species was volatile and remained with the HF after distillation.

The initial powerful oxidant, then, has either changed or reacted to produce a mild oxidizing species. One explanation might be that the oxidant freed from the solid attacked the Kel-F containers but we could find no evidence of this. There was also no evidence for the liberation of fluorine gas either from pressure measurements or from the fluorination of AgF which takes place rapidly in its presence.

At present, we are unable to identify the oxidized species in this system or to give an adequate explanation of why UF_6 and AgF combined in this manner should produce a powerful oxidant.

ACKNOWLEDGMENTS

I would like to thank F. Schreiner for many useful discussions. I would like to thank D. Cohen for his help with spectrophotometric determinations of the uranium valence in H_3PO_4 solutions of solids; E. Appelman for help with the iodometric titrations; A. Essling and I. Fox for chemical analyses; E. Sherry for x-ray powder patterns; J. Norris for ESR results; J. Huston of Loyola University for the mass spectrometric studies; and R. Langley of University of Wisconsin at River Falls for Raman data on the solids.

REFERENCES

1 See the review article by M.F.A. Dove and A.F. Clifford in 'Chemistry' in 'Nonaqueous Ionizing Solvents', (G. Jander, H. Spandau, and C.C. Addison, eds.) Vol. II, part 2, Pergamon Press: Oxford, 1971, p. 121.

2 M. Baluka, N. Edelstein, and O. O'Donnell, Inorg. Chem. 20(1981) 3279.

3 M. Baluka, S. Yeh, R. Banks and N. Edelstein, Inorg. Nucl. Chem. Lett. 16(1980) 75.

4) P.W. Wilson, J. Chem.Soc., Chem. Commun. (1972) 1241; R.T. Paine, R.R. Ryan, and L.B. Asprey, Inorg. Chem. 14(1975) 1113; E. Jacob, and W. Polligkeit, Z. Naturforsch 28(1974) 303.

5 Iv. V. Drobyshevskii, V.N. Prusakov, V.F. Serik, and V.B. Sokolov, Radiokhimia 22(1980) 591.

6 H. Martin, A. Albers, and H.P. Dust, Z. anorg. allgem. Chem. 265 (1951) 128.

7 J.G. Malm, H. Selig, and S. Siegel, Inorg. Chem. 8(1966) 130.

8 R. Bougon, P. Charpin, J.P. Desmoulin, and J.G. Malm, Inorg. Chem. 15(1976) 2532.

9 H.H. Hyman and J.J. Katz in 'Non-aqueous Solvent Systems' (T.C. Waddington, Ed.) Academic Press:London, 1965, p. 64.

10 J.G. Malm, J. Inorg. Nucl. Chem. 42(1980) 993.

11 R. Bougon and P. Plurien, C.R. Acad. Sci. Paris 260(1965) 4217. P. Charpin, C.R. Acad. Sci. Paris 260(1965) 1914.

12 I. Sheft, H.H. Hyman, and J.J. Katz, Am.Chem.Soc. 75(1953) 5221.

13 A.F. Clifford, W.D. Pardieck, and M.W. Wadley, J. Phys. Chem. 70 (1966) 3241.