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THE PREPARATION AND PROPERTIES OF $AgUF_6$ AND $AgUOF_5$*

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Abstract—$AgUF_6$ and $AgUOF_5$ are formed by precipitation from liquid hydrogen fluoride. Chemical and physical properties are described.

INTRODUCTION

Earlier studies[1] have given evidence that the compounds $AgUF_6$ and Ag_3UF_8 can be formed by heating mixtures of AgF and UF_5 at 350–400°C. Salts of UF_5 with the alkali metal fluorides have been formed in the same manner[2]. Similarly, X-ray and vibrational studies gave evidence for formation of the compounds $MUOF_5$ ($M = K$, Rb, Cs) when the insoluble UOF_4 is slurried with alkali metal fluorides in liquid hydrogen fluoride or liquid sulfur dioxide[3].

In the studies reported here, we show that it is possible to precipitate highly insoluble silver salts directly from solutions of the UF_6^- and UOF_5^- anions in anhydrous hydrogen fluoride.

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 nickel vessel with 2 atm of fluorine for several days. The excess fluorine was removed by pumping on the liquid at −78°C. When purified in this manner, the liquid HF had a specific conductivity of $10^{-4}\,\Omega^{-1}\,cm^{-1}$ and showed no reaction with UF_6, which is extremely sensitive to traces of moisture or reducing impurities. Silver fluoride, typically of greater than 99.5% purity, was obtained from CERAC, Inc. Spectrographic analysis showed only traces (0.001%) of metal impurities. Uranium hexafluoride of very high purity was purchased from Union Carbide Corp.

Uranium pentafluoride was prepared by reacting PF_3 (Ozark Mahoning) with excess UF_6 in liquid HF; after the reaction was complete, the supernatant solution was poured off. The product was washed with fresh HF and then pumped to a good vacuum. The UF_5 was dissolved in HF containing a base, either H_2O or NaF, to give the blue solutions of $H_3O^+UF_6^-$ or $Na^+UF_6^-$[4].

Experimental procedure. The reactions were carried out in all Kel F systems consisting of 30 cc tubes fitted with valves and connected with 1/4 inch o.d. tubing and fittings. Once the apparatus was in place, the reactions and subsequent manipulations could be carried out without exposing these very hygroscopic materials to the atmosphere.

Preparation of $AgUOF_5$. Approximately 0.040 cc (2.22 mmol) of H_2O was dissolved in 4.5 cc of HF. This was poured into a solution of 0.5794 g of AgF in HF. This mixture was cooled to 0°C, and a solution containing 3.32 mmol of UF_6 was poured onto it. After mixing, the concentrations were AgF 0.25 M; UF_6 0.19 M, H_2O 0.126 M. After several minutes the solution turned yellow, and then the dark red solid $AgUOF_5$ precipitated. After 90 minutes, the supernatant solution was poured off, and 4 cc of HF was distilled back for washing. This was poured off, and the product was pumped to a good vacuum. The product weighted 0.9158 g (2.01 mmol of $AgUOF_5$).

Preparation of $AgUF_6$. $AgUF_6$ was prepared by addition of AgF to solutions of $H_3O^+UF_6^-$ or $Na^+UF_6^-$ in HF. In one experiment, 0.688 g of AgF was dissolved in 6 cc of HF and then poured into a tube containing about 5.3 cc of 0.54 M $H_3O^+UF_6^-$. The very pale yellow $AgUF_6$ precipitated immediately. The supernatant solution was poured off. About 8 cc of HF were distilled back and the precipitate was washed. The wash solution was poured off, and the solid was pumped to a good vacuum. The product weighed 1.3220 g.

In another preparation, about 1.5 cc of a solution containing 0.32 M NaF and 0.18 M UF_6^- was diluted to 8 cc. To this was added a solution of 0.2211 g of AgF in 8 cc of HF. After pouring off the supernatant solution and washing, the dry product weighed 0.1155 g.

Solubility determination. The solubility of $AgUF_6$ in anhydrous hydrogen fluoride was determined by equilibrating a large sample of $AgUF_6$ with a weighed quantity of pure HF and then pouring the liquid into another tube. The weight loss of the original sample and the weight gain after evaporating the solvent were taken as a measure of the solubility. Successive measurements with the same sample were in good agreement and eliminated the possibility that the weight changes were caused by impurities in the sample. The solubility in the presence of excess AgF was determined by analysis of uranium in the solution.

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 weighed sample, the fluoride was collected and determined by potentiometric titration with thorium solution.

RESULTS AND DISCUSSION

$AgUF_6$

$AgUF_6$ is precipitated quantitatively when silver fluoride is added to a solution of $H_3O^+UF_6^-$ or $Na^+UF_6^-$ in anhydrous hydrogen fluoride. The solid is a very pale yellow. Chemical analyses showed 23.1% Ag, 50.8% U and 24.5% F^-. (Calc for $AgUF_6$: 23.46% Ag, 51.75% U, 24.78% F^-.) The X-ray powder data were indexed as tetragonal, $a = 5.4491(8)$ Å, $C = 7.9704(12)$ Å, $z = 2$ and $D_x = 6.455$ g/cc. This was found in the literature as a =

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5.423 Å, c = 7.950 Å, Z = 2, space group $P4_2/mcm$[1]. The compound prepared in this manner gave no evidence of Ag_3UF_8, which had been previously prepared by heating UF_5 with excess AgF. No change was observed when $AgUF_6$ was contacted with a 7 M solution of AgF in hydrogen fluoride for several days.

The Raman spectra of the solid showed only an intense band at 596 cm^{-1}. This is considerably lower than the frequencies observed in related solid species $H_3O^+UF_6^-$ (625 cm^{-1})[4] and $NO^+UF_6^-$ (618 cm^{-1})[5].

The solubility of $AgUF_6$ in HF is 0.29 g/100 g at 25°C. In 0.6 M AgF solution, the solubility is reduced to 0.02 g/100 g at 25°C. This solubility is much lower than that of the analogous silver salts of NbF_5, TaF_5 and SbF_5[6].

Thermal decomposition was monitored with a mass spectrometer. UF_6 was first observed at 225° with copious amounts being evolved at 286°.

$AgUF_6$ reacts with dilute aqueous acid, disproportionating to give equimolar amounts of soluble uranyl ion and insoluble UF_4.

An interesting aqueous reaction was observed for the first time. When $AgUF_6$ containing a large excess of silver fluoride is hydrolyzed in 0.5 M $HClO_4$, all of the uranium(V) is oxidized to hexavalent uranium, and silver is precipitated as the metal. 0.0065 mmol of $AgUF_6$ mixed with 4 mmol of AgF was hydrolyzed with 0.5 M $HClO_4$ and produced 0.006 mmol of silver metal, which was identified by its X-ray powder pattern.

$AgUOF_5$

After a brief induction period, $AgUOF_5$ is precipitated quantitatively when excess UF_6 is added to a hydrogen fluoride solution of AgF containing H_2O. The precipitate is a very dark red. The solid is hydroscopic and must be handled in a dry atmosphere.

Chemical analyses showed Ag, 21.5%; U, 52.6%; F, 21.2%; O, 4.7% by difference. (Calc for $AgUOF_5$: Ag, 23.62%; U, 52.09%; F, 20.79%; O, 3.50%.

The X-ray powder pattern was indexed as tetragonal, a = 5.370(3) Å, c = 8.043(3) Å, Z = 2 and D_x = 6.85 g/cc. This indicates the compound to be isostructural with $AgUF_6$[1].

$AgUOF_5$ dissolves in dilute acid to give a clear yellow solution of UO_2^{2+}.

When heated under vacuum at 200°C, the red solid becomes yellow and UF_6 is evolved. This is similar to the decomposition observed for UOF_4. When thermal decomposition is monitored with a mass spectrometer, UF_6 is observed at 105°, and copious amounts are released at 136°. No volatile oxyfluoride species were observed.

Raman spectra of solid $AgUOF_5$ were obtained using the 6470 Å exciting line of a Kr^+ laser. Extensive decomposition of the compound occurred if the 5145 Å line of the Ar^+ laser was used. The strong Raman bands observed at 795 and 575 cm^{-1} can be assigned respectively to the U–O and U–F stretching vibrations. Both are about 20 cm^{-1} lower than the frequencies observed for the analogous $CsUOF_5$[3]. This difference is about the same as that observed when H_3O^+ or Na^+ are replaced by Ag^+ in MUF_6 salts.

The solubility in HF could not be determined because of reaction with the solvent. When $AgUOF_5$ is washed with HF, AgF is slowly removed from the compound:

$$AgUOF_5 + HF \rightarrow UOF_4 + Ag^+ + HF_2^-.$$

A 0.8580 g sample of $AgUOF_5$ was contacted with 10 cc of HF for several hours. The supernant was poured to another tube and then distilled back. This procedure was repeated five times. In this way the red $AgUOF_5$ was converted to 0.6530 g of yellow solid, which was identified as UOF_4 by X-ray powder pattern and strong Raman bands at 890 and 660 cm^{-1}[7]. Chemical analysis of the yellow solid showed it to be UOF_4 containing some unconverted $AgUOF_5$.

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