Preparation and Characterization of the Uranyl Fluoride–Antimony Pentafluoride Adduct, $UF_2O_2{\cdot}4SbF_5$

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When $UF_4O{\cdot}2SbF_5$ is treated with anhydrous hydrogen fluoride a slow reaction in solution takes place. Investigation of this reaction and those of $UF_4O–SbF_5–HF$ solutions on standing have shown that, in both cases, UF_6 and a new uranyl fluoride derivative, $UF_2O_2{\cdot}4SbF_5$, are produced.

RECENT studies have shown that the interaction of the uranium fluoride oxides, UF_4O and UF_2O_2, with antimony pentafluoride give rise to the adducts, $UF_4O{\cdot}nSbF_5$ (n = 1—3) [1,2] and $UF_2O_2{\cdot}nSbF_5$ (n = 2 or 3) [3] respectively. During work on the UF_4O adducts, when experiments designed to remove one mole of SbF_5 from $UF_4O{\cdot}2SbF_5$ by treatment with anhydrous HF were carried out, and when attempts were made to prepare the 1 : 1 adduct from stoicheiometric quantities of UF_4O and SbF_5 in HF, it became evident that $UF_4O–SbF_5–HF$ solutions are unstable. A slow reaction took place on standing which appeared to produce uranium hexafluoride and a uranyl fluoride-antimony fluoride adduct. The chemistry of this reaction has been investigated *via* two different approaches: (*i*) the room temperature (r.t.) decomposition of $UF_4O{\cdot}2SbF_5$ dissolved in anhydrous HF and (*ii*) the slow reaction of $UF_4O–SbF_5–HF$ mixtures on standing at r.t.

EXPERIMENTAL

Uranium tetrafluoride oxide was prepared as described by Wilson [4] and its purity monitored by *X*-ray diffraction and vibrational spectroscopy. Antimony pentafluoride and anhydrous hydrogen fluoride were prepared and purified as described previously.[3] The solution reactions were carried out using approximately 0.5 mmol samples of UF_4O. To avoid the possibility of diffusion of atmospheric moisture through the walls of the reaction vessels the solution reactions were carried out in thick-walled Kel-F tubes fitted with Teflon valves and experiments were conducted in a nitrogen-filled dry box. The solutions were allowed to stand for periods of up to 36 h.

Other apparatus used and instruments employed for the characterizations have been described previously.[2,3] Elemental analyses were performed by the Analytical Laboratories, Engelskirchen, Germany.

RESULTS AND DISCUSSION

When $UF_4O{\cdot}2SbF_5$ is dissolved in a large excess of anhydrous HF rapid exchange with the solvent is evidenced by the one broad ^{19}F n.m.r. resonance which appears at *ca.* 160 p.p.m. (upfield from external reference CCl_3F) at temperatures down to −50 °C. When such solutions are allowed to stand for 8 h or more at room temperature, the orange colour is lost and pale yellow crystals of UF_6, identified by Raman spectroscopy, appear. The Raman spectra of the solutions exhibit lines attributable to the $[SbF_6]^-$ ion. Removal of volatiles leaves a solid, white residue, the *X*-ray powder diffraction of which indicates a new phase, together with lines attributable to $[H_3O]^+[SbF_6]^-$,[†] or a species isostructural with $[H_3O]^+[SbF_6]^-$.[‡] After subtracting the impurity lines the residual pattern is clearly different from those of $UF_2O_2{\cdot}3SbF_5$, $UF_2O_2{\cdot}2SbF_5$, and UF_2O_2 [5] itself. Infrared spectra were generally uninformative but a peak at 1 010 cm^{-1} is clearly associated with the ν_3 vibration of the uranyl ion (*cf.* i.r. data for $UF_2O_2{\cdot}3SbF_5$ and $UF_2O_2{\cdot}2SbF_5$ in ref. 3). The Raman spectrum of the solid, using the 647.1 nm line of a red laser, exhibits a strong shift at 926 cm^{-1} which can be assigned to the ν_1 vibration of the $[UO_2]^{2+}$ cation on the basis of the relationship $\nu_1 = 0.912\nu_3 - 1.04$ cm^{-1}.[6] The spectrum also showed bands at 660 and 685 cm^{-1} which can be attributed to ν(Sb–F). When the green (514.5 nm) line is used the characteristic fluorescence spectrum of the uranyl ion is observed. The chemical analysis (Found: F, 38.6; Sb, 40.9; U, 19.8. Calc. for $UF_2O_2{\cdot}4SbF_5$: F, 35.5; Sb, 41.4; U, 20.2%) yields Sb : U and F : U ratios of 4.03 : 1 and 24.4 : 1 respectively which implies possible formulations of $UF_4O{\cdot}4SbF_5$ or $UF_2O_2{\cdot}4SbF_5$. The first can be ruled out on the basis of the spectroscopic data, the weight of product obtained, and the fact that solvation in HF tends to remove SbF_5 from $UF_4O{\cdot}2SbF_5$ rather than to add to it. The theoretical weight of product, calculated on the assumption that equimolar

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[†] Unpublished observations from P. Charpin and R. Bougon (CEN-Saclay, France), J. Fawcett and D. R. Russell (University of Leicester), and K. O. Christe (Rocketdyne) indicate that $[H_3O]^+[SbF_6]^-$ is cubic.

[‡] Because of the fact that no $[H_3O]^+[SbF_6]^-$ or related species were detected in $UF_2O_2–SbF_5–HF$ reactions which employed HF from the same source, and in view of the great precautions taken to eliminate water from the reactions, the origin of this impurity is not clear. The species may originate from H_2O contamination, from oxygen arising from the decomposition of UF_4O, or it may be another salt such as $[H_2F]^+[SbF_6]^-$. However, since chemical analytical results always agree closely with the bulk product being $UF_2O_2{\cdot}4SbF_5$ and differ markedly from theoretical values for possible solid mixtures such as $UF_2O_2{\cdot}(4-n)SbF_5–n([H_3O]^+[SbF_6]^-)$ (n = 1—3), the level of contamination must be small. The fact that $[H_3O]^+[SbF_6]^-$ or a related species is so readily detected may be due to its cubic nature and its high crystallinity relative to that of the uranyl fluoride adduct.

quantities of UF_6 and $UF_2O_2{\cdot}4SbF_5$ are produced, coincided with the weight of product obtained and the spectroscopic data, suggesting an overall reaction scheme according to equation (1).

$$2\,(UF_4O{\cdot}2SbF_5) \xrightarrow[\text{r.t.}]{\text{HF}} UF_6 + UF_2O_2{\cdot}4SbF_5 \quad (1)$$

The solid white adduct can also be obtained from solutions of UF_4O and SbF_5 in anhydrous HF after standing at r.t. for several hours. In a typical experiment a solution in which the molar composition $UF_4O : SbF_5 : HF$ was 1 : 5 : 30 was examined by ^{19}F n.m.r. and Raman spectroscopy. The ^{19}F n.m.r. spectrum of the initially orange solution exhibited a broad resonance at +118 p.p.m. (upfield from CCl_3F); the shift from that observed for the solution of $UF_4O{\cdot}2SbF_5$ in HF is explained by the change in molar ratio of the constituents. The Raman spectrum of the initially orange solution exhibited lines associated with UF_4O–SbF_5 adducts [1,2] but, on standing, the intensities of these lines diminished as lines due to UF_6 appeared. After several hours the solution became clear and crystals of UF_6 were deposited. When volatiles were removed the residual solid exhibited the same vibrational spectrum and X-ray powder diffraction pattern as that of the solid resulting from the reaction of $UF_4O{\cdot}2SbF_5$ in anhydrous HF and again exhibited extra lines attributable to $[H_3O]^+[SbF_6]^-$ (see footnote †).

Reactions with UF_4O–(excess)SbF_5 mixtures in a variety of ratios all gave the same product in a yield consistent with the weight expected for dismutation of uranium tetrafluoride oxide to uranyl fluoride and uranium hexafluoride and subsequent formation of $UF_2O_2{\cdot}4SbF_5$, and it is concluded that this product arises from the initial formation of $UF_4O{\cdot}2SbF_5$. The adduct $UF_2O_2{\cdot}4SbF_5$ is not obtained by direct synthesis, even when large excesses of SbF_5 are used.[3] It is presumed that it is obtainable only in the dismutation reaction because the direct synthesis route does not provide a sufficiently high activation energy or for some other thermodynamic reason.

The mechanism by which the dismutation occurs is not clear. However, plutonium tetrafluoride oxide has been shown previously to be unstable in anhydrous HF giving PuF_2O_2 and PuF_6.[7] Although UF_4O is stable in HF at r.t., on heating the solid above 230 °C, uranyl fluoride and UF_6 are formed [4] and it is not unreasonable to expect that, in an acid mixture such as HF–SbF_5, dismutation [equation (2)] may occur.

$$2\,UF_4O \longrightarrow UF_2O_2 + UF_6 \quad (2)$$

Since the initial effect of anhydrous HF on $UF_4O{\cdot}2SbF_5$ has previously been shown to result in the removal of SbF_5 to give $UF_4O{\cdot}SbF_5$[2] the following mechanism [equations (3)—(7)] for the decomposition of UF_4O–SbF_5–HF solutions is likely.

$$UF_4O + SbF_5(\text{excess}) \xrightarrow{\text{HF}} UF_4O{\cdot}2SbF_5(\text{excess}) \quad (3)$$

$$UF_4O{\cdot}2SbF_5 \xrightarrow{\text{HF}} UF_4O{\cdot}SbF_5 + SbF_5 \quad (4)$$

$$UF_4O{\cdot}SbF_5 \rightleftharpoons [UF_3O]^+ + [SbF_6]^- \quad (5)$$

$$2\,[UF_3O]^+ \longrightarrow UF_6 + [UO_2]^{2+} \quad (6)$$

$$[UO_2]^{2+} + 2\,[SbF_6]^- + 2SbF_5 \xrightarrow{\text{HF}} UF_2O_2{\cdot}4SbF_5 \quad (7)$$

As expected for these strongly acidic solutions, no evidence was found in the Raman spectra for fluoride acceptance by UF_4O to give $[UF_5O]^-$. The observed fluorine exchange, therefore, must involve the removal of a fluorine species from UF_4O by a reaction such as that represented in equation (5). Furthermore, it should also be mentioned that the instability of the postulated intermediate, $[UF_3O]^+$ [equation (6)], is also to be expected in view of the low co-ordination number implied for this ion.

Since $UF_2O_2{\cdot}3SbF_5$ has been previously characterized,[3] the thermal decomposition of a sample of $UF_2O_2{\cdot}4SbF_5$ was studied. On heating at 70 °C for 40 h under dynamic vacuum, SbF_5, characterized by its i.r. spectrum, was released and the i.r. spectrum of the residue exhibited a sharp peak at 1 012 cm^{-1} coincident with that due to $\nu_3(UO_2^{2+})$ in $UF_2O_2{\cdot}3SbF_5$. A cluster of peaks between 750 and 400 cm^{-1} close to those associated with ν[SbF(terminal)], ν[Sb $\cdots$ F(bridging)], and ν[U $\cdots$ F(bridging)] in $UF_2O_2{\cdot}3SbF_5$[3] were also observed. At the same time, peaks between 3 300 and 3 100 cm^{-1} due to traces of $[H_3O]^+[SbF_6]^-$ or related species disappeared which indicates that the compound dissociated or reacted with the uranium compounds.

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REFERENCES

[1] R. Bougon, J. Fawcett, J. H. Holloway, and D. R. Russell, *C.R. Acad. Sci., Ser. C*, 1978, **287**, 423.

[2] R. Bougon, J. Fawcett, J. H. Holloway, and D. R. Russell, *J. Chem. Soc., Dalton Trans.*, 1979, 1881.

[3] J. Fawcett, J. H. Holloway, D. Laycock, and D. R. Russell, *J. Chem. Soc., Dalton Trans.*, 1982, 1355.

[4] P. W. Wilson, *J. Inorg. Nucl. Chem.*, 1974, **36**, 303.

[5] W. H. Zachariasen, *Acta Crystallogr.*, 1948, **1**, 277.

[6] K. W. Bagnall and M. W. Wakerley, *J. Inorg. Nucl. Chem.*, 1975, **37**, 329.

[7] R. C. Burns and T. A. O'Donnell, *Inorg. Nucl. Chem. Lett.*, 1977, **13**, 657.