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Properties of Uranium(V) in Hydrofluoric Acid Solution; the New Compounds $HUF_6 \cdot 2.5H_2O$ and $HUF_6 \cdot 1.25H_2O$[1]

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Anhydrous UF_5 is very soluble in concentrated aqueous HF; the resulting solutions of U(V) in *ca.* 10–27 *M* HF are remarkably stable. Blue crystals of $HUF_6 \cdot 2.5H_2O$ are formed when a 5 *M* solution of U(V) is cooled from 25 to −10°. The spectrum of $HUF_6 \cdot 2.5H_2O$ crystals shows prominent absorption at 1.36 μ, strikingly similar to that shown by anhydrous $LiUF_6$, $NaUF_6$, and $CsUF_6$. UF_5 is essentially insoluble in anhydrous liquid HF but $HUF_6 \cdot 2.5H_2O$ dissolves. A lower hydrate, $HUF_6 \cdot 1.25H_2O$, is obtained from a solution of U(V) in 85–90% HF. The anhydrous acid, HUF_6, could not be prepared. Cesium and rubidium form macrocrystalline salts, $CsUF_6$ and $RbUF_6$, which are precipitated readily by addition of CsF or RbF to a solution of U(V) in aqueous HF. A nonuranyl structure, UF_6^-, is postulated as the form of U(V) in the hydrates of HUF_6 and in concentrated aqueous hydrofluoric acid solutions.

Introduction

The chemistry of pentavalent uranium is complicated by the fact that U^{+5} is hydrolyzed in aqueous solution to UO_2^+, which is extraordinarily unstable to disproportionation.[2] Because of this difficulty, prior study[3] of the aqueous chemistry of uranium in its pentavalent state has been restricted to very dilute solutions ($\sim 10^{-3}$ *M*) of UO_2^+ in a narrow pH range of 2–4. In stronger acid, UO_2^+ disproportionates rapidly into U^{+4} and UO_2^{+2}.

Fluoride complexes of the pentavalent transition metals, tantalum and niobium, are known,[4,5] and analogous compounds of pentavalent uranium would be expected. We recently prepared, by anhydrous methods, a series of fluoride complexes containing pentavalent uranium.[6,7] Such fluoride complexes of U(V) could exist in solution provided that these complexes were sufficiently stable so that U(V) would not hydrolyze to UO_2^+ and subsequently disproportionate. The report[8] that $NH_4F \cdot UF_5$ dissolved in concentrated aqueous HF without disproportionation led us to study U(V) in fluoride solution. We found that UF_5 itself is remarkably soluble in concentrated aqueous HF, forming stable solutions of U(V) from which hydrates of the acid HUF_6 could be obtained. The properties of the solutions and of the solid phases are reported in this paper.

Experimental

Materials.—Reagent grade aqueous 48% HF and certified alkali fluorides (>99%) were used. Anhydrous HF and UF_6 were distilled. Anhydrous α-UF_5 was prepared by treating high surface area UF_4 with gaseous UF_6 above 150° in a nickel reactor.[7] The yield was improved by a brief pretreatment of the UF_4 with F_2 (1 atm.) at 40° for 20 min. To prevent reaction of UF_5 with moisture, it was weighed and handled in a dry helium atmosphere. Both α- and β-UF_5 were used in the initial work. However, a stock of UF_5 was not all used in one run and some slow degradation was observed on the surface of the UF_5 remaining in the storage tube. With α-UF_5 (light gray) this discoloration was easy to observe and the layer was discarded. With β-UF_5 (faint yellow) this was more difficult. Therefore, α-UF_5 was used in later runs.

Solubility of UF_5 in Aqueous HF.—Several grams of UF_5 was weighed into a tube in the inert atmosphere box and the tube was stoppered. A few ml. of 48% HF was placed in a plastic 15-ml. centrifuge cone. Both tubes were transferred into a flexible plastic bag which was flushed with helium. The UF_5 powder was then added slowly to the vigorously stirred HF solution. Heat is evolved so the temperature of the HF solution was kept near room temperature by controlling the rate of UF_5 addition and by use of a coolant. In a typical experiment, 10 g. of UF_5 and 4 g. of 48% HF were used. After centrifugation the temperature was brought to 25°. The volume of the deep blue supernatant solution was about twice the volume of initial 48% HF. A waxed, calibrated pipet was used to withdraw a known volume of liquid which was evaporated in a Pt dish and ignited to U_3O_8. In several experiments, a solubility of 1.19 g. of U/ml. at 25° (5.0 *M*) was found. Upon cooling and after removal of $HUF_6 \cdot 2.5H_2O$ (described below), the solubility of U(V) in the saturated solutions was found to be 4.05 *M* at 0° and 3.19 *M* at −26°.

Spectrum of U(V) in Aqueous HF.—Solutions of U(V) in 24% HF were placed in polyethylene bags (0.002-in. wall) which were squeezed between two parallel glass plates to produce a thin film of liquid. Known path lengths of less than 1 mm. were used to permit measurements in the 14,000 Å. region (where water absorbs strongly) and still have reasonable slit widths on a Cary Model 14-MR spectrophotometer. The spectrum is shown in Fig. 1. Without special precautions, at 25° the blue color of U(V) changed slowly over a period of several hours as the yellow color of UO_2F_2 grew in and green UF_4 precipitated. However, when kept cold and protected from air and moisture, the blue solution (and crystals described below) remained unchanged for weeks.

Preparation of $HUF_6 \cdot 2.5H_2O$.—Several ml. of a saturated solution of U(V) in HF was prepared at 25°, stoppered, and placed in a refrigerator at −10°. Large blue crystals (up to 3 mm. on an edge) then formed. Since the crystals redissolved in the mother liquor on warming, the excess liquid was decanted in the cold. The crystals were blotted using filter paper, dried in a stream of helium, and then analyzed for fluoride by pyrohydrol-

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[1] This work was sponsored by the U. S. Atomic Energy Commission.

[2] J. J. Katz and G. T. Seaborg, "The Chemistry of the Actinide Elements," John Wiley and Sons, Inc., New York, N. Y., 1957, Chapters V and XI.

[3] K. A. Kraus, F. Nelson, and G. L. Johnson, *J. Am. Chem. Soc.*, **71**, 2510 (1949); K. A. Kraus and F. Nelson, *ibid.*, **71**, 2517 (1949).

[4] B. Cox, *J. Chem. Soc.*, 876 (1956).

[5] H. Bode and H. Dohren, *Naturwissenschaften*, **44**, 179 (1957).

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[8] G. A. Rampy, GAT-T-697, 11-2-59, Goodyear Atomic Corp., available from the U. S. Dept. of Commerce, Office of Technical Services, Washington 25, D. C.

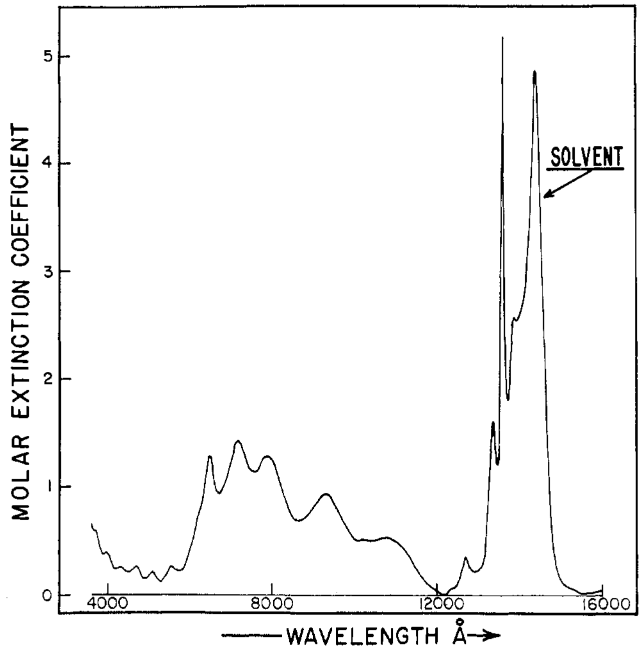

Fig. 1.—Absorption spectrum of 5 *M* U(V) in 24% HF; path length = 0.05 cm.

ysis.[9,10] The residue was weighed as U_3O_8. From these data the formula weight per mole of uranium and the fluorine to uranium ratio were calculated. Results are given in Table I.

TABLE I

ANALYSIS OF $HUF_6{\cdot}2.5H_2O$ (FORMULA WT. = 398)

Wt. of crystals, g.	Wt. of U_3O_8, g.	Formula wt. calcd.	F/U
0.4893	0.3470	396	6.02
0.7417	0.5279	394	6.03
1.0687	0.7561	397	6.10
7.9556	5.5619	401	. . .

Preparation of $HUF_6{\cdot}1.25H_2O$.—To the U(V)-rich supernatant liquid remaining after removal of $HUF_6{\cdot}2.5H_2O$ at −10°, 3-5 volumes of anhydrous HF were added. On cooling to −80°, fine blue crystals of a lower hydrate were obtained. These were washed with anhydrous HF and dried in helium. In one case the crystals were redissolved in 97% HF and reprecipitated by cooling. This analysis showed no change in the mole ratio of water to uranium.

TABLE II

ANALYSIS OF $HUF_6{\cdot}1.25H_2O$ (FORMULA WT. = 375.6)

Wt. of crystals, g.	Wt. of U_3O_8, g.	Formula wt. calcd.
0.8967	0.6727	374
1.8194	1.3564	376
3.1290	2.3438	375

Attempted Preparation of Anhydrous HUF_6.—Anhydrous HF was condensed onto a few grams of α-UF_5 contained in a translucent Kel-F tube. The tube was warmed to ~20° to allow the liquid HF to boil. No reduction in the volume of solid was noted, nor was there a significant amount of uranium found in the supernatant liquid. After decanting the bulk of the liquid, the temperature was raised and the excess HF was removed by distillation. The powdered residue was then transferred to an inert box and an X-ray capillary filled. The X-ray powder pattern showed that the starting material, α-UF_5, had converted to β-UF_5, the low-temperature form.[11]

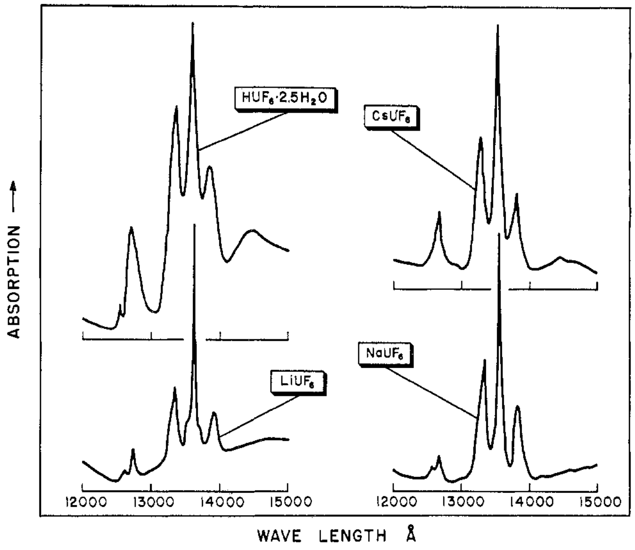

Fig. 2.—Absorption spectra of mulls of the anhydrous solids, $LiUF_6$, $NaUF_6$, $CsUF_6$, compared with $HUF_6{\cdot}2.5H_2O$.

Preparation of Salts of HUF_6.—Addition of a saturated solution of RbF or CsF in 48% HF to a solution of U(V) in HF resulted in immediate precipitation of insoluble $RbUF_6$ or $CsUF_6$. However, addition of KF led to formation of mixtures of K_2UF_7 and KUF_6. LiF and NaF are sufficiently insoluble so that $LiUF_6$ and $NaUF_6$ are best prepared by heating LiF or NaF with UF_5.[6,7] The X-ray powder patterns and absorption spectra of $RbUF_6$ and $CsUF_6$ prepared by precipitation from U(V) solution agreed exactly with those obtained from anhydrous $RbUF_6$ and $CsUF_6$ made by the direct reaction of UF_5 and the alkali fluorides (X-ray data appear in ref. 7 and will not be repeated here).

Absorption Spectra of $LiUF_6$, $CsUF_6$, $HUF_6{\cdot}2.5H_2O$, and $HUF_6{\cdot}1.25H_2O$.—Mulls of these compounds were mounted between CaF_2 flats and measured using a Cary Model 14-MR spectrophotometer. $HUF_6{\cdot}2.5H_2O$ and $HUF_6{\cdot}1.25H_2O$ were examined as the hydrate; the other compounds were prepared by anhydrous reactions (MF + UF_5). The spectra are shown in Fig. 2. The lower hydrate, $HUF_6{\cdot}1.25H_2O$, gave a spectrum qualitatively similar to that of $HUF_6{\cdot}2.5H_2O$ with the main peaks at 1.3-1.4 μ shifted ~25 Å. toward longer wave lengths. A much smaller absorption at 1.18 μ also appears in the lower hydrate, apparently absent in $HUF_6{\cdot}2.5H_2O$.

Discussion

Two other pentafluoride–hydrofluoric acid–water systems have been reported. In contrast with our finding an acid hydrate with the composition $HUF_6{\cdot}2.5H_2O$, Nikolaev and Buslaev[12,13] report the polymeric compounds, $HNb_2F_{11}{\cdot}4H_2O$ and $HTa_2F_{11}{\cdot}4.5H_2O$, which have a fluorine:metal ratio of 5.5. Since we find a F:U ratio of 6, we cannot have similar polymeric compounds (although we could have a dimer, $H_2U_2F_{12}{\cdot}5H_2O$).

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The same authors report a lower hydrate monomer for each element, $HNbF_6 \cdot 1.3H_2O$ and $HTaF_6 \cdot 1.5H_2O$ (occurring at higher HF concentrations), which may be compared with our compound $HUF_6 \cdot 1.25H_2O$, obtained from >90% HF. (Actually N and B report the formula $HNbF_6 \cdot H_2O$, but we calculate $1.3H_2O$/Nb from their data.)

We were not able to prepare the anhydrous acid, HUF_6, in very concentrated or even anhydrous HF. This finding is in agreement with the Russian work in which neither anhydrous $HNbF_6$ nor $HTaF_6$ could be prepared.

Of great chemical interest is the fact that there is no uranyl-like ion either in the hydrates of HUF_6 or in the concentrated HF solutions of U(V). Their nearly identical spectra show that U(V) has the same environment in the anhydrous salts $LiUF_6$, $NaUF_6$, and $CsUF_6$ as it has in the hydrates of HUF_6. The absorption spectrum of U(V) in aqueous HF is also very similar, suggesting strongly a species such as UF_6^-. However, since water is necessary for UF_5 to dissolve in HF, either UF_6^- ion or the released H^+ must be hydrated.

Support for the existence of the UF_6^- ion is given by recent work on niobium(V) involving Raman spectra[14] and n.m.r. techniques.[15] It was shown unequivocally that pentavalent niobium occurs predominantly as the NbF_6^- ion in fluoride solutions, with no evidence for the higher complex, NbF_7^{-2}. In this connection the near identity of their X-ray powder patterns shows that $CsTaF_6$, $CsNbF_6$, and $CsUF_6$ are isostructural and of very similar cell size.[7] The U^{+5} radius is not sufficiently large to accommodate 8F/U, but falls nicely in the range for F/U = 6. This $KOsF_6$ type[16] of structure can be viewed as a distorted CsCl type with the MF_6^- anion at 0,0,0 positions and Cs^+ at $^1/_2,^1/_2,^1/_2$.

The stability of UF_6^- in concentrated aqueous HF solutions contrasts strongly with and indeed is surprising when viewed against the well-known instability of UO_2^+ in acid. Obviously, F^- can coordinate sufficiently strongly to *pentavalent* uranium in concentrated aqueous HF to prevent hydrolysis. However, when a U(V) solution in 24% HF is diluted with water, oxygen replaces fluorine, forming uranyl(V) which is unstable, and disproportionation results. Reproportionation does not occur on subsequently increasing the concentration of HF since UF_4 is insoluble and is removed from reaction.

The effect of charge is brought out strongly when the hydrolysis of U(IV), U(V), and U(VI) is considered. The U^{+4} ion is only slightly hydrolyzed to UOH^{+3} in molar acid[17]; U^{+6} exists only as UO_2^{+2}. In the pentavalent case, the attraction for oxygen is still sufficient so that the aqueous ion is UO_2^+ in dilute acid. As shown in this paper, fluoride is an effective competitor with oxygen and the UF_6^- ion can exist in concentrated HF solution. However, with *hexavalent* uranium (even when starting with U(VI) as the complex fluoride, Na_2UF_8), we found that hydrolysis to UO_2F_2 occurred immediately in 48% aqueous HF.[18]

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[18] NOTE ADDED IN PROOF.—A crystal-field treatment of the optical absorption spectrum of $CsUF_6$ has been developed by M. J. Reisfeld of this laboratory and G. A. Crosby (University of New Mexico). The UF_6^- ion is shown to possess very nearly octahedral symmetry. This work will be submitted for publication in *Inorganic Chemistry*.