[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF OAK RIDGE NATIONAL LABORATORY]

A Synthetic Uranyl Silicate Hydrate

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A uranyl silicate hydrate was prepared by the reaction of an aqueous UO_2F_2 solution with silica at 300°. The chemical analysis of this yellow crystalline solid indicated the probable composition to be either $(UO_2)_2SiO_4 \cdot 3H_2O$ or $(UO_2)_3Si_2O_7 \cdot 3H_2O$. The compound is virtually insoluble in HCl, HNO_3 or H_2SO_4. It is thermally stable to approximately 400°.

Introduction.—In the course of early experimental investigation of the UO_3–HF–H_2O system at high temperature in silica tubes,[1] a yellow insoluble product was obtained. This product was analyzed by chemical methods which indicated a uranyl silicate hydrate. The stoichiometric compound most nearly corresponding to the analyses was uranyl orthosilicate trihydrate. A description is given of the synthesis and properties of the compound.

Experimental Procedure.—A silica liner containing 5.6% aqueous UO_2F_2 solution was held at 300° for 16 hours in a commercial high pressure bomb after which time the bomb was cooled and opened. The solid solution of $UO_2(OH)_2$ and $UO_2(OH)F \cdot {}^1/_2H_2O$ which forms under the above conditions[1] had redissolved upon cooling the contents of the bomb. However, two insoluble solids remained, these being bright yellow crystals and white particles. These solids presumably were formed by reaction of the solution components with the silica liner since they were not observed under similar conditions in a gold-lined bomb. After thorough washing of the solids by centrifugation techniques, separation was accomplished by making use of the different settling characteristics and of the large difference in densities of the two solids. Upon centrifuging a "slurry" mixture, the much heavier yellow solid would form a bottom layer in the centrifugation tube and the white solid would settle on top with very little mixing at the interface. The bulk of the white solid could be slurried off, thus leaving only the yellow solid and a small amount of white solid. By carefully repeating this procedure, practically 100% separation was attained.

The white solid was identified as silica by spectrography and by reaction with aqueous hydrogen fluoride in a platinum crucible to form volatile SiF_4. No residue remained in the crucible after evaporation of the liquid under a heat lamp.

The yellow product was identified as a uranyl silicate hydrate by analyses for water, silicon and uranium. Several analytical procedures were used for comparison of results. In the first procedure, water was determined from the differences in weight of a sample before and after ignition at 1000° to produce the non-volatile decomposition products, U_3O_8 and SiO_2 (samples 1, 3, 5, 6). The weight difference was multiplied by a "water correction factor" as follows to account for the loss of oxygen thus giving a close approximation of the weight loss attributed to the water of hydration

$$(UO_2)_2SiO_4 \cdot 3H_2O \longrightarrow 2/3\ U_3O_8 + SiO_2 + 3H_2O \uparrow + 2/3\ [O] \uparrow$$

"water correction factor"
assuming uranyl orthosilicate
trihydrate

$$= \frac{3H_2O}{3H_2O + 2/3\ [O]} = 0.8352$$

The "water correction factor" is 0.7716 assuming uranyl disilicate trihydrate. Silicon was determined by final difference in weight of the ignited sample after volatilization of SiF_4 produced by treatment with aqueous HF and subsequent ignition at 1000° of the U_3O_8 residue (sample 1). Uranium was then determined from the final weight of U_3O_8.

The second procedure was to decompose the compound with a 1:1 mixture of concentrated HNO_3 and H_2SO_4 (sample 2). The gelatinous silica which was formed was separated by centrifugation and analyzed by gravimetric ignition. The supernatant solution was analyzed gravimetrically for uranium. The third method combined the silica determination of Scott[2] with a subsequent gravimetric analysis (sample 3). In the fourth procedure uranium was determined potentiometrically by the Analytical Chemistry Division of this laboratory (sample 4).

The oxidation state of uranium was assumed to be hexavalent by observation of the bright yellow color of the compound which is characteristic of most hydrated compounds of hexavalent uranium. Moreover, it was unlikely that the initial U(VI) of UO_2F_2 would be reduced to U(III) or U(IV) at high temperature in the absence of an active reducing agent. No cases of reduction of uranyl ion under similar experimental conditions have been encountered with any of several uranyl compounds.

Analysis for trace amounts of fluorine was carried out by addition of ground silica and concentrated H_2SO_4 to a washed sample thereby converting fluoride to SiF_4, distillation of the SiF_4, and subsequent spectrophotometric determination of the distillate for fluoride.[3] These analyses indicated approximately 0.4% fluorine impurity in the silicate compound.

TABLE I

POWDER PATTERN X-RAY DIFFRACTION LINES FOR URANYL SILICATE HYDRATE (Cu Kα RADIATION)

Relative peak height	*d*	Relative peak height	*d*	Relative peak height	*d*
44	6.108	3	2.099	4	1.465
14	4.720	17	2.076	4	1.451
20	4.575	4	2.056	3	1.441
81	4.450	8	2.028	12	1.402
14	3.723	16	1.963	8	1.398
66	3.282	16	1.895	2	1.380
22	3.209	6	1.875	5	1.367
3	3.119	17	1.846	6	1.350
16	2.952	15	1.758	5	1.344
7	2.767	3	1.726	6	1.328
41	2.687	7	1.696	4	1.294
5	2.622	8	1.669	3	1.281
2	2.568	11	1.657	6	1.263
2	2.525	9	1.653	3	1.240
29	2.462	18	1.638	8	1.219
15	2.438	14	1.634	3	1.198
3	2.374	9	1.590	5	1.164
10	2.309	8	1.574	5	1.162
11	2.238	5	1.560	5	1.157
8	2.190	4	1.545	7	1.148
4	2.159	7	1.508	7	1.146
3	2.136	4	1.489	4	1.135

The principal X-ray powder pattern lines and their relative intensities given in Table I were obtained by B. S. Borie of this Laboratory from the crystalline solid by means of a recording X-ray diffractometer utilizing Cu Kα radiation (λ = 1.54 Å.). The structure analysis of a complex silicate

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[1] W. L. Marshall, J. S. Gill and C. H. Secoy, THIS JOURNAL, **76**, 4279 (1954).

[2] W. W. Scott, "Standard Methods of Chemical Analysis," Ed. by N. H. Furman, 5th ed., Vol. 1, D. Van Nostrand Co., New York, N. Y., 1939, p. 804.

[3] J. E. Lee, Jr., J. H. Edgerton and M. T. Kelley, *Anal. Chem.*, **28**, 1441 (1956).

is a difficult one, especially if only the powder pattern is available and if the compound contains heavy uranium as well as light oxygen, silicon, and hydrogen atoms.

Data and Discussion.—Analytical samples were limited to 0.100 g. since only a small over-all amount of compound was available. The analytical accuracy of approximately ±0.3% for uranium is much better than was attained for silicon or for water due to the very large atomic weight of uranium. Therefore, greater reliance should be placed on the uranium analyses.

Analytical data for uranium, silicon and water were compared with theoretical values for the stoichiometric compounds UO_2SiO_3, $(UO_2)_2SiO_4$, $(UO_2)_3Si_2O_7$ and their hydrates to a maximum of four waters of hydration. These compounds were selected in order to encompass a plausible stoichiometry of the solid. With the exception of two of the compounds, all were rejected as possibilities by virtue of considerable disagreement with the analytical values.

In Table II the data are compared with theoretical values for the two most plausible uranyl silicates. From the data it appears that $(UO_2)_2SiO_4 \cdot 3H_2O$ is the more probable of the two compounds. Uranyl disilicate trihydrate does not fit the analyses as well as the ortho compound since high silicon (and, consequently, low water) values would be expected as a result of possible incomplete dehydration of the silica upon ignition analysis and incomplete initial separation from the original white SiO_2. There is a possibility, however, that the solid is non-stoichiometric as, for example, soddyite, $12UO_3 \cdot 5SiO_2 \cdot 14H_2O$[4] and the indication of a stoichiometric compound may be fortuitous. The nearest simple whole number mole ratio for uranium, silicon and water is 5:3:7, respectively.

TABLE II

ANALYTICAL DATA FOR THE URANYL SILICATE HYDRATE

Sample	Uranium, wt. %	Silicon, wt. %	Water, wt. % Assuming the orthosilicate	Water, wt. % Assuming the disilicate
Experimental				
1	69.16	5.16	6.6	6.1
2	69.25	4.54		
3	69.83	4.6	7.37	6.81
4	69.27			
5			7.79	7.20
6			7.79	7.20
Av.	69.38	4.77	7.39	6.83
Theoretical				
$(UO_2)_2SiO_4 \cdot 3H_2O$	69.38	4.09	7.88	
$(UO_2)_3Si_2O_7 \cdot 3H_2O$	69.18	5.44		5.23

The formation of silica and a uranyl silicate hydrate from aqueous UO_2F_2 solution and SiO_2 glass may be explained by the hydrolysis of UO_2F_2 to form free HF and UO_2^{++} or $U_2O_5^{++}$ type ions. Hydrofluoric acid in turn reacts with SiO_2 glass to produce SiF_4 or H_2SiF_6. These products may combine with UO_2^{++} or $U_2O_5^{++}$ probably to form an intermediate product which hydrolyzes to uranyl silicate hydrate. Silica solid is produced by hydrolysis of SiF_4 or H_2SiF_6.

This uranyl silicate hydrate is insoluble or difficultly soluble in concentrated or dilute HNO_3, HCl and H_2SO_4 but soluble with precipitation of silicic acid in concentrated $HClO_4$ or in a mixture of concentrated HNO_3 and H_2SO_4. The compound is thermally stable to approximately 400° but liberates water between 400 and 450° with possible additional decomposition to a light reddish solid which may be a mixture of UO_3, UO_2 and SiO_2.

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(4) A. Schoep, *Compt. rend.*, **174**, 1066 (1922).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE GEORGE WASHINGTON UNIVERSITY]

On the Existence of the Fluoroplatinite Ion in Aqueous Solution

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A study was undertaken to determine whether the divalent platinum fluoride complex, the fluoroplatinite ion, could be synthesized in aqueous solution. The use of a full variety of reducing agents with fluoroplatinic acid and its salts under various conditions failed to provide any substantial evidence to indicate the formation of the fluoroplatinite ion. An estimate of the electrode potential suggests the instability of the fluoroplatinite ion with regard to disproportionation in an aqueous solution.

This paper presents a summary of the efforts directed toward the preparation of fluoroplatinous acid and its salts.

In order to ascertain whether the fluoroplatinate ion reacts with reducing agents much in the same manner as the chloroplatinate ion, the preliminary experiments were simply a modification of the procedures employed in the preparation of the chloroplatinites from the chloroplatinates. When these failed to produce effective results, other measures were adopted.

Experimental

Reagents.—Fluoroplatinic acid and potassium fluoroplatinate were prepared as previously reported.[2,3] In order to eliminate any substitution in the fluoroplatinate ion by the chloride ion, stannous fluoride was used instead of stannous chloride as a reducing agent. Chloride-free stannous fluoride was prepared by the following procedure. Ammonium hydroxide was added to a solution of stannous chloride. The precipitate of stannous hydroxide was washed thoroughly until free of chloride. To this precipitate, a quantity of 48% hydrofluoric acid was added which just dissolved all of the stannous hydroxide. The solution of stannous

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(1) Abstracted from a portion of the thesis submitted by David E. Icenhower in partial fulfillment of the requirements for the degree of Master of Science.

(2) T. P. Perros and C. R. Naeser, THIS JOURNAL, **75**, 2516 (1953).

(3) T. P. Perros, C. R. Naeser and T. E. Wheeler, *ibid.*, **77**, 3488 (1955).