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 $\pm0.3\%$ 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 $(UO_2)_2SiO_4\cdot3H_2O$ 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, $12UO_3\cdot5SiO_2\cdot14H_2O$[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.

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

TABLE II

ANALYTICAL DATA FOR THE URANYL SILICATE HYDRATE

Sample	Uranium, wt. %	Silicon, wt. %	Water, wt. % Assuming the orthosilicate	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		
$(UO_2)_2SiO_4\cdot3H_2O$	69.38	4.09	7.88	
$(UO_2)_3Si_2O_7\cdot3H_2O$	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.

OAK RIDGE, TENNESSEE

On the Existence of the Fluoroplatinite Ion in Aqueous Solution

BY THEODORE P. PERROS, WILLIAM F. SAGER AND DAVID E. ICENHOWER[1]

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.

(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.

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

(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).

fluoride was diluted so that its concentration was approximately 0.1 N. The remainder of the chemicals were of reagent grade.

Attempted Reduction of Potassium Fluoroplatinate.—Twenty-five ml. of a 0.025 M potassium fluoroplatinate solution was placed in a 50-ml. flask and stirred constantly with a mechanical stirrer while the flask was in a water-bath kept at a temperature of 85–90°. A freshly prepared saturated sulfur dioxide solution was added slowly with sufficient time lapse between additions for all of the sulfur dioxide odor to disappear. No evidence of reaction was noted. Further, the absorption spectrum of the crystallized residue was characteristic of the fluoroplatinate ion.

This procedure was repeated using a potassium oxalate solution in place of the sulfur dioxide solution without any evidence of a reaction.

A 0.025 M solution of hydrazine was prepared and added to a 0.025 M solution of potassium fluoroplatinate. The result was an immediate reduction to platinum. Solutions of hydrazine of a decreased concentration when treated with potassium fluoroplatinate gave the same results although in very dilute solutions the formation of platinum occurred slowly. In no instance was there any evidence of a reduction to the fluoroplatinite ion.

A similar sequence of tests was run with hydroxylamine sulfate at various pH levels. In no case was there any evidence of reduction.

A 0.025 M solution of stannous fluoride was added to a 0.025 M solution of potassium fluoroplatinate. There was a formation of a precipitate which quickly changed color from deep red to dark brown. The precipitate was gelatinous in appearance and was shown to be platinous hydroxide. The precipitate was insoluble in hydrofluoric acid but dissolved readily with hydrochloric acid to produce the deep red color characteristic of the chloroplatinite ion. If stannous chloride is used as the reducing reagent, no precipitate is formed and the solution becomes colored red as previously described. This identical color is obtained if a solution of potassium chloroplatinate is treated with stannous fluoride or chloride.

A 0.1 N solution of sodium stannite was added to a solution of potassium fluoroplatinate. Reduction of the fluoroplatinate ion was the result. If less than stoichiometric quantities of sodium stannite were used, upon removal of the platinum by filtration, the characteristic color of the fluoroplatinate ion was detected easily. Variations in the concentrations of the reagents failed to produce any change in the end-products.

The reduction of solid potassium fluoroplatinate at room temperature with gaseous hydrogen resulted in the decomposition of the salt to platinum. Dilution of hydrogen with helium produced the same result at a reduced rate. There was no evidence of any intermediate reduction product.

Attempted Reduction of Fluoroplatinic Acid.—The reactions described for potassium fluoroplatinate were repeated with solutions of 0.075 and 0.003 N fluoroplatinic acid. In each instance the outcomes were essentially identical.

In addition, fluoroplatinic acid was treated separately with methanol and 3% hydrogen peroxide. With methanol, after several hours of constant agitation a slow precipitation

of platinum was observed. There was no evidence of a reaction with hydrogen peroxide.
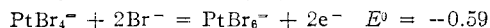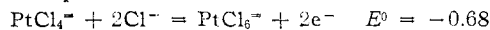
Discussion of Results

The experiments which were conducted seemed to confirm the belief that the fluoroplatinite ion cannot exist in aqueous solution or if it can be formed, its existence is transitory.
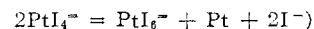
Additional support for this thought is derived from the approximation of the electrode potential for the reaction
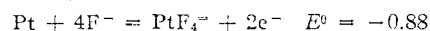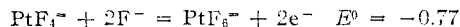
$$2PtF_4^- = PtF_6^- + Pt + 2F^-$$
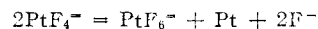
By accepting the literature values for the indicated reactions[4] and assuming that the variation in electrode potentials is uniform

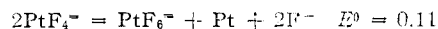$$PtCl_4^- + 2Cl^- = PtCl_6^- + 2e^-   E^0 = -0.68$$
$$PtBr_4^- + 2Br^- = PtBr_6^- + 2e^-   E^0 = -0.59$$

(The iodoplatinite ion is unstable, the reaction taking place

$$2PtI_4^- = PtI_6^- + Pt + 2I^-)$$
$$Pt + 4Cl^- = PtCl_4^- + 2e^-   E^0 = -0.73$$
$$Pt + 4Br^- = PtBr_4^- + 2e^-   E^0 = -0.58$$

then the potentials for the reactions may be estimated as

$$PtF_4^- + 2F^- = PtF_6^- + 2e^-   E^0 = -0.77$$
$$Pt + 4F^- = PtF_4^- + 2e^-   E^0 = -0.88$$

From these it is possible to obtain the potential for the reaction

$$2PtF_4^- = PtF_6^- + Pt + 2F^-   E^0 = 0.11$$

It is apparent that the fluoroplatinite ion is unstable and tends to disproportionate. Thus any reducing agent which could bring about the reduction of the fluoroplatinate ion to the fluoroplatinite ion would reduce it to platinum if the reducing agent were present in excess and, if not, the fluoroplatinite ion would disproportionate. This seems to be in accord with the experimental results.

Conceivably the fluoroplatinite ion would be stable in a large fluoride ion concentration. A sample calculation indicates that this could be done if the fluoride concentration were in the order of 45 M.

(4) W. Latimer. "Oxidation Potentials." Prentice-Hall, Inc., New York, N. Y., 2nd Edition. 1952, pp. 204–206.

Washington, D. C.