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Osmium Hexafluoride and its Identity with the Previously Reported Octafluoride^{1,2}BY BERNARD WEINSTOCK³ AND JOHN G. MALM

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The reaction between osmium metal and fluorine gas had been reported in 1913 by Ruff and Tschirch to yield three products, OsF₄, OsF₆ and OsF₈. A repetition of their synthesis led to the formation of only the most volatile of these, the yellow solid that they identified as osmium octafluoride. Our measurements of the melting point, 32.1°, and the boiling point, 45.9°, establish the identity of our product with their octafluoride. However, our molecular weight determinations and chemical analysis show the composition of this compound to be OsF₆ rather than OsF₈. This conclusion is also supported by X-ray diffraction measurements and infrared and Raman spectroscopy. It therefore appears very likely that the compound known now for many years as osmium octafluoride is in fact osmium hexafluoride and that the compound previously called OsF₆ also was identified incorrectly.

Introduction

Over forty years ago Ruff and Tschirch⁴ described the preparation, identification and some properties of three osmium fluorides, OsF₄, and OsF₆ and OsF₈, formed by the interaction of a stream of elemental fluorine with samples of heated osmium metal. They pointed out that the discovery of the octafluoride was of particular interest because it not only confirmed the octavalency of osmium originally found in the tetroxide, OsO₄, but also represented the first synthesis of a binary compound with eight univalent atoms attached to a single central atom. Despite this distinction, which has remained until this day, very few studies have been reported with the octafluoride since the original work; two reports that have appeared are the electron diffraction measurements of Braune and Knoke⁵ and the determination of the solid density by Henkel and Klemm.⁶ Because of our interest in the series of hexafluorides formed by the actinide elements, uranium, neptunium and plutonium, we have had occasion to consider the physical properties of the analogous series of hexafluorides formed by osmium and its neighbors, tungsten, rhenium and iridium. This revealed that the values of the melting point and boiling point reported for OsF₆⁴ are markedly higher than the corresponding values for the other members of this group while the values of these quantities reported for OsF₈⁴ are very close to what one would predict for OsF₆ from interpolation of the properties of WF₆, ReF₆ and IrF₆ (Table I). These observations suggested the possibility that the identification of the volatile yellow solid as the octafluoride might have been incorrect and that this compound might in fact be a hexafluoride. If this turned out to be true than the less volatile green compound described as the hexafluoride would also have been incorrectly identified. This paper will describe the preparation of a volatile osmium fluoride and some studies that were made of its properties with the intention of helping to resolve these questions.

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(4) O. Ruff and F. W. Tschirch, *Ber.*, **46**, 929 (1913).

(5) A. H. Braune and S. Knoke, *Nature*, **21**, 349 (1933).

(6) P. Henkel and W. Klemm, *Z. anorg. allgem. Chem.*, **222**, 65 (1935).

TABLE I

HEXAFLUORIDES	REPORTED MELTING POINTS AND BOILING POINTS OF 5d	
	M.p., °C.	B.p., °C.
WF ₆	2.3	17.5
ReF ₆	18.8	47.6
OsF ₆	50-120	205
OsF ₈	34.4	47.3
IrF ₆	44.4	53

Experimental

Materials.—Finely divided osmium metal, which showed only traces of impurity on spectrochemical analysis, was used for the preparation. Volatilization of the osmium as osmium tetroxide by heating in a stream of oxygen showed the non-volatile residue to be 0.4 weight %. The fluorine gas obtained from the Pennsylvania Salt Manufacturing Company analyzed to greater than 99% fluorine and was purified from HF before use by condensation with liquid nitrogen.

Preparation.—The reaction obtained by the passage of fluorine gas at a pressure of 250 mm. over osmium metal heated in a Pyrex furnace tube was studied. Under these conditions all but a few tenths of a per cent. of the osmium was found to have volatilized at the end of the experiment. Two Pyrex U-tubes were provided downstream to collect the volatile reaction products; the first U-tube was cooled with solid CO₂ and the second with liquid nitrogen. Only a single volatile reaction product was observed to collect, a brightly colored yellow solid. All of this material was usually found in the first U-tube although occasionally a small amount was also found in the second U-tube where it was presumed to have been blown by the fluorine stream. The volatile product was purified by U-tube to U-tube distillation under high vacuum conditions; the details of this method and the techniques used in this Laboratory for the purification, handling and storage of reactive volatile fluorides have been reported elsewhere.⁷ Some osmium fluoride is lost during this vacuum purification if solid CO₂ is used as the refrigerant, such loss being avoided by the use of the -100° eutectic provided by the mixture of 31 weight % chloroform and 69% trichloroethylene. The yield of volatile product was determined after purification by PVT measurement assuming one osmium atom per molecule of gas. In the initial experiment, when solid CO₂ was used for the purification, an 84% yield of osmium fluoride was obtained from 1.35 g. of metal; in the next experiment the -100° bath was used and a 100% recovery of volatile fluoride was obtained from 3.50 g. of osmium metal.

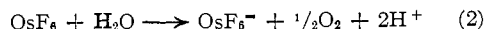
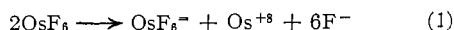
Molecular Weight Determination.—The molecular weight of the yellow fluoride was determined by weighing a quantity of gas collected under conditions of known pressure, volume and temperature in a Pyrex glass bulb provided with a miniature valve. All weighings were made with a similar evacuated bulb used as a tare. The bulb was thermostated during filling and the pressure measurements were made with a quartz sickle gauge. The bulb was flamed, pumped to a good vacuum, 10⁻⁶ mm. and sometimes weighed before fill-

(7) B. Weinstock and John G. Malm, *J. Inorg. Nucl. Chem.*, **2**, 380 (1956).

ing. After determining the weight of the bulb filled with the osmium compound, the bulb was emptied by distillation and its weight determined evacuated.

Chemical Analysis.—A weighed sample of osmium fluoride sealed in a Pyrex flask and cooled with solid CO_2 was hydrolyzed by admitting a solution of NaOH through a break seal. The hydrolysis was observed to proceed smoothly with the liberation of heat and the evolution of a gas that was insoluble in the alkaline solution. The color of the hydrolyzed fluoride varied from a deep reddish brown in concentrated solution to a light yellow in dilute solution. The fluorine was separated from the osmium before measurement by the use of the Willard and Winter distillation from perchloric acid⁸ to which ferrous ion is added to prevent the distillation of OsO_4 . The fluoride in the distillate was titrated spectrophotometrically with thorium nitrate using sodium alizarin sulfonate as indicator. The osmium was determined colorimetrically by measurement of the absorption of the thiourea complex,⁹ $[\text{Os}(\text{NH}_2\text{CSNH}_2)_6]^{+3}$, at $480 \text{ m}\mu$ after oxidation of the osmium to the octavalent state. The color was developed in 50 ml. of 10% thiourea in 6 N HCl as recommended by Hoffman, *et al.*¹⁰

Chemistry of the Hydrolysis.—The standard osmium solution used to test the analytical procedures was prepared from a weighed amount of OsO_4 by hydrolysis; this quantity of OsO_4 itself representing the complete recovery of a known amount of osmium metal volatilized in an oxygen stream. Besides the above mentioned method other procedures had been attempted for the analysis of the osmium fluoride. These included for osmium: (1) reduction with ethyl alcohol followed by adjustment to pH 4 to precipitate the hydrated oxide and (2) reduction with ethyl alcohol and precipitation with H_2S in alkaline medium followed by adjustment to pH 4. In both cases the precipitate is filtered on a Gooch crucible, reduced to the metal with hydrogen and weighed. These procedures both gave reliable results with synthetic osmium solutions containing a 6:1 molar ratio of fluoride and enough H_2BO_3 to complex the fluoride and prevent glass attack. The average composition of osmium in the standard tetroxide solution obtained in these measurements corresponded to the formula $\text{OsO}_4.04$. A gravimetric procedure for the determination of fluorine as PbClF also was found to give reliable results when tested with the above solution. However, when these procedures were used with the hydrolyzed osmium fluoride only 10% of the osmium and of the fluorine were recovered. A possible scheme explaining this behavior is



It is then postulated that 20% of the osmium fluoride hydrolyzes by disproportionation according to equation 1 and the remainder by the oxidation of water with the liberation of oxygen, equation 2. Only the octavalent osmium and the corresponding fluorine appear in the last mentioned analytical methods, the remainder being strongly complexing as OsF_6^- and as such escaping detection. In the method described in the preceding section this difficulty was avoided by oxidizing all of the osmium to the octavalent state. Equation 2 was tested by the hydrolysis of a 1.017-g. sample of the yellow fluoride with a degassed sample of dilute alkali. From this 0.00130 mole of O_2 (identified mass spectrometrically) was recovered in agreement with the 0.00134 mole predicted by equation 2 (after correction for the fraction hydrolyzing according to equation 1). An unsuccessful attempt was made to identify the presence of OsF_6^- by Raman spectroscopy. In order to do this the solution was first decolorized by electrolytic reduction of the Os^{+8} to the metal; as with the other reduction procedures 10% of the osmium was recovered in this way.

Results and Discussion

Method of Preparation.—Some differences were found in the present work when osmium was heated in a stream of fluorine than were reported

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(10) I. Hoffman, J. E. Schweitzer, D. E. Ryan and F. E. Beamish, *Anal. Chem.*, **25**, 1092 (1953).

by Ruff and Tschirch. A probable explanation lies in the difficulties that they report being faced with arising from the variable nature and limited supply of their fluorine stream and from their inability to remove air completely from their system. Thus, the incomplete volatilization of osmium from the reaction zone with the formation of three reaction products that they report could be due to an inadequate supply of fluorine to complete the reaction and to the presence of moisture in their system. The presence of water and HF in their system most probably explains the apparent reactivity of their product toward glass in contrast to the present experience.

Physical Properties.—The melting point found for the yellow fluoride in this work is 32.1° in agreement with the value of 34.4° previously reported. Present preliminary vapor pressure measurements are compared with the the previously reported values in Fig. 1 and also found to be in agreement; the current results extrapolate to a boiling point of 45.9° compared to the former value of 47.3° . This similarity of physical properties as well as the similar method of preparation make it very probable that the yellow solid prepared here is identical with the octafluoride of Ruff and Tschirch.

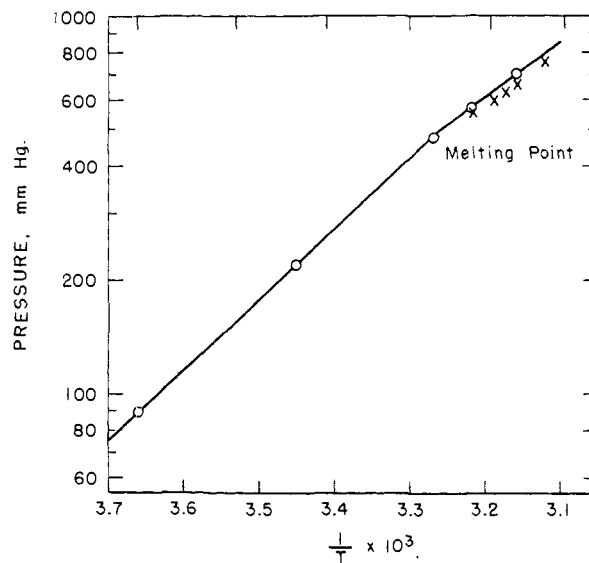


Fig. 1.—Vapor pressure of OsF_6 : O, this research; X, Ruff and Tschirch (OsF_6).

Molecular Weight Determination.—Some pertinent data and the calculated molecular weights are given in Table II. The uncertainty of the determination is about 1% largely because of the increase in weight of the bulb during exposure to the osmium fluoride. Two values of the molecular weight are recorded: one based on the initial weight of the bulb when available and the other on the final weight of the evacuated bulb. The average of all these values is $307.6 \pm 3.9 \text{ g.}$, in agreement with the formula weight of the hexafluoride. Ruff and Tschirch measured the molecular weight by the Victor Meyer method and reported an average value of $355 \pm 13 \text{ g.}$ in agreement with the formula weight of the octafluoride. In their work the osmium fluoride samples were transferred and

weighed while exposed to air. This feature of the earlier technique as well as the unsuitability of the Victor Meyer method for vapor density measurements with reactive compounds would make the present measurements appear the more reliable of the two.

TABLE II
MOLECULAR WEIGHT DETERMINATIONS

Pressure, mm.	Wt. of gas, g.	Increase in wt of bulb, g.	Mol. wt.	
			Initial bulb wt., g.	Final bulb wt., g.
232.56	0.3144	311.1
225.52	.3030	0.0021	310.3	308.2
225.18	.3047	309.1
95.67	.1279	.0063	317.7	302.8
196.98	.2591	.0076	308.7	299.9
206.00	.2817	.0012	304.5	303.2

Av. value 307.6 \pm 3.9

Formula weights: OsF₆—304.2 g., OsF₈—342.2 g.

Chemical Analysis.—A sample of the yellow fluoride weighing 1.4914 g. gave an average analysis of F, 0.5710 g., and Os, 0.9356 g., in agreement with the values of F, 0.5589 g., and Os, 0.9325 g., calculated on the basis of the formula OsF₆. The atom ratio of F to Os from these measurements is 6.11. Ruff and Tschirch reported chemical analyses that agreed with the formula OsF₈. The high fluorine content that they observed could be explained as due to the contamination of their samples with HF, which would give a high fluorine content without appreciably affecting the total weight of the sample.

X-Ray Diffraction.—As an additional method of determining the composition of the yellow fluoride powder patterns were obtained by X-ray diffraction with both this compound and IrF₆.¹¹ Both compounds were found to have similar patterns and consequently the same structure. From these measurements the cell of the osmium fluoride was determined to be body centered cubic with $a_0 = 6.23$ Å. and volume equal to 243 Å.³ with two osmium atoms per cell. If the volume occupied by a fluorine atom is 19 Å.³ the hexafluoride would occupy a cell of 228 Å.³ while the octafluoride would require 304 Å.³ Thus, the similarity of the X-ray patterns of IrF₆ and the osmium fluoride as well as estimates of unit cell sizes both favor the identification of the yellow compound as the hexafluoride. By assuming the fluorine atoms to be octahedrally bonded to the osmium, the Os-F distance is estimated to be 2.07 Å.

Infrared and Raman Spectra.—The infrared spectrum of the vapor of the yellow solid has been found to be very similar to that found for other hexafluorides and has been analyzed successfully on the basis of the structure of a regular octa-

hedron.¹² There are three Raman active fundamentals for this structure and two of them have been observed for the liquid. The third was not obtained because of absorption by the liquid in the yellow. All of the observed frequencies have been assigned and the Raman frequencies agree with those derived from the infrared combination bands to within 1–2 cm.⁻¹. The completeness of the explanation of the spectra and the absence of spurious bands attest to the reliability of the model and the purity of the compound. An octafluoride of cubic symmetry cannot be ruled out completely without tortuous arguments; it would have four Raman active fundamentals.

Summary and Conclusions.—It appears very likely from the present results that the volatile yellow fluoride of osmium is the hexafluoride and not the octafluoride as reported by Ruff and Tschirch. This removes another anomaly pointed out by Sidgwick¹³ in connection with the formation of stable addition compounds between "OsF₈" and alkali fluorides that was reported by the previous workers. Such compounds would require an extension of the covalency limit from 8 to either 9 or a possible maximum of 10. On the other hand the formation of stable addition compounds between hexafluorides and alkali fluorides is not at all uncommon.¹⁴ Although no attempt to synthesize and identify the compound described by the previous authors as OsF₈ has been made in the present work, it follows that this compound also had been incorrectly identified.

It seems reasonable to explain the failure of Ruff and Tschirch in the identification of these compounds as due to the limited facilities available to them for their work. This handicap was augmented by the greater reactivity and complexity of the chemistry of osmium hexafluoride as compared with many other hexafluorides more successfully studied by Ruff and his co-workers. The fact that these errors have persisted in the chemical literature for so many years without serious questioning and in spite of the unique status of the alleged octafluoride attests to the nature of the difficulties involved.

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