

Reductive Syntheses of Transition Metal Fluoride Compounds. Synthesis of Rhenium, Osmium, and Iridium Pentafluorides and Tetrafluorides¹

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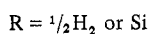
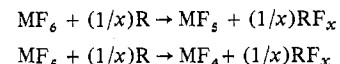
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Two simple syntheses of third-row transition series pentafluorides MF₅ and tetrafluorides MF₄ (M = Re, Os, Ir) from the corresponding hexafluorides are described. The success of the syntheses depends upon the ease of reduction of the corresponding metal hexafluorides by hydrogen gas or silicon metal in anhydrous HF at room temperature. The pentafluorides and tetrafluorides have been characterized and the data are discussed in the light of known properties of similar compounds. The reaction of silicon in liquid HF is also described.

Introduction

Binary fluorides of groups VIb–VIIIb, second- and third-row transition metals, are known with oxidation states ranging from VII to II. The higher oxidation states VII and VI are easily obtained by direct fluorination of the metal usually at an elevated temperature (200–400°).² The MF₇ and MF₆ compounds are obtained in good yields and with high purity, and their reaction chemistry is well studied.² Unfortunately, no one reaction has been reported for the synthesis of intermediate oxidation state metal fluorides of the type MF₅, MF₄, and MF₃. Over the years, a number of relatively specific syntheses have evolved, most of which provide low yields of impure metal fluoride products.² As a result, the reaction chemistry of MF₅, MF₄, and MF₃ compounds has not been adequately explored.

As part of a program to develop further and exploit the reaction chemistry of intermediate oxidation state metal fluorides we have attempted to devise a convenient, general synthesis of metal pentafluorides and tetrafluorides. This paper reports on the successful high-yield syntheses of MF₅ and MF₄ (M = Re, Os, Ir) from simple reduction reactions of the type



Some new characterization data for these compounds are presented and the potential utility of the reaction scheme is discussed.

Experimental Section

The manipulation of the volatile compounds was accomplished in a Monel vacuum line³ fitted with auxiliary Kel-F reaction tubes. The metal hexafluorides ReF₆,⁴ OsF₆,⁵ and IrF₆ were prepared by direct high-pressure (4 atm) fluorination of the metal at elevated temperature. The resulting hexafluorides were purified by trap to trap vacuum distillation. Hydrogen fluoride was purchased from Matheson Co. The crude gas was purified by trap to trap distillation, dried for 24 hr over K₂NiF₆, and stored in Kel-F containers. The high-purity silicon powder was purchased from Alfa Chemical Co.

The mass spectra were recorded with a Bendix Model MA-2 time-of-flight mass spectrometer operating with an ionization voltage of 70 eV and source temperature of 25°. The samples were introduced into the ionization chamber with a standard heated-solids probe. Infrared spectra were recorded with a Perkin-Elmer 521 spectrometer (4000–400 cm⁻¹). The electronic spectra were recorded with a Cary 14 spectrometer and the Kel-F reaction tubes served as cells for the HF solutions. The Raman spectra of the solids were recorded with a Cary 82 spectrometer using 6471-Å Kr⁺ laser excitation. The samples were contained in sealed thin-wall glass tubes.

Synthesis of Pentafluorides. In a typical one-electron silicon redox reaction, 5.0 mmol of MF₆ and 10 ml of anhydrous HF are combined in a Kel-F reaction tube⁶ with 1.2 mmol of pure silicon powder frozen in 10 ml of HF. *Caution! Metal hexafluorides should not be condensed directly onto bare silicon powder. Explosions may result.* The contents are warmed to room temperature and stirred. The reaction is complete in 30 min–6 hr with the ReF₆ reduction being

slowest. Completion of the reaction is evidenced by the disappearance of the silicon powder, and the formation of a colored solution, e.g., ReF₅ yellow-green, OsF₅ blue, or IrF₅ yellow-green. Vacuum distillation of the volatile products (HF and SiF₄) provides powders of ReF₅, OsF₅, and IrF₅ in 95–100% yields based on silicon.

In a typical one-electron hydrogen redox reaction 5.0 mmol of MF₆ and 10 ml of anhydrous HF are combined in a Kel-F reaction tube.⁶ Hydrogen gas, 2.4 mmol, P₀ = 2500 Torr, is admitted to the solution at room temperature and the solution stirred. Iridium hexafluoride is reduced rapidly (ca. 2–3 hr.) in room light, but ReF₆ and OsF₆ are reduced slowly (ca. 1–2 days). The rates are greatly enhanced by placing a small piece of Pt gauze in the reaction solution and irradiating the solution with a low-pressure mercury lamp. Under these conditions ReF₆ and OsF₆ are completely converted to the pentafluorides in 3–4 hr and IrF₆ is converted to IrF₅ in 1 hr. The reactions do not appear to be noticeably dependent on the reaction tube material. The solids are recovered by evaporating the HF solvent. This reduction can also be accomplished in the gas phase without HF, but the rates are slower.

Synthesis of Tetrafluorides. The reductions to the tetrafluorides are best accomplished by starting with the isolated pentafluorides prepared as described above. In a typical reaction, 3.0 mmol of metal pentafluoride is dissolved in 10 ml of anhydrous HF and 1.5 mmol of H₂ gas is admitted to the solution. The resulting solution is stirred in the presence of Pt gauze and uv radiation for 1–12 hr. The reactions of OsF₅ and ReF₅ are the slowest and their rates are enhanced by heating the solution to 50°. The respective tetrafluorides precipitate from solution leaving blue (ReF₄), yellow-brown (OsF₄), and red-brown (IrF₄) powders. Only OsF₄ and IrF₄ are produced directly from the hexafluorides and only then by hydrogen reduction. Unless great care is taken, mixed-valence-state compounds are obtained in the one-step, two-electron reductions with silicon metal. The tetrafluorides are obtained in 95–100% yields from the hydrogen reduction systems.

Reaction of Silicon with HF. In a typical reaction, 30 mg of Si powder and 10 ml of anhydrous HF are combined in a Kel-F tube with a Teflon-coated stir bar. The slurry is stirred at room temperature for up to 12 hr and the pressure in the system monitored with a metal-diaphragm pressure transducer. The slurry is frozen periodically, e.g., every hour, and any noncondensable gas pumped off. A small amount of noncondensable gas is evolved and it is identified as H₂. Attempts to follow the low rate of evolution of H₂ quantitatively have not been successful due mainly to drift in the transducer. We estimate the rate of evolution of hydrogen to be less than 0.1 mmol/hr at 23°. No HF soluble products were detected by visible–uv or Raman spectroscopy.

Characterization of Products. All of the pentafluorides and tetrafluorides are very moisture and air sensitive so that all manipulations of the compounds are performed in an inert-atmosphere box. The pentafluorides are observed to melt sharply within the ranges previously reported⁷ and they are easily purified by vacuum sublimation. The pentafluorides are soluble to at least 1 M in anhydrous HF. Some trouble is encountered in redissolving OsF₅ and IrF₅ if they have stood for more than 1 week as powders. The tetrafluorides are momentarily soluble as formed in HF, but they precipitate on standing and cannot be redissolved in HF up to 50°. Chemical analyses for F in all compounds and Re agree within 1% of the expected formula compositions. The *d* values from powder X-ray patterns are available.⁸

Table I. Mass Spectra of MF₅ and MF₄ (70 eV)

Ions	ReF ₅	ReF ₄	OsF ₅	OsF ₄	IrF ₅	IrF ₄
M ₃ F _x ⁺ ΣI ^a	20	16	32	28	15	16
M ₂ F _x ⁺ ΣI ^a	25	18	36	29	17	20
MF ₅ ⁺	17	10	12	18	12	6
	8	6	7	10		
			4	7	7	2
			4	6		
MF ₄ ⁺	100	41	100	30	100	26
	54	52	63	19	69	15
			39	12		
			31	10		
MF ₃ ⁺	36	100	41	100		
	20	52	27	64	42	100
			17	39	27	67
			13	30		
MF ₂ ⁺	17	31	23	37		
	10	18	15	23	21	45
			9	14		
			7	10	12	27
MF ⁺	8	9	11	17		
	5	5	7	11	9	12
			4	7	5	7
			7	6		
M ⁺	5	9	4	4	3	5
			2	2		
	3	6	1	1	2	3
			1	1		

^a The individual ion peaks at high mass were not well resolved so these intensities are listed as an approximate sum of intensities for the entire envelope. ^b All intensities are expressed as relative intensities normalized to the most intense ion.

Table II. Infrared Spectra of MF₅ and MF₄ (cm⁻¹)

ReF ₅ (thin film, -196°)	ReF ₄ (thin film, 23°)	OsF ₅ (mull, -196°)	OsF ₄ (mull, 23°)	IrF ₅ (thin film, -196°)	IrF ₄ (powder, 23°)
743 m, sh					
721 s, sh	722 s		719 w, sh		
		712 m, sh	702 s	715 s, sh	
693 s	696 s	691 s		699 s, sh	691 m, sh
	680 w, sh			678 vs	688 s
660 s	661 m	657 s	660 m	642 s	
535 m, br	528 s, br	530 s, br	532 br, s	533 m, br	545 s, br
	318 vw				
	279 w				

The polyisotopic mass spectrum of each compound is listed in Table I. Careful ion intensity vs. ionization voltage studies were not made, but spectra recorded at 20 eV show the greatest intensities in the (MF_{5-x})_{2,3}⁺ and (MF_{4-x})_{2,3}⁺ envelopes. The intensities of the low-mass ions are greatly reduced at low voltages. Ion source pressures are estimated to be about 8 × 10⁻⁵ Torr. The infrared spectrum of the pentafluorides (-196°, thin film)⁹ and tetrafluorides (mull) are summarized in Table II. The Raman spectra of ReF₅ and IrF₅ melts show the following bands (cm⁻¹): 746 s (pol), 690 w, 215 w; 718 s (pol), 705 w, 701 w, 687 w, 673 w, 646 m, 258 m, 237 w, 224 w. Raman spectra of the remaining compounds could not be recorded in our experimental arrangement without significant decomposition induced by the laser.

The visible spectra of the HF solutions are as follows: ReF₅, 752 nm; ReF₄ 970, 745, 579.5, 445 nm; OsF₅, 1135, 1020, 960, 623, 562, 517 nm; IrF₅ 840, 683 nm.

Results and Discussion

Prior to this work the pentafluorides MF₅, M = Re, Os, and Ir, have been prepared from the reactions of ReF₆¹⁰ and OsF₆¹¹ with W(CO)₆, ReF₆ with PF₃,¹² OsF₆ with IF₅ or light,¹¹ IrF₆ with glass,¹³ and ReF₆ and OsF₆ with a hot filament.¹⁴ The tetrafluorides have been prepared from the reactions of IrF₆ with a hot filament,¹⁴ thermal decomposition of OsF₅¹⁵ and ReF₅,¹⁰ decomposition of ReF₆ over Re,¹⁶ and the reaction of ReF₆¹⁰ and OsF₆¹¹ with W(CO)₆. Not one of the reaction types, however, has been found to be general or to give high yields.

The present study shows that the easily obtained starting

materials ReF₆, OsF₆, and IrF₆ can be readily reduced to the corresponding pentafluorides and tetrafluorides in a stepwise procedure. One-electron reductions to MF₅ are efficiently accomplished using silicon in anhydrous HF solution or hydrogen with or without HF as the reducing agent. The reactions are rapid (30 min–6 hr) and the resulting pentafluorides are pure as evidenced by their sharp melting points and mass spectra. High yields (95–100%) are always obtained. The best route to the tetrafluorides involves the isolation of the pentafluoride and dissolution in liquid HF followed by a photolytically enhanced one-electron reduction with hydrogen.

The one-step, two-electron reduction of ReF₆ and OsF₆ with silicon usually produces mixed-valence-state compounds of variable composition and very little tetrafluoride. A one-step, two-electron reduction of ReF₆ and OsF₆ in liquid HF can be realized with hydrogen if the solution is irradiated and warmed to 50°. Iridium hexafluoride is reduced directly to IrF₄ with either silicon or hydrogen in stoichiometric amounts.

The mechanism for the hydrogen reducing system probably depends on the formation of hydrogen atoms as qualitatively evidenced by the increased reaction rate with uv radiation. The mechanism for the silicon reducing system is less certain. It is observed that the rates of reduction of the hexafluorides by H₂ and Si are roughly comparable. It might be expected that a reaction summarized by the equation Si + 4HF → SiF₄ + 2H₂ occurs and the evolved hydrogen is responsible for the reduction of the hexafluoride. If this is the case, then the Si–HF reaction must be fast in order for the rates of the two reduction reactions to be comparable. Examination of the Si–HF reaction in the absence of metal fluorides indicates that H₂ is evolved but at a rate apparently too slow to be important. The direct reaction of silicon metal with the hexafluoride must control the reaction rate.

The pentafluorides and tetrafluorides have been characterized by chemical analyses, by powder X-ray patterns, by mass spectrometry and, in part, by vibrational spectroscopy. The characterization data fully supported the composition of the compounds. Three points are worth discussion. The ReF₅ and OsF₅ X-ray powder patterns cannot be indexed with the unit cell parameters determined by single-crystal studies.^{17,18} In addition, for ReF₅, comparison of our film data with two other workers' data¹⁹ indicates that the patterns vary as a function of several preparation methods. It is concluded that the pentafluorides and perhaps the tetrafluorides may be polymorphic.

Several pentafluoride crystal structures^{2,7,17,18} have been determined and all are dominated by extensive metal–fluorine bridging which results in the formation of tetrameric or linear chain networks. The crystal structures of the tetrafluorides have not been reported, but they also are expected to be dominated by M–F–M bridging.

The gas-phase structures of MF₅ and MF₄ are of considerable interest. The mass spectra of the vapors above the MF₅ solids (23°) and MF₄ solids (100–200°) are shown in Table I. The pentafluorides show significant intensity in the dimer and trimer ion envelopes²⁰ in agreement with the recent detailed molecular beam study by Falconer and coworkers.²¹ Previously we reported the observation of oligomer ions for MoF₄.²² As seen in Table I, ReF₄, OsF₄, and IrF₄ also display ion envelopes assigned to M₂F_x⁺ and M₃F_x⁺ species. Two factors preclude formation of these ions in the ion source. First, all spectra are recorded at relatively low ion source pressures, ca. 8 × 10⁻⁵ Torr. Second, spectra recorded at 20 eV show greater relative intensities for M₃F_x⁺, M₂F_x⁺, MF₄⁺, and MF₃⁺ ions and lesser intensities for MF_{2,1}⁺ ions. Although careful variable ionization energy studies and neutral progenitor identifications have not as yet been made, the data in hand are consistent with the presence of neutral oligomers in the

gas phase above MF₅ and MF₄. Further studies of these vapors are warranted.

The infrared spectra listed in Table II show one common band in each compound: a broad absorption at about 530 cm⁻¹. From this work and earlier studies,²³ the assignment of the band as an M-F-M bridge mode appears to be certain. This band is further evidence for highly bridged polymeric structures of both the pentafluorides and tetrafluorides.

Registry No. ReF₅, 30937-52-1; ReF₄, 15192-42-4; OsF₅, 31576-40-6; OsF₄, 54120-05-7; IrF₅, 14568-19-5; IrF₄, 10025-97-5; ReF₆, 10049-17-9; OsF₆, 13768-38-2; IrF₆, 7783-75-7; Si, 7440-21-3; H₂, 1333-74-0; HF, 7664-39-3.

Supplementary Material Available. A listing of powder pattern *d* values for ReF₄, OsF₅, OsF₄, IrF₅, and IrF₄ will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.50 for microfiche, referring to code number AIC40513T.

References and Notes

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Synthesis, Characterization, and Structure of Uranium Oxide Tetrafluoride¹

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The synthesis of uranium oxide tetrafluoride from the combination of uranium hexafluoride and quartz wool (SiO₂) in anhydrous hydrogen fluoride solution is reported. The slow reaction 4HF + SiO₂ → SiF₄ + 2H₂O provides a stoichiometric, one-step, controlled, partial hydrolysis of UF₆. The characterization of UOF₄ including electronic and vibrational spectra of the solid is presented. The crystal structure as determined from three-dimensional single-crystal X-ray data collected by counter methods is described. A full-matrix least-squares refinement using 300 observed reflections resulted in a final *R* = 4.2%. The structure refines in the trigonal space group *R*3*m*. The hexagonal cell constants are *a* = 13.22 (1) Å and *c* = 5.72 (1) Å with *V* = 865.7 cm³, *d_c* = 5.70 g/cm³, and *Z* = 9. The idealized coordination sphere of UOF₄ consists of a pentagonal bipyramid of light atoms surrounding the central uranium. An oxygen atom and fluorine atom occupy indistinguishable axial positions with the U-O and U-F distances in the range 1.77-1.79 (3) Å. The equatorial belt contains one unique unbridged fluorine (U-F_{eq} = 1.98 (3) Å) and four bridged fluorines (U-F_{br} = 2.25-2.29 (3) Å). The observed chemistry and structure are compared and discussed in relation to transition metal oxide tetrafluorides and previously reported uranium oxide fluorides.

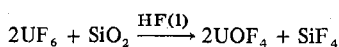
Introduction

The simple yet important compound uranium oxide tetrafluoride, UOF₄, has had an uncertain history. It was first suggested by Brooks and coworkers² that UOF₄ might be the principal product of a gas-phase reaction of UF₆ with very low partial pressures of water. Surprisingly, their experiments indicated that, in the presence of excess hexafluoride, UF₆ and water combine in a 1:3 ratio to give a mixture of UO₂F₂ and UO₂F₂·2H₂O. Bartlett and Robinson,³ as part of a study of the fluorination properties of SeF₄, reported the formation of a cream-colored solid from the reaction of UO₃ and SeF₄. The compound analyzed as UOF₄. A subsequent reinvestigation of this reaction by Otey and LeDoux⁴ was unsuccessful in producing UOF₄. In the same study, Otey and LeDoux, outlined a detailed investigation of the gas-phase, water-deficient hydrolysis of UF₆. They identified one new compound, U₃O₅F₈, and suggested the presence of an intermediate compound, U₂O₃F₆, but found no evidence for UOF₄. Until

very recently, the synthesis of UOF₄ apparently received little further attention.

We previously reported a simple, high-yield synthesis of ReOF₄,⁵ MoOF₄,⁶ and WOF₄⁶ from the controlled hydrolysis of the corresponding hexafluorides. Because of this success and the uncertainty surrounding the existence of UOF₄, we initiated a study of the controlled-hydrolysis chemistry of UF₆. During the course of our study two additional reports on syntheses of UOF₄ appeared. Wilson⁷ and Jacob and Pollick⁸ allowed UF₆ to react with dilute solutions of water in liquid HF. In each study an orange powder was collected and identified as UOF₄.

We report here a simple high-yield synthesis of UOF₄ from a solution-phase controlled-hydrolysis reaction. The synthesis is summarized by the equation



The UOF₄ was characterized, and the crystal structure was