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THE SYNTHESIS AND CHARACTERIZATION OF SOME OXIDE FLUORIDES OF RHENIUM AND OSMIUM

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SUMMARY

Existing synthetic methods for oxide fluorides of rhenium and osmium have been reviewed. New syntheses, using static heating, have been developed for OsO_3F_2, OsO_2F_3, $OsOF_5$, $OsOF_4$, ReO_3F, ReO_2F_3, $ReOF_5$, and $ReOF_4$. The products were characterized principally by mass spectroscopy, with supporting information from X-ray powder diffraction, chemical analysis, and molecular beam electric deflection. Tables of the mass spectra and the electric deflection data are presented.

INTRODUCTION

Synthetic methods are available in the literature for OsO_3F_2, OsO_2F_3, $OsOF_5$, and $OsOF_4$ [1-4] and for $ReOF_5$, ReO_2F_3, ReO_3F, $ReOF_4$, and $ReOF_3$ [1]. In addition, an unidentified four-coordinate osmium oxide fluoride, probably OsO_3F or OsO_2F_2, has been studied crystallographically by Burbank [5]. Available syntheses were not found to be universally convenient, or sufficiently clean for certain structural investigations underway in our laboratory. Therefore, new synthetic methods have been developed for several oxide fluorides of osmium and rhenium. This paper briefly describes these new syntheses, reviews existing methods, and describes the characterization of the compounds obtained with particular emphasis on their mass spectra.

Mass spectra were obtained using a modulated molecular beam source mass spectrometer [6]. Polarity of the neutral molecular beam species was determined by electrostatic deflection in a quadrupole electric field [6,7].

Osmium Oxide Fluorides

The possible simple oxide fluorides of osmium are listed in Table 1. Only OsO_3F_2, OsO_2F_3, $OsOF_5$ and $OsOF_4$ are known, plus either OsO_2F_2 or OsO_3F identified crystallographically. Attempts to prepare the six and seven coordinated eight valent osmium compounds OsO_2F_4 and $OsOF_6$ have not been successful. Quite likely, OsO_2F_4 disproportionates at modest temperatures, while $OsOF_6$ is unstable because of ligand crowding. The lower valent, less coordinated oxide fluorides present difficulties not only of synthesis, but of separation and characterization. Examination with the molecular beam mass spectrometer, so useful in characterizing the volatile species, has aided in identifying decomposition products of involatile lower oxide fluorides of osmium, but the stoichiometry or purity of these samples could not be determined.

TABLE 1

Oxide Fluorides of Osmium

Formal Valence State	Compound		
8	OsO_3F_2	OsO_2F_4	$OsOF_6$
7	OsO_3F	OsO_2F_3	$OsOF_5$
6		OsO_2F_2	$OsOF_4$
5		OsO_2F	$OsOF_3$
4			$OsOF_2$
3			$OsOF$

OsO_3F_2

Hepworth and Robinson [8] prepared osmium trioxide difluoride by reaction of OsO_4 with BrF_3 and by the oxyfluorination of Os sponge in a flow system. The resulting OsO_3F_2 was an orange solid, M.P. ~ 170°C, with three known crystalline modifications [9]. We were unable to free samples prepared by the BrF_3 - OsO_4 reaction completely of interfering bromine containing species. Therefore, we attempted to prepare OsO_3F_2 by direct fluorination of OsO_4.

Heating a 2:1 F_2:OsO_4 mixture at 300°C for ~ 50 hours converted OsO_4 into OsO_3F_2. The orange solid melted at 172° - 173°C. Chemical analysis gave Os = 70%, F = 14.4% (required for OsO_3F_2: Os = 68.9%, F = 13.8%). The mass spectrum, Table 2, is reasonable for OsO_3F_2, and is consistent with that of a sample prepared by reaction of BrF_3 and OsO_4 with contaminant peaks omitted.

OsO_2F_3

By reacting equimolar mixtures of OsO_4 and OsF_6 at 150°C for 17 hr in an openable Monel reactor, a yellow-green powder was obtained on the cooler, upper portions of the reactor. The same product was obtained by heating $OsOF_4$ and OsO_3F_2 for 12 hours at 100°C in a rotatable Raman cell with a Monel body and a sapphire window. This material was identified by elemental analysis, Raman spectroscopy, magnetic susceptibility, and mass spectrometry to be osmium dioxide trifluoride [4]. On heating sufficiently for a mass spectrum to be obtained, OsO_2F_3 disproportionates and a composite spectrum of OsO_2F_3, OsO_3F_2, and $OsOF_4$, with slight contamination by OsO_4, is observed at ~ 60°C. At higher temperatures, ~ 110°C, OsO_4 and OsF_6 mass spectra are also seen. The mass spectrum of OsO_2F_3, obtained by subtracting contributions from $OsOF_4$ and OsO_3F_2 from a composite spectrum is presented in Table 2.

The focusabilities of OsO_3F_2, OsO_2F_3, and $OsOF_4$ were obtained on characteristic mass peaks of the same mass

TABLE 2

Relative Ion Abundances for Some Oxide Fluorides of Osmium

	$OsOF_4$ 50° C	$OsOF_5$ 25° C	OsO_2F_3 80° C	OsO_3F_2 115° C
Os^+	20	28	19	18
OsO^+	8	12	17	18
OsF^+	16	28	24	12
OsO_2^+			9	14
$OsOF^+$	13	18	25	22
OsF_2^+	18	31	16	9
OsO_3^+				14
OsO_2F^+			38	30
$OsOF_2^+$	36	24	47	16
OsF_3^+	11	23	10	
OsO_3F^+				100
$OsO_2F_2^+$			100	32
$OsOF_3^+$	100	37	28	
OsF_4^+	10	17		
$OsO_2F_3^+$			17	
$OsOF_4^+$		100		
OsF_5^+		10		
$OsOF_5^+$		14		

Note: All Percentages based on 192 Isotope of Osmium. Contributions to oxide fluoride or oxide ions from 189 Isotope have been subtracted out.

spectrum. The amount of refocusing of $OsOF_4$ is notably higher than that for OsO_3F_2 and OsO_2F_3, as seen from the data in Table 3. Thus the focusing behavior is a diagnosti for mixtures with $OsOF_4$.

$OsOF_5$

Osmium oxide pentafluoride was prepared by Bartlett, Jha, and Trotter [10,11] by the fluorination of OsO_2 or the

TABLE 3

Focusing Characteristics of Some Rhenium and Osmium Oxide Fluorides

Molecule	%Refocusing	Refocusing Potential (KV)	Orifice Diameter (cm)
OsO_2F_3	5	5	.044
OsO_3F_2	5	5	.044
$OsOF_5$	20	5	.032
$OsOF_4$	35	5	.044
ReO_2F_3	5	5	.013
ReO_3F	15	5	.013
$ReOF_5$	25	5	.032
$ReOF_4$	15	5	.013
$Re_2O_4F_6$	Defocuses	20	.013

oxyfluorination of Os metal. Holloway, et al. [12] reported better yields by the static oxyfluorination of the metal. A substantial yield of $OsOF_5$ is also obtained from the fluorination of OsO_3F_2 in excess fluorine at 180°C [10].

By reacting a 3:1 OsF_6/OsO_4 mixture for 17 hours at 150-200°C, $OsOF_5$ and $OsOF_4$ were formed in about a 2:1 ratio. The OsF_6 was entirely consumed. $OsOF_5$ was the only product volatile at 0°C and thus was readily recovered. Its mass spectrum, Table 2, is identical with that of samples prepared by oxyfluorination of osmium powder. $OsOF_5$ can also be prepared by fluorination of $OsOF_4$ at 175°C with a modest excess of F_2, but because of the relative difficulty in obtaining $OsOF_4$, this synthetic route is not attractive.

$OsOF_4$

Osmium monoxide tetrafluoride has been prepared in small amounts by reduction of $OsOF_5$ on a hot tungsten wire [3]. It is also formed by static heating of stoichiometric amounts of the elements, but with heavy contamination by OsF_5 which is difficult to remove. Reaction of OsF_6 with Pyrex or quartz wool gives a yellow material, predominately $OsOF_4$ and OsF_5, but $OsOF_4$ could not be cleanly separated from this mixture [13].

From the reaction of OsF_6 with OsO_4, above, the non-volatile product is green or blue-green $OsOF_4$. To minimize contamination of the $OsOF_4$ by OsF_5, the optimum ratio of OsF_6 to OsO_4 is 2.5:1, and 175°C is a satisfactory reaction temperature. The mass spectrum, Table 2, is identical with that reported previously [3]. The material melts at 82 ± 1 °C.

OsO_3F, OsO_2F_2

From the yellow product of the reaction of OsF_6 with Pyrex glass, one small, nearly colorless crystal was obtained in a quartz capillary in a thermal gradient [13]. The structure of this material, which is neither OsO_4 nor OsF_4, shows it to be four-coordinated osmium [5]. Its volatility suggests the formulations OsO_3F or OsO_2F_2 as being most likely.

Lower Valent Osmium Oxide Fluorides

By fluorinating OsO_2 either with F_2 or OsF_6 under relatively mild conditions, a major volatile product is OsO_4. At 200°C, with a 4:1 fluorine to OsO_2 ratio, impure OsO_3F_2 is formed as a solid product, presumably by the fluorination of the OsO_4. At 150°C and below, black solids are obtained which evolve OsO_4 on heating to temperatures between 150 and 300°C and above. The black materials must be lower oxide fluorides of osmium, which disproportionate on heating to give largely OsO_4 and osmium fluorides. The black powders are crystalline, but essentially uncharacterized.

Rhenium Oxide Fluorides

The possible simple oxide fluorides of rhenium are listed in Table 4. The three seven valent species ReO_3F, ReO_2F_3, and $ReOF_5$, and six valent $ReOF_4$ have been well characterized [1, 14]. $ReOF_3$ is also suggested in the literature [14,15]. In addition, Ruff and Kwasnik [16] suggested the synthesis of ReO_2F_2 and $ReOF_2$, but later experiments by Peacock, et al. [15,17] indicated that these assignments were erroneous. As with the osmium compounds, the lower oxide fluorides of rhenium have not been isolated or characterized, although heating of involatile residues from attempted syntheses indicates the existence of one or more additional species.

TABLE 4

Oxide Fluorides of Rhenium

Formal Valence State	Compounds		
7	ReO_3F	ReO_2F_3	$ReOF_5$
6		ReO_2F_2	$ReOF_4$
5		ReO_2F	$ReOF_3$
4			$ReOF_2$
3			ReOF

ReO_3F

Per-rhenyl fluoride was first convincingly made by Engelbrecht and Grosse [18] by the interaction of ReO_3Cl

and anhydrous HF. It has also been obtained in good yield by refluxing finely divided $KReO_4$ in IF_5 [19]. The material is yellow, M.P. 147°C and B.P. 164°C.

We have prepared ReO_3F by reacting 0.5g ReF_7 with 2.3g Re_2O_7 at 150°C for 20 hours in a 250 cm^3 Monel reactor with an openable top. A hard, blue green material was recovered. This was heated to 65°C in a quartz tube. Yellow material which sublimed to the cooled part of the tube gave a mass spectrum entirely consistent with the composition ReO_3F (see Table 5) with minor contamination by ReO_2F_3 which could be removed by careful sublimation. Using a slight excess of Re_2O_7 (mole ratio $Re_2O_7:ReF_7$ of 3.6:1) eliminated the ReO_2F_3 contaminant. The ReO_3F could more readily be sublimed away from the excess Re_2O_7 to give a yellow product which did not yield a melting point as the material blackened and apparently decomposed at 110°-115°C.

ReO_2F_3

Rhenium dioxide trifluoride has been prepared [17] with 10 - 30% $ReOF_5$ by the fluorination of ReO_2 or $KReO_4$ in a glass flow system. ReO_2F_3 is a pale yellow solid, M.P. 90°C and B.P. 185°C [20].

In a static Monel system, no reaction was observed on heating $KReO_4$ with excess F_2 to 350°C. However, when a little powdered quartz was admixed with the $KReO_4$, both $ReOF_5$ and ReO_2F_3 were produced. In the absence of glass, the fluorination of ReO_2 with a 2:1 mole ratio $F_2:ReO_2$ in a static Monel system occurred readily at 400°C but not at 275°C. Relatively pure samples of both $ReOF_5$ and ReO_2F_3 were obtained. The same products were obtained by heating a 1:1 mixture of F_2 and ReO_3 at 200°C.

The fluorination of Re_2O_7 at 200°C for 65 hours with a 4:1 mole ratio of F_2 to Re_2O_7 yielded an almost white solid which melted at 115°C to give a pale yellow liquid. Chemical analysis gave F:20.6%, Re:67.6% (expected for ReO_2F_3: F:20.7%, Re:67.7%). Its mass spectrum, Table 5, is that to be expected for ReO_2F_3. No impurities were detected. Focusing experiments showed ReO_2F_3 to be polar.

TABLE 5

Relative Ion Abundances for Some Oxide Fluorides of Rhenium

	ReO_3F 57°C	ReO_2F_3 79°C	$ReOF_4$ 67°C	$ReOF_5$ 25°C
Re^+	12	11	10	8
ReO^+	15	10	5	5
ReF^+	4	9	11	13
ReO_2^+	18	8		
$ReOF^+$	14	16	14	15
ReF_2^+		9	14	18
ReO_3^+	21			
ReO_2F^+	31	12		
$ReOF_2^+$		17	20	21
ReF_3^+		5	12	18
ReO_3F^+	100			
$ReO_2F_2^+$		100		
$ReOF_3^+$		16	100	37
ReF_4^+			6	11
$ReO_2F_3^+$		2		
$ReOF_4^+$			19	100
ReF_5^+				8
$Re_2O_4F_5^+$		2		

$ReOF_5$

Rhenium oxide pentafluoride was the minor product from the fluorination of ReO_2 or $KReO_4$ in a flow system ,and it is readily separable from ReO_2F_3 by sublimation [17]. Better yields were obtained by the static fluorination of ReO_2

[12,21]. It is a cream colored, relatively volatile material, M.P. 41°C and B.P. 73°C [20].

Fluorination of $ReOF_4$ at 300°C in a 50% excess of F_2 in a Monel reactor with a top cooled to 10°C quantitatively yielded $ReOF_5$, which could be readily sublimed from the reactor. The material was cream colored and gave a mass spectrum expected for $ReOF_5$ (Table 5). $ReOF_5$ could also be prepared by fluorination of ReO_2 at 250°C for 25 hours and by fluorination of ReO_3 at 200°C for 17 hours. The latter method also produced some ReO_2F_3, which could be separated by sublimation.

$ReOF_4$

Blue, crystalline rhenium oxide tetrafluoride can be synthesized by the reaction of ReF_6 with metal carbonyls [15]. It is more cleanly made by the controlled but rather slow hydrolysis of ReF_6 by SiO_2 [22]. The partial hydrolysis of ReF_6 in HF is a very satisfactory way to prepare $ReOF_4$ [23]. An equimolar quantity of ReF_6 is added to a solution of HF containing a given quantity of H_2O. The HF and any excess ReF_6 are pumped off the blue solution to yield the blue $ReOF_4$ powder. $ReOF_4$ has M.P. 108°C and B.P. 172°C [19], with both trimeric [24] and infinite fluorine bridged chain [25] crystal modifications.

The oxyfluorination of rhenium powder with a stoichiometric amount of 1:4 O_2:F_2 mixture at 300°C for 17 hours gave a good yield of blue, crystalline $ReOF_4$ and some yellow ReF_6 which was readily removed by sublimation. The characteristic mass spectrum of $ReOF_4$ was used for identification (Table 5). The melting point was 107 ± 2°C.

The fluorination of ReO_3 at 200°C with a 2:1 mole ratio F_2 to ReO_3 also yields $ReOF_4$, but with considerable ReO_2F_3 contamination which is difficult to separate.

$ReOF_3$

Black, involatile rhenium oxide trifluoride is formed [19] by the attack of $ReOF_4$ on Pyrex glass at 250°C. It has a tetragonal crystal habit.

Lower Valent Rhenium Oxide Fluorides

A number of residues from reactions of ReF_7 and Re_2O_7, $ReOF_5$ and KF, ReO_2F_3 and Si, and $ReOF_4$ and Si evolved ReO_3F and some other oxide fluorides at temperatures between 200 and 500°C, much higher than the normal volatilization temperatures of the known oxyfluorides of rhenium. Effort is being made to characterize the residues, but tentatively they represent one or more lower oxide fluorides which disproportionate to give the more stable species such as ReO_3F. In this regard, ReO_3F plays a comparable role to OsO_4 in the osmium systems.

DISCUSSION

Mass spectral analysis was made on all solid and gas samples prepared. Solids were heated in a Monel oven until the vapor pressure behind the orifice increased to the point where sufficient molecular beam intensity was obtained. Orifice diameters ranging from 0.013 to 0.044 cm were used because of the tendency of osmium oxide fluorides, when heated to their melting point, to plug a small orifice. Small diameters were used whenever possible to minimize consumption of the sample. A variable temperature Monel inlet with fixed 0.032 cm orifice was used for gas phase samples.

The mass spectra of Tables II and V were taken at 70 eV electron energy. No correction has been made for quadrupole mass filter transmission loss with ions of increasing mass [26] because mass filter ion energy was programmed to partially compensate for this effect.

Magnitudes of the electric deflection polarity measurements were subject to many variables [7,27]. The geometry of the stopwire, source, detector, and defining orifices particular to this instrument determined the amount of refocusing that could be observed. Refocusing for a given molecule was higher with a large diameter orifice than with a small one. Relatively small source misalignments were found to be capable of altering the refocusing magnitude by a factor of two. Consequently, electric deflection data were primarily used qualitatively. An indication of sensitivity for detection of polar species was given by 15% refocusing on ReO_3F, with a dipole moment of 0.82 Debye [28].

Focusabilities listed in Table III were calculated as the fraction of the beam, with stopwire out, that could be returned with the stopwire in and a potential applied to the quadrupole rods. Of the molecules studied, only the dimer of ReO_2F_3 failed to indicate a positive electric deflection (Table III). Because OsO_2F_3, OsO_3F_2, and ReO_2F_3 refocus, they cannot possess static D_{3h} symmetry with axial oxygen atoms for OsO_2F_3 and ReO_2F_3 and with axial fluorine atoms for OsO_3F_2. These molecules must not have electrically centro-symmetric structure.

Phase measurements from the modulated molecular beam can be of particular value when mixtures of different species or of monomer and polymers of the same species are encountered [6]. Only for ReO_2F_3 was a dimer observed and a dimer versus monomer phase relationship obtained. A 3 to 10 degree phase difference between $ReO_2F_2^+$ and $Re_2O_4F_5^+$ was measured at temperatures of 75 to 90°C. The calculated phase difference between the neutral parents ReO_2F_3 and $Re_2O_4F_6$ at 80 hertz chopping frequency was 43 degrees. Therefore, the molecular beam was composed of a mixture of monomer and dimer. Since $Re_2O_4F_6$ defocused and ReO_2F_3 refocused slightly, a small amount of polar ReO_2F_3 was mixed with or produced by decomposition of non-polar $Re_2O_4F_6$. Decomposition could occur by the breakdown of a possible double fluorine bridged, square bipyramidal $Re_2O_4F_6$, with planar oxygen atoms, into polar, trigonal bipyramidal ReO_2F_3 with axial fluorine atoms.

X-ray powder diffraction pictures were made of starting materials, prepared samples, and residues after many mass spectral analyses. At this time we have been unable to identify the powder pattern residues from samples which gave off ReO_3F or OsO_4 as decomposition products. From residue analysis it was determined that the reaction $3ReO_3 \rightarrow Re_2O_7 + ReO_2$ takes place at temperatures above 330°C.

CONCLUSION

Static heating of the proper ratio of starting materials on Monel surfaces has proved successful in the preparation of rhenium and osmium oxide fluorides. Impurity levels, determined by mass spectrometry, ranged from not detectable to less than five per cent.

Mass spectrometry proved to be a practical method for characterizing materials and determining the levels of impurities in the samples analyzed. Problem analyses were resolved by x-ray powder patterns and electric quadrupole deflection measurements.

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