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Contribution from the Department of Chemistry and the Materials Research Center, Northwestern University, Evanston, Illinois 60201

Partial Hydrolysis of Rhenium and Osmium Hexafluorides. An Improved Synthesis and Characterization of Rhenium Oxide Tetrafluoride

R. T. Paine[1]

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Simple transition metal oxide tetrafluoride compounds, MOF_4, have been known for some time. A convenient, general synthesis for the compounds, however, has not been described. In particular, rhenium oxide tetrafluoride was reported by Hargreaves and Peacock[2] as an unexpected but major product of the reaction between ReF_6 and metal carbonyls, *e.g.*, $W(CO)_6$. In our laboratory only small amounts of $ReOF_4$ have been isolated from this reaction. This observation is in agreement with a recent study by O'Donnell and Phillips[3] which indicated that under rigorously dry conditions a rhenium carbonyl fluoride, $Re(CO)_3F_3$, is the major product of the above reaction. Osmium oxide tetrafluoride was recently reported by Falconer and coworkers[4] to be a product of the reduction of $OsOF_5$ by a hot tungsten filament.

In the light of these studies, a general, improved synthesis for MOF_4 compounds was desired. We report here on a simple, high-yield synthesis of $ReOF_4$ from the partial hydrolysis of ReF_6. The initial hydrolysis chemistry of ReF_6 and OsF_6 also is qualitatively compared.

Experimental Section

The manipulation of the volatile compounds was accomplished in a Monel vacuum line[5,6] fitted with Pyrex glass reaction vessels and auxiliary Kel-F U traps. The metal vacuum line and Kel-F U traps were conditioned with fluorine and ClF_3. The glass reaction vessels were flamed and/or evacuated as described below but were not chemically conditioned. The ReF_6 and OsF_6 were prepared by known methods.[7,8] The metal hexafluorides were freed of trace amounts of HF by pumping on the samples held at −78°. Conductivity grade anhydrous HF was provided by L. A. Quarterman, Argonne National Laboratory.[9]

The mass spectra were recorded with a modified Bendix Model 12 time-of-flight mass spectrometer. The vapors above the solids (25°) were sampled directly into the ion source region. Thin-film infrared spectra were recorded on a Beckman IR-9 spectrophotometer (4000–400 cm^{-1}); the low-temperature cell will be described elsewhere.[10] The Raman spectra were recorded on the instrument described by Claassen and coworkers.[11] The 4880-Å Ar^+ laser excitation line was used, and the $ReOF_4$–HF (conductivity grade) solution was contained in a $^1/_4$-in. o.d. Kel-F sample tube. The conductivity of $ReOF_4$–HF solutions was measured as described by Frlec and Hyman.[12] The cell constant was 0.04214 cm^{-1} and all measurements were recorded at 0°.

Hydrolysis of ReF_6. A new 250-ml Pyrex flask was thoroughly evacuated and flamed until a good vacuum was obtained (*ca.* 10^{-6} Torr).[13] A 2.0-mmol sample of ReF_6 was condensed into the flask; the flask was closed with a high-pressure valve and warmed to 25°. After 2 weeks no reaction was detected, and the ReF_6 was quantitatively recovered.

In a second procedure a new 250-ml Pyrex flask was pumped for 1 hr to *ca.* 10^{-4} Torr without flaming. A 4.0-mmol sample of ReF_6 was condensed into the flask and then held at 25° for 2 weeks. The volatile products were vacuum distilled and retained as follows: HF, BF_3, SiF_4 (−196°), ReF_6 (−78°). About 80% of the ReF_6 was recovered. A small amount of blue crystalline material was sublimed at 60° from the glass reactor. When an identical reaction was run at 70°, conversion of the ReF_6 went noticeably faster and blue crystals sublimed out of the heated zone onto cooler surfaces of the flask. The volatile products were vacuum distilled as outlined above and about 40% of the ReF_6 was recovered unreacted. Higher reaction temperatures generally led to significant decomposition of the blue solid.

In a third system a new 250-ml Pyrex flask was loosely packed with Pyrex wool and the flask pumped for 30 min to *ca.* 10^{-4} Torr. A 5.0–7.0-mmol sample of ReF_6 was condensed into the flask; the flask was closed with a high-pressure valve and warmed to 25°. The glass wool was slowly coated with a gray-brown deposit and tiny blue crystals. After 7–10 days, the volatile reaction products were distilled as described above. About 30% of the ReF_6 was recovered unreacted and about 1 g of blue solid was collected (*ca.* 60% yield $ReOF_4$). Similar reactions run at higher temperatures (50–70°) resulted in a faster reaction, but more gray deposits and less blue solid were produced. The blue solid was characterized as outlined below and found to be $ReOF_4$.

The 1:1 reaction of water and ReF_6 also was investigated. In all experiments less than 10% $ReOF_4$ was obtained, and considerable quantities of black nonvolatile solids were formed.

Hydrolysis of OsF_6. A 5.0-mmol sample of OsF_6 was condensed into a thoroughly flamed and evacuated (*ca.* 10^{-6} Torr[13]) Pyrex reaction vessel. The flask was held at 25° for 5 days with no apparent reaction. In a second procedure, a 3.2-mmol sample of OsF_6 was condensed into a new 250-ml Pyrex flask which had been pumped for 1 hr to *ca.* 10^{-4} Torr. The flask was held at 25° for 5 days with no apparent reaction. In a third procedure, a new 250-ml Pyrex flask loosely packed with Pyrex wool was pumped for 30 min to *ca.* 10^{-4} Torr without flaming. A 4.0-mmol sample of OsF_6 was condensed into the flask. The flask was held at 25° for 2 weeks with no apparent reaction. Similar reactions run at higher temperatures (70–80°) produced small yields (*ca.* 20% OsF_6 consumed) of a slightly volatile yellow solid. The yellow solid sublimed with decomposition at 90°.

Characterization of Products. The blue, moisture-sensitive, crystalline solid obtained from the hydrolysis of ReF_6 was found to sublime at *ca.* 60° and melt at *ca.* 109°. The mass spectrum of the vapors above the solid at 25° was recorded and the principal ions are listed here [*m/e* (assignment) relative intensity]: 279 ($^{187}ReOF_4^+$) 16, 277 ($^{185}ReOF_4^+$) 9, 263 ($^{187}ReF_4^+$) 3, 261 ($^{185}ReF_4^+$) 2, 260 ($^{187}ReOF_3^+$) 100, 258 ($^{185}ReOF_3^+$) 53, 257 ($^{187}ReO_2F_2^+$) 3, 255 ($^{185}ReO_2F_2^+$) 2, 244 ($^{187}ReF_3^+$) 5, 242 ($^{185}ReF_3^+$) 3, 241 ($^{187}ReOF_2^+$) 10, 239 ($^{185}ReOF_2^+$) 7, 225 ($^{187}ReF_2^+$) 8, 223 ($^{185}ReF_2^+$) 4, 222 ($^{187}ReOF^+$) 6, 220 ($^{185}ReOF^+$) 4, 206 ($^{187}ReF^+$) 7, 204 ($^{185}ReF^+$) 4, 203 ($^{187}ReO^+$) 3, 201 ($^{185}ReO^+$) 2, 187 ($^{187}Re^+$) 2, 187 ($^{187}Re^+$) 10, 185 ($^{185}Re^+$) 6. The infrared spectrum of a cold (−196°), sublimed thin-film sample was recorded and the absorptions (cm^{-1}) are as follows: 1075 (s), 710 (sh, m), 655 (s), 605 (sh, m), 555 (m). The Raman spectrum of a 3.8 *m* solution of $ReOF_4$ in HF was recorded at 25°. The bands (cm^{-1}) are 1072 (vs, pol), 667 (w), 303 (m), 256 (m), 245 (m), 168 (w, br). The solution was dark blue. The specific conductance of anhydrous HF at 0° was $\kappa_{solv} = 2.593 \times 10^{-5}$ ohm^{-1} cm^{-1}. The specific conductance at 0° of a 0.1004 *M* HF solution of $ReOF_4$ was $\kappa_{soln} = 35.8 \times 10^{-5}$ ohm^{-1} cm^{-1} which results in $\kappa_{soln}{}^{cor} = 33.2 \times 10^{-5}$ ohm^{-1} cm^{-1}. The equivalent conductance

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(1) Address correspondence to the author at CNC-4, Los Alamos Scientific Laboratory, P.O. Box 1663, Los Alamos, N. M. 87544.

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and degree of ionization were calculated: $\mu_{\mathrm{soln}} = 3.6$ ohm^{-1} cm^{-1} mol^{-1} and $\alpha \leq 1\%$.

The yellow solid obtained from the hydrolysis of OsF_6 has not been completely characterized due to the extreme reactivity of the compound.

Results

The slightly volatile, crystalline product isolated from the hydrolysis of ReF_6 was characterized by its melting point, mass, infrared, and Raman spectra, and conductivity in HF solution. Some details of the characterization are of interest.

The deep blue color and melting point (109°) of the solid are consistent with reported properties of $ReOF_4$ (mp 108°).[2] The mass spectrum of the vapors above the blue solid shows a low-intensity parent ion, $ReOF_4^+$ (relative intensity 16), and the fragmentation pattern is similar to the molecular beam mass spectrum of $ReOCl_4$ recorded by Singleton and Stafford.[14] No evidence for the existence of dimers ($Re_2O_2F_8$) or other rhenium oxide fluorides in the vapor phase is obtained from the mass spectrometric measurements. The infrared spectrum of a frozen (−196°), sublimed thin film of $ReOF_4$ shows three main bands and two shoulders at frequencies in agreement with data recorded by Edwards and Jones[15] on a powdered $ReOF_4$ sample. The absorption at 1075 cm^{-1} can be assigned to ν_1 which corresponds to a terminal Re=O stretch. The Raman spectrum of HF solutions of $ReOF_4$ shows seven bands (two polarized), and the band at 1072 cm^{-1} can be assigned to ν_1. Additional details of these vibrational spectra and infrared data obtained on $ReOF_4$ isolated in an Ar matrix will appear in a later publication.[10] The electrical conductivity measurements of $ReOF_4$-HF solutions show a small increase in specific conductance over the specific conductance of pure anhydrous HF, and a small degree of ionization (≤1%) is calculated. This result is consistent with the presence of a small amount of conducting impurity in the $ReOF_4$ or a slight ionization of $ReOF_4$ according to the equation $ReOF_4 + 2HF \rightleftharpoons H_2F^+ + ReOF_5^-$, but the principal rhenium species in HF solution must be $ReOF_4$.

Discussion

Several nonmetal fluoride compounds are known to undergo slow hydrolysis in moist glass. In several cases the normally undesirable hydrolysis reaction has been found to provide the simplest pathway to oxide fluoride derivatives. Two such reactions are

$$XeF_6 + \text{glass wool} \xrightarrow[H_2O]{25^\circ,\ \text{trace}} XeOF_4 + 2HF^{16}$$

$$IF_7 + \text{glass wool} \xrightarrow[H_2O]{25^\circ,\ \text{trace}} IOF_5 + 2HF^{17}$$

Trace amounts of water absorbed on the glass wool are thought to initiate the hydrolysis reaction. The subsequent cyclic HF-glass reaction $4HF + SiO_2 \rightarrow SiF_4 + 2H_2O$ provides a continuing source of water for the hydrolysis. At least one group of workers[2] has noticed that ReF_6 undergoes a similar reaction in glass, but no reports on the details or synthetic utility of the reaction have appeared.

The present study reveals that ReF_6 and OsF_6 are definitely stable at 25° in thoroughly dry Pyrex vessels but that both undergo hydrolysis in moist Pyrex reactors. It was found that the hydrolysis of ReF_6 proceeds at a reasonable rate either in a Pyrex flask held at *ca.* 70° or in a Pyrex flask filled with glass wool at 25° when no special care was taken to predry the flasks. Both procedures provide a convenient, high-yield (60–70%) synthesis of $ReOF_4$. The $ReOF_4$ is easily separable from the other products HF, SiF_4, BF_3, ReF_6, and ReO_2, and the unreacted ReF_6 may be recovered and reused. This simple reaction offers a significantly improved synthesis for $ReOF_4$.

Osmium hexafluoride on the other hand appears to be less susceptible to hydrolysis, reacting with moisture on the glass at 80°, but not at 25° even in the presence of glass wool. The hydrolysis pathway of OsF_6 is uncertain. The initial hydrolysis product (yellow solid), though not conclusively identified at this time, closely resembles the yellow by-product of a Os + F_2 (O_2 impurity) reaction reported briefly by Hargreaves and Peacock.[18] They suggested, on the basis of an osmium analysis, that the yellow solid was $OsOF_4$. This assignment, however, is not in agreement with the recent work of Falconer and coworkers.[4]

Studies directed toward the further characterization of the osmium system and the systematization of the hydrolysis chemistry of the remaining metal hexafluorides are in progress.

Registry No. ReF_6, 10049-17-9; $ReOF_4$, 17026-29-8; OsF_6, 13768-38-2; $OsOF_4$, 38448-58-7.

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Contribution from the Department of Chemistry, Massachusetts
Institute of Technology, Cambridge, Massachusetts 02139

Successful Fluorination of Neopentane. A Challenge Met by Direct Fluorination

N. J. Maraschin and R. J. Lagow*

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The fluorination of neopentane has been a goal toward which fluorine chemists have directed considerable effort since the end of the Manhattan project. This symmetrical, highly branched hydrocarbon has been found to be very difficult to fluorinate because it is sterically crowded and vibrational relaxation of the energy released is hindered. Careful studies of the reaction of neopentane with CoF_3[1] and with fluorine[2] using more conventional techniques have established that no perfluoroneopentane was formed by these

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