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

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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Successful Fluorination of Neopentane. A Challenge Met by Direct Fluorination

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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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methods. In 1955, a communication by Dresdner on the pyrolysis of CF_3SF_3 with C_3F_6 reported that a mixture of perfluoropentanes had been formed including perfluoroneopentane.[3] The compound was later purified and characterized by melting point[4] and ir[5] and nmr.[6]

Perfluoroneopentane, $C(CF_3)_4$, is also of interest because it possesses high symmetry. It is perhaps the most nearly spherical molecule known and its exterior surface is almost entirely fluorine bound to carbon. Unusual physical properties might be expected from interaction of the projecting nonbonding electrons and from the inert nature of the surface.

The apparatus and technique used to fluorinate neopentane has been described in general by Lagow and Margrave[7] and the new cryogenic reactor developed in our laboratory has been described in detail.[8] This cryogenic fluorination system consists of a 1-in. i.d. nickel reaction tube packed with fluorinated fine copper filings, immersed in a series of four cold baths to carefully control the reaction temperatures and to move a zone of reactants slowly along the length of the reactor, while exposing its surface to fluorination.

Neopentane (2.052 g, 2.82×10^{-2} mol) was condensed into the first two traps of the cold reactor, which had been flushed with helium and cooled to −78°. The helium flow was initiated at 20 cc/min and the fluorine flow at 1.5 cc/min and continued for 48 hr. The first trap of the cold reactor was allowed to warm and the third trap was cooled. The helium flow was shut off and 1.5 cc/min of pure fluorine passed through the system. Twenty-four hours later, the last trap was cooled to −78° and the second trap was warmed. A glass trap at the end of the system, filled with NaF, was also cooled to −78°. After 24 hr, the third trap was warmed and following another 24 hr, the fluorine was shut off, a helium flow of 20 cc/min was begun, and the last trap of the cold reactor was warmed. Helium was passed through the system for 12 hr after the last trap had reached room temperature. The glass trap was removed from the system, cooled in liquid nitrogen, and evacuated. The trap was then allowed to warm to room temperature and was shaken periodically for 12 hr. The volatile material was pumped off into a liquid nitrogen cooled vial, diluted with CCl_4, and subsequently separated by gas chromatography. A 10 ft × 0.25 in. column of 10% SE-30 on Chromosorb P was held at 0° for the separation. Perfluoroneopentane had a retention time of 3.5 min from injection. Perfluoroneopentane (0.849 g, 0.294×10^{-2} mol) was obtained which corresponds to a 10.4% yield. The melting point was determined in a sealed capillary and found to be 72.5-73° in agreement with the reported value.[4] *Anal.* Calcd for C_5F_{12}: C, 20.84; F, 79.15. Found: C, 20.67; F, 79.23. The gas-phase infrared spectrum contained three strong bands at 1300, 980, and 720 cm^{-1} and a very weak band at 1190 cm^{-1}, in agreement with the reported spectrum. The ^{19}F nmr spectrum consisted of a singlet at −13.92 ppm from an external trifluoroacetic acid reference. A value of −13.8 ppm has been reported for perfluoroneopentane.[6] The mass spectrum of the compound at 70 eV does not contain a parent peak but exhibits a strong P − 19 peak at 269. The CF_3^+ ion is the most intense peak in the spectrum. The known physical properties of this unusual, colorless, and extremely volatile fluorocarbon pose a very interesting problem. The intermolecular forces in fluorocarbons are not well understood; however, one would expect that any attraction would be due primarily to van der Waals interactions. The boiling points of the perfluoropentane isomers, *n*-perfluoropentane and isoperfluoropentane, are known to be 29.3 and 29.9-30.1°, respectively.[1] In contrast, the melting point of perfluoroneopentane is 72.5-73°. Of course, the molecular weights are the same. One might expect that perfluoroneopentane would have a higher melting point that the other two isomers since it should exhibit more regular stacking in its crystalline form. However, one would predict that the normal and iso structures would have stronger van der Waals interactions. Unless the van der Waals interactions have a positive effect on volatility, this disparity in physical properties is striking. It has been observed that highly branched hydrocarbons often have higher melting and boiling points than linear isomers.

Registry No. $C(CF_3)_4$, 374-51-6; neopentane, 463-82-1; fluorine, 7782-41-4.

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Kinetic Study of the Association between Chromium(VI) and[1] Aquopentaamminecobalt(III) in Aqueous Perchlorate Media

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In a previous study of this system[2] a limited amount of data was presented which indicated an observable time-dependent step prior to the establishment of equilibrium concentrations of the species. The present communication presents the results of a more detailed kinetic study for the reaction in which an inner-sphere complex ion is formed presumably by substitution on the chromate ion.

Experimental Section

Reagents. The preparation and standardization of stock solutions of perchloric acid, lithium perchlorate, sodium dichromate, and aquopentaamminecobalt(III) perchlorate have been described in a previous publication.[2] The preparation of the diaquotetraamminecobalt(III) perchlorate has been described by White and Newton.[3]

Procedures. Kinetic measurements were made with a Durrum stopped-flow spectrophotometer thermostated at 25.0 ± 0.1°. The reactions were carried out with large excess of the cobalt salts at 255 and 260 nm for the aquopentaamminecobalt(III) and 290 nm with the diaquotetraamminecobalt(III). Hydrogen ion concentrations of the equilibrium mixtures were determined as previously described.[2] Stock solutions were prepared just prior to use. The reaction system was flushed with these solutions until constant A_e values were obtained and then kinetic traces recorded for the reactions. Triplicate determinations were carried out for each set of concentrations. The kinetic traces (at least 15 A, time data points) were analyzed as a first-order process. The data were adjusted in terms of the expression

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