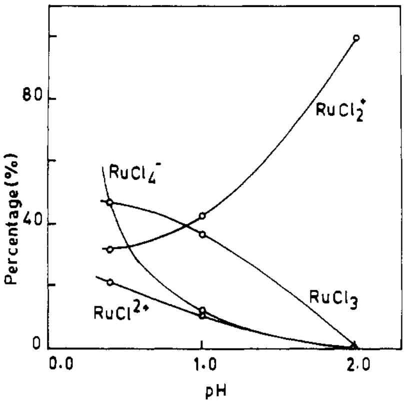
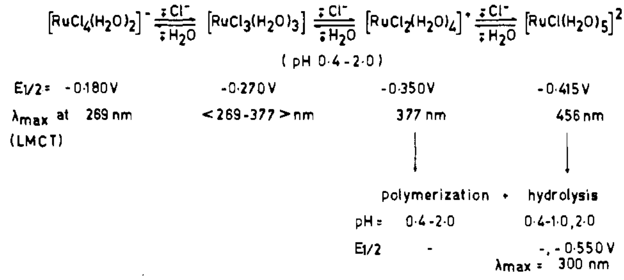


Figure 6. Distribution of the percentage of ruthenium(III) chloro complexes with solution pH (t = 25 °C, μ = 0.1 M (KCl)).

Scheme I



Halpern et al.,[8] these species are highly labile and exist to a maximum concentration in hydrochloric acid upto 4 N. These labile species on dilution to lower pH (0.4–2.0) dissociate to their lower chloro complexes and attain an equilibrium in solution as described in Scheme I. Of these species, $[RuCl_2(H_2O)_4]^+$ ions are the most stable in the pH range investigated and the rest, which are less stable, get converted to the former stable species under the experimental conditions. However, when they age, $[RuCl_2(H_2O)_4]^+$ ions become unstable and polymerize extensively as evidenced by nonreducibility at the DME. The species $[RuCl(H_2O)_5]^{2+}$ also undergo polymerization (pH 0.4 and 1.0) along with hydrolysis (pH 2.0).

Moreover, the observation of the color changes in experimental solutions from yellowish brown to light yellow (pH 0.4), colorless (pH 1.0), and light brick red (pH 2.0), slow precipitation in stored solutions at pH 7.0, and immediate formation of black precipitate at pH 3.0 strengthen the formation of polymeric species in solution.

The equilibria existing in solutions for the various ruthenium(III)–chloro species in the pH range studied may be expressed by

$$[RuCl(H_2O)_5]^{2+} + Cl^- \overset{K_1}{\rightleftharpoons} [RuCl_2(H_2O)_4]^+ + H_2O \quad (1)$$

$$[RuCl_2(H_2O)_4]^+ + Cl^- \overset{K_2}{\rightleftharpoons} [RuCl_3(H_2O)_3] + H_2O \quad (2)$$

$$[RuCl_3(H_2O)_3] + Cl^- \overset{K_3}{\rightleftharpoons} [RuCl_4(H_2O)_2]^- + H_2O \quad (3)$$

With use of the data on the percentage of each species (Figure 6) in solution, these constants K_1, K_2, and K_3 ($0.4 < pH < 2.0$) can be calculated with the help of appropriate equations by assuming a constant excess of chloride ion concentration. These constants at 25 °C (μ = 0.1 M KCl, pH 1.0) are 4.05, 0.86, and 0.33, respectively.

The constants K_1, K_2, and K_3 reported by Ohyoshi et al.[19] in $HClO_4$–HCl medium at 6 °C (μ = 0.46) with the help of the electrophoresis technique are 20, 2.8, and 0.6, respectively. These values, however, cannot be compared directly with our results because of the difference in experimental conditions.

Registry No. $[RuCl(H_2O)_5]^{2+}$, 26167-23-7; $[RuCl(H_2O)_5]^+$, 35594-90-2; $[RuCl_2(H_2O)_4]^+$, 99922-04-0; $[RuCl_2(H_2O)_4]$, 100017-79-6; $[RuCl_3(H_2O)_3]$, 15203-91-5; $[RuCl_3(H_2O)_3]^-$, 99922-05-1; $[RuCl_4(H_2O)_2]^-$, 100017-77-4; $[RuCl_4(H_2O)_2]^{2-}$, 100017-78-5; Ru, 7440-18-8; KCl, 7447-40-7.

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Formation of Actinide Hexafluorides at Ambient Temperatures with Krypton Difluoride

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A second low-temperature agent, krypton difluoride, for generating volatile plutonium hexafluoride is reported (dioxygen difluoride is the only other reported agent). Plutonium hexafluoride is formed at ambient or lower temperature by the treatment of various solid substrates with krypton difluoride. Volatilization of uranium and neptunium from solid substrates using *gaseous* krypton difluoride is also reported for the first time. The formation of actinide hexafluorides has been confirmed for the reaction of krypton difluoride in anhydrous HF with UO_2 and with uranium and neptunium fluorides at ambient temperatures. Treatment of americium dioxide with krypton difluoride did not yield americium hexafluoride under the conditions studied.

Introduction

The use of elemental fluorine on uranium, neptunium, and plutonium substrates at or above 300 °C has been the only known method of economically converting these materials to the volatile hexafluorides.[1-3] We recently reported that ambient-temperature dioxygen difluoride (O_2F_2) gas will smoothly and efficiently convert U_3O_8 to UF_6.[4] Plutonium tetrafluoride, oxide, and oxyfluorides are all readily fluorinated to PuF_6 by gaseous O_2F_2 or O_2F_2/HF solutions at *or below* room temperature.[5] Similarly, we have shown that neptunium substrates can be fluorinated to NpF_6 with dioxygen difluoride.[6]

Soviet authors Drobyshevskii et al.[7,8] have reported the ambient-temperature or lower temperature fluorination of the oxides and tetrafluorides of uranium, neptunium, and americium and the oxyfluorides of neptunium with krypton difluoride in bromine

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pentafluoride or anhydrous HF to obtain the respective hexafluorides. German workers have briefly mentioned the generation of UF_6 by treating UF_4 with KrF_2.[9] Peacock and Edelstein[10] have reported the fluorination of $NpOF_4$ to NpF_6 with KrF_2 in anhydrous HF, while Brown et al.[11] have reported the oxidation of PuF_3 to PuF_4 with krypton difluoride at room temperature or lower.

There is no mention in the literature of the reaction of plutonium substrates with KrF_2 to produce PuF_6 and no description of gaseous KrF_2–solid actinide substrate reactions. We now report that KrF_2 will oxidatively fluorinate not only uranium and neptunium oxides and fluorides but plutonium tetrafluoride as well at ambient temperature. Further, these reactions can be carried out by using gaseous KrF_2. However, we have been unable to prepare AmF_6 from AmO_2 in anhydrous HF by this method, in contrast to an earlier report.[7]

Experimental Section

Caution! Krypton difluoride is one of the most potent oxidation fluorinating agents known, so great care must be taken to anticipate violent reactions. Further, KrF_2 thermally decomposes to gaseous products, so that pressure increases on storage must also be expected. The hexafluorides of U, Np, and Pu are also strong fluorinating agents. Of course, Np, Pu, and Am materials must be handled appropriately because of their severe radiotoxicity.

Krypton difluoride was prepared by the method of Bougon[12] in the identical apparatus we used for preparing dioxygen difluoride.[13] Using a fluorine:krypton ratio of 2:1, we could prepare KrF_2 at a rate approaching 300 mg/h. The freshly prepared krypton difluoride was held in a trap at −78 °C while the unreacted starting materials were removed under vacuum. The solid material is stable indefinitely at −78 °C.

Uranium dioxide fuel pellets (fired at 1750 °C for 24 h) supplied by Westinghouse Electric Corp. were treated with oxygen at 500 °C for conversion to U_3O_8 powder. Uranium, neptunium, and plutonium fluoride or oxyfluoride substrates were prepared by photolytic or hydrolytic decomposition of the gaseous hexafluorides or by their reduction on metal surfaces. Neptunium-237 and plutonium-239 were the isotopes used for the Np and Pu work. Americium-243 oxide was supplied by Oak Ridge National Laboratory. Plutonium dioxide containing 5% americium-241 oxide was supplied locally by the MST Division, Los Alamos National Laboratory. Infrared spectra were obtained with a Nicolet 20SX Fourier transform infrared (FTIR) spectrometer operating at 1-cm^{-1} resolution, using Monel gas cells fitted with AgCl windows.

Passivation normally consisted of prolonged treatment with elemental fluorine at room temperature followed by KrF_2 or O_2F_2, and finally with NpF_6 or PuF_6. The latter treatment inevitably is accompanied by formation of nonvolatile decomposition products, which as shown below could be refluorinated to the respective volatile fluorides.

Actinide substrates were treated with KrF_2 as described in the following experiments.

1. In a 100-mL quartz bulb, about 50 mg of PuF_6 was decomposed by UV light, heated to several hundred degrees Celsius, and allowed to cool. The PuF_4 product was then treated with about 50 torr of KrF_2. Infrared spectroscopy and visual examination showed that PuF_6 was formed continuously over a period of hours. There was no evidence of SiF_4 in the infrared spectrum and no obvious etching of the container, which demonstrates that quartz vessels are suitable for such KrF_2 applications.

2. Krypton difluoride was periodically added to a well-passivated metal vacuum line in which NpF_6 and PuF_6 had been handled. Over a period of several days, NpF_6 was continuously generated; eventually PuF_6 was also observed in the infrared spectrum.

3. An ambient-temperature metal process loop (essentially all nickel or Monel, with a surface area of 1.13×10^4 cm^2) equipped with an in-line infrared cell and recirculating bellows pump was treated by allowing several hundred milligrams of PuF_6 to decompose, giving a surface coating of nonvolatile plutonium fluorides and oxyfluorides. Krypton difluoride (144 torr) was admitted to the loop, and within minutes PuF_6 was formed, as determined by infrared spectroscopy. The KrF_2 absorbance smoothly diminished, and the PuF_6 absorbance increased with time, with a peak PuF_6 generation rate of about 13 mg/h (Figure 1). A KrF_2 half-life of about 4 h under these conditions was observed, and even after 24 h some KrF_2 was still present.

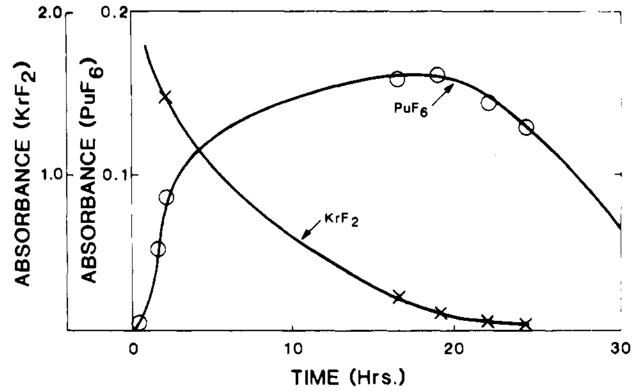

Figure 1. Disappearance of KrF_2 and ingrowth of PuF_6 with time in a metal process loop, as measured by gas-phase Fourier transform infrared spectroscopy (experiment 3). Peak absorbances were taken for the KrF_2 asymmetric stretching mode component at 596 cm^{-1} (P-branch) and for the Q-branch of the PuF_6 asymmetric stretching mode at 616 cm^{-1}.

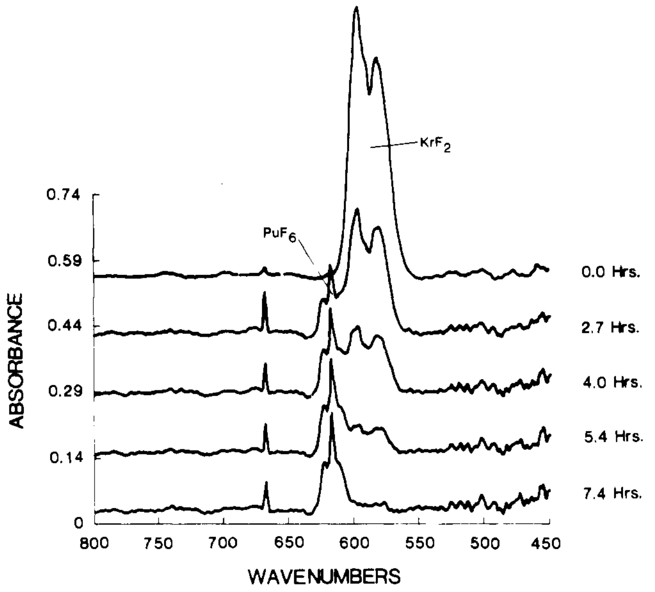

Figure 2. Infrared spectrum of the gas mix resulting from KrF_2 treatment of the metal process loop containing photoproduct (experiment 4). The peak at 667 cm^{-1} is due to carbon dioxide external to the infrared cell.

4. A total of 34 mg of PuF_4 was photodecomposed to nonvolatile PuF_4 in the process loop described above. Since this loop had been exposed to PuF_6, nonvolatile plutonium materials in addition to photoproduct were present. Krypton difluoride (11 torr) and argon (96 torr) were added and recirculated through the loop. Again, the concomitant appearance of PuF_6 and disappearance of KrF_2 were observed (by FTIR) over a period of hours, with a maximum PuF_6 generation rate of about 18 mg/h and a total of about 73 mg of PuF_6 recovered. Figure 2 illustrates the resulting infrared spectrum in the 450–800-cm^{-1} region over a period of 7.4 h.

5. Uranium oxide as U_3O_8 (59.6 mg) was treated with approximately 1 g of KrF_2 in 2.6 mL of anhydrous HF in a Kel-F reactor at ambient temperature. After 1 day, all of the black oxide had dissolved to give a colorless solution. On evacuation of the Kel-F reactor, all of the contents were found to be volatile. Following separation of the HF, infrared spectroscopy revealed only UF_6 plus trace impurities.

6. Krypton difluoride was stored at −78 °C in a stainless-steel cylinder that had been treated previously with uranium hexafluoride and then evacuated. After several days, the container was warmed to room temperature and the KrF_2 was removed. Uranium hexafluoride was observed in the off-gas by infrared spectroscopy, due to fluorination of nonvolatile uranium solids in the reactor.

7. Krypton difluoride was added to a Kel-F tube in which several milligrams of $^{243}AmO_2$ and 2 mL of anhydrous HF were placed. Over a period of several hours at ambient temperature, the mixture became orange; however, on removal of volatiles there was no evidence for any

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transport of the americium γ activity. Likewise, when the HF suspension was heated gently to 50–60 °C for approximately 1 h in the presence of KrF_2, there was no evidence for the formation of AmF_6. A similar reaction involving 95% PuO_2/5% AmO_2 powder also gave no evidence for the formation of americium hexafluoride.

Results and Discussion

The experiments described above demonstrate conclusively that not only uranium and neptunium, as previously reported,[7-10] but also plutonium substrates can be converted to volatile hexafluorides by using KrF_2. Krypton difluoride thus becomes only the *second* reported molecular agent for plutonium volatilization at room temperature or below. The experiments not only confirm that KrF_2 solutions in anhydrous HF form UF_6 and NpF_6 from lower valent solids but also demonstrate that UF_6, NpF_6, *and* PuF_6 can be produced from solid substrates by using *gaseous* KrF_2. A noteworthy feature of the KrF_2 treatments described above is that violent and unpredictable decomposition has *not* been observed, as is seen occasionally with O_2F_2.[5,6,13]

In agreement with the reports of Soviet workers[14] but in contrast to other reports,[15] our experiments indicate a surprisingly long lifetime of KrF_2 in metal and glass systems. Figure 1 illustrates the growth of PuF_6 and disappearance of KrF_2 with time in an essentially all-metal recirculating loop. The disappearance of PuF_6 after 20 h is due to decomposition onto the metal surface in the absence of KrF_2. These experiments unequivocally demonstrate the possibility of generating PuF_6 in practical process systems.

Experiment 2 demonstrates that NpF_6 is preferentially evolved when both Np and Pu substrates are present. While it is possible that the formation of NpF_6 is kinetically as well as thermodynamically favored over PuF_6, it is also clear that PuF_6 will fluorinate Np substrates. During one KrF_2 treatment, both NpF_6 and PuF_6 were observed with KrF_2 still present, but with time the NpF_6 absorbance increased while the PuF_6 and KrF_2 absorbances disappeared. This suggests that NpF_6 and PuF_6 could be formed at comparable rates and that a subsequent reaction occurs between PuF_6 and the neptunium solid to generate NpF_6 and PuF_4.

Treatment of U_3O_8 powder with a KrF_2/HF solution at room temperature provides slow but quantitative conversion to UF_6 with only traces of easily separated gaseous impurities. With highly refractory UO_2 powder derived from the crushing of fuel pellets, the conversion rate and yield were much less. Reaction rates with uranium fluoride/oxyfluoride residues arising from UF_6 treatment of an unconditioned metal storage tube, on the other hand, appear to be much faster.

Soviet workers have reported the preparation of thermally unstable AmF_6 by heating HF suspensions of AmF_4 with KrF_2.[7] However, in several experiments we were unable to identify such a species from similar treatments of americium oxides.

No attempts were made to identify actinide fluorides or oxyfluorides (e.g., MF_5, MOF_4, or MO_2F_2) in these reactions, although they very likely were formed as intermediates. Such intermediates will be the focus of further work.

The ability of KrF_2 to volatilize actinides at ambient temperature and at moderate rates could have a significant impact in the areas of actinide recovery and decontamination, among many other potential applications. The enormously longer lifetime and nonviolent reactivity of KrF_2 compared to the case of O_2F_2 should more than offset its lower reaction rate for some applications. Optimization of reaction variables (reactor design, solvent, stoichiometry, temperature, etc.) should improve the overall yield of the hexafluorides.

Acknowledgment. We are grateful to Dr. J. G. Malm, Dr. B. I. Swanson, and Dr. R. A. Penneman for many helpful discussions and encouragement throughout the course of this work. The authors are indebted for the use of the $^{243}AmO_2$ to the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, through the transplutonium element production facilities at Oak Ridge National Laboratory. We thank Bruce Neuman, Westinghouse Electric Corp., for providing the UO_2 fuel pellets.

Registry No. KrF_2, 13773-81-4; U_3O_8, 1344-59-8; PuF_4, 13709-56-3; PuF_6, 13693-06-6; NbF_6, 14521-05-2; UF_6, 7783-81-5; $^{243}AmO_2$, 53754-11-3.

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Photolysis of Group 6 Metal Hexacarbonyl Solutions Containing Diimine Ligands. Spectral Characterization and Reaction Kinetics of a Photoproduced Intermediate, Monodentate $M(CO)_5$(diimine)

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Electronic absorption spectra have been obtained immediately following the photolysis of $M(CO)_6$ solutions containing diimine ligands (1,10-phenanthroline, 2,2′-bipyridine, 1,4-diazabutadiene, or their derivatives) with the use of a microprocessor-controlled diode-array UV–visible spectrophotometer. The time-dependent spectra illustrate rapid formation of a reaction intermediate that is assigned to be $M(CO)_5L$, where L is a diimine ligand coordinated in a monodentate fashion. Monodentate $M(CO)_5L$ subsequently extrudes CO thermally via a first-order kinetic process to form stable $M(CO)_4L$. No discernable $M(CO)_5L$ intermediates were observed when L = 1,10-phenanthroline (phen) or a phen derivative consistent with the rigid coplanar nature of these ligands. In contrast, the chelation of $M(CO)_5L$ complexes, where L = 2,2′-bipyridine, 1,4-diazabutadiene, or derivatives, proceeds with considerably slower reaction rates. The rate data are interpreted in terms of the stereochemistry of the monodentate intermediate. For a given ligand, the reaction rate decreases in the sequence Mo > Cr > W, analogous to the order of CO release in $M(CO)_6$; this ordering suggests that the predominant barrier to chelation involves breaking of the M–C bond. Derived activation energy parameters indicate that the chelation reaction is enthalpy-controlled. The marked dependence of reaction rate on diimine and resulting negative activation entropy values imply that the chelation mechanism proceeds with a substantial associative component.

Introduction

The photochemistry of metal carbonyl complexes has, for a number of years, received a great deal of attention.[1] Recently, this interest has been further stimulated because of the importance of these molecules in the design of homogeneous catalytic processes and as models in mechanistic organometallic chemistry.[2-5] Despite

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