-196 °C into a 200-mL quartz vessel. After it was warmed from -196 to +25 °C over a period of 1 h, the quartz vessel was photolyzed for 1 h at 3000 Å. The quartz vessel was evacuated, leaving a nonvolatile viscous liquid. This viscous compound on analysis was found to be [CF$_3$(C$_2$F$_5$)NN(CF$_3$)CF$_2$NN(C$_2$F$_5$)CF$_3$]$_2$ in ~93% yield. Spectral data were as follows. MS (CI$^+$) [m/e (species), intensity]: 734 (C$_{11}$F$_{28}$N$_5^+$), 0.59; 651 (C$_{10}$F$_{25}$N$_4^+$), 4.92; 601 (C$_9$F$_{23}$N$_4^+$), 3.93; 563 (C$_9$F$_{21}$N$_4^+$), 0.26; 513 (C$_8$F$_{19}$N$_4^+$), 2.38; 413 (C$_6$F$_{15}$N$_4^+$), 5.17; 385 (C$_6$F$_{15}$N$_2^+$), 9.02; 335 (C$_5$F$_{13}$N$_2^+$), 41.88; 285 (C$_4$F$_{11}$N$_2^+$), 6.82; 247 (C$_4$F$_9$N$_2^+$), 17.34; 119 (C$_2$F$_5^+$), 21.57; 114 (C$_2$F$_4$N$^+$), 18.89; 69 (CF$_3^+$), 100. IR (liquid) 1229

b, vs, 1098 w, 1077 s, 972 w, 954 s, 805 m, 739 s, 664 w, 534 w cm^{-1}; ^{19}F NMR: ϕ -55.71 to -63.94 (NCF$_3$, mult), -67.18 (NCF$_2$N, mult), -83.86, -85.54 (CF$_3$CF$_2$, mult), -96.14 to -100.9 (CF$_3$CF$_2$, mult). Density: 2.14 g/mL at 23 °C. Anal. Calcd for C$_{16}$F$_{42}$N$_8$: C, 17.42; F, 72.41; N, 10.16. Found: C, 17.55; F, 72.7; N, 10.21.

Oxidation of Trivalent Plutonium in Acid Solution by Xenon Difluoride and by the Fluoroxysulfate Ion, SO$_4$F^{-1}

Richard L. Cook,† Mary Woods,‡ James C. Sullivan,* and Evan H. Appelman*

Stopped-flow spectrophotometry was used to study the oxidation of plutonium(III) to plutonium(IV) in 1 M HClO$_4$ by XeF$_2$ and by the fluoroxysulfate ion, SO$_4$F$^-$. In both reactions, 2 mol of Pu(III) is oxidized per 1 mol of oxidant consumed, and neither Pu(V) or Pu(VI) appears to be formed either as an intermediate or as an initial product, although an excess of XeF$_2$ does slowly oxidize the Pu(IV) product to Pu(VI). At 2 °C the reactions have respective bimolecular rate constants of 1160 ± 70 and 120 ± 9 M^{-1} s^{-1}, expressed in terms of -d[Pu(III)]/dt. Over the temperature range 2-24 °C, the activation parameters for the XeF$_2$ reaction are $\Delta H^* = 39.5 \pm 8.6$ kJ/mol and $\Delta S^* = -48.3 \pm 29$ J/(mol K), while those for the SO$_4$F$^-$ reaction are $\Delta H^* = 30.8 \pm 2.3$ kJ/mol and $\Delta S^* = -98.5 \pm 7.8$ J/(mol K). Mechanisms are postulated that invoke a sequence of two one-electron-oxidation steps.

Introduction

Molecular fluorine has a standard electrode potential in aqueous solution of 3.1 V, and many of its compounds have potentials well in excess of 2 V. Their reactions with reducing substrates are therefore highly exoergic, and such reactions may at least in principle proceed by pathways that are inaccessible to milder oxidants. While fluorine itself has a limited solubility and vanishingly short liftime in aqueous solution,[2] some reactive fluorine compounds are both substantially soluble and reasonably long-lived in water. Two such compounds are xenon difluoride, XeF$_2$, and the fluoroxysulfate ion, SO$_4$F$^-$.

Xenon difluoride dissolves in water to the extent of about 0.15 M at 0 °C, apparently as the unchanged molecule, and it oxidizes water with a half-time of about 7 h at the ice point,[3] the half-time decreasing to about 30 min at room temperature.[4] Aqueous XeF$_2$ is estimated to have a standard electrode potential of 2.7 V for the half-reaction[5]

$$XeF_2 + 2H^+ + 2e^- \rightleftharpoons Xe + 2HF$$
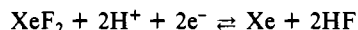
Although the kinetics of the reaction of XeF$_2$ with water itself have been studied,[4,6] and qualitative reports of its behavior as an aqueous oxidant have been published,[7] only a relatively limited number of kinetic investigations of its reactions with aqueous reductants have been reported.[8]

The fluoroxysulfate ion is usually prepared in the form of its cesium salt, CsSO$_4$F, which is soluble in water to the extent of about 0.5 M at room temperature.[9] The half-time for oxidation of water by the fluoroxysulfate ion increases from about 15 min at room temperature to about 3.6 h at the ice point.[10] The half-reaction

$$SO_4F^- + 2H^+ + 2e^- \rightleftharpoons HSO_4^- + HF$$
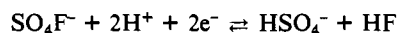
has a standard electrode potential of 2.47 V,[11] making fluoroxysulfate thermodynamically a somewhat less potent oxidant than

XeF$_2$. The kinetics of reactions of fluoroxysulfate with several aqueous reductants have been reported in two papers.[10,12]

Of particular interest concerning the reactions of these powerful oxidizing agents is the question of whether they act as one- or two-electron oxidants. Trivalent plutonium can potentially be oxidized to Pu(IV), Pu(V), and Pu(VI), and all four of these plutonium oxidation states are interrelated by electrode potentials around 1 V.[13] Furthermore, the interconversion of these states by way of reactions among themselves generally takes place relatively slowly,[13] making it feasible to draw conclusions about the mechanism of oxidation of Pu(III) from the identity of the initial products. With these considerations in mind, we have undertaken the present kinetic study of the reaction of Pu(III) with xenon difluoride and with the fluoroxysulfate ion.

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Experimental Section

Materials. Xenon difluoride was obtained from PCR, Inc., and was used as received. Cesium fluoroxysulfate was prepared by fluorination of an aqueous solution of cesium sulfate.[14] The precipitated salt was filtered, vacuum-dried, and stored in a −15 °C freezer when not in use. Iodometric analysis indicated a purity of 98%, the balance being largely cesium persulfate. Plutonium-242 was obtained from Oak Ridge National Laboratory as PuO_2. It was dissolved in nitric acid, purified by ion-exchange chromatography,[15] fumed with perchloric acid, and finally reduced electrolytically to Pu(III).[16] Distilled water was redistilled first from alkaline permanganate and then from acidic dichromate. Other materials were commercial products of reagent grade.

Analytical Procedures. Xenon difluoride and the fluoroxysulfate ion were analyzed iodometrically by titration with standard thiosulfate solution after reaction with acid iodide. In the case of fluoroxysulfate, this method is only entirely accurate for freshly prepared solutions, since the reaction of fluoroxysulfate with water produces some peroxymonosulfate, SO_4OH^-, and lesser amounts of hydrogen peroxide, both of which oxidize iodide.[10]

The absolute analysis of trivalent plutonium was carried out by titrating with a standard Ce(IV) solution in sulfate medium and determining the end point photometrically. At high sulfate concentrations, the product of the oxidation is Pu(IV).[17] Routine Pu(III) assays were carried out spectrophotometrically with a Perkin-Elmer Model 330 spectrophotometer, using an empirically determined extinction coefficient of 36.2 M^{-1} cm^{-1} at 601 nm.

Stoichiometry Experiments. Reaction stoichiometries were determined both by spectrophotometric analysis and by cerimetric titration of the Pu(III) remaining after reaction with an insufficiency of oxidant. Spectrophotometry was also used to verify the absence of significant amounts of higher oxidation states of plutonium, particularly Pu(VI). (Since Pu(VI) has an extinction coefficient of 550 M^{-1} cm^{-1} at 830 nm, this is a sensitive test.[18]) In addition, stoichiometries were estimated from the net decrease in absorbance in stopped-flow experiments in which the Pu(III) was present in excess.

Kinetic Measurements. Kinetic measurements were made with a Hi-Tech Scientific SF-51 thermostated stopped-flow spectrophotometer system containing an observation cell of 0.5-cm^3 volume and 0.2-cm light path. The drive syringes delivered equal volumes of the two reagents, with a mixing time of about 2 ms. Pu(III) was monitored by its absorption at 601 nm, which was found empirically to have an extinction coefficient of 35.8 M^{-1} cm^{-1} in this instrument. The voltage output of the spectrophotometer was amplified by a line-driver amplifier and then digitized by a data system consisting of a Digital Equipment Co. LSI 11/23 minicomputer connected via a parallel interface to a LeCroy 8013A CAMAC crate controller containing a TR8818 transient recorder. The processed data were stored on disk and subsequently transferred to a VAX 11/780 computer for analysis. The analysis consisted of converting the digitized voltages to optical densities and fitting to a three-parameter bimolecular rate equation for nonstoichiometric initial concentrations, by using a nonlinear least-squares program. In this analysis the stoichiometry, $\Delta[Pu(III)]/\Delta[SO_4F^-]$, was assumed to be 2, and Pu(III) and Pu(IV) were taken to be the only absorbing species, with extinction coefficients of 35.8 and 2.0 M^{-1} cm^{-1}, respectively.

A serious experimental difficulty in these studies was the instability of the oxidant solutions. These solutions were made up at the ice point and brought to temperature in the spectrophotometer immediately before use. Nevertheless, significant decomposition took place during the time it took to carry out a series of measurements, particularly at the highest temperatures. The solution of oxidant was analyzed iodometrically at the beginning and end of the series, and in the case of the XeF_2 experiments, this permitted a rather accurate interpolation of the concentration of oxidant at the time of each run. This correction was less satisfactory for the fluoroxysulfate measurements, because of the buildup of peroxymonosulfate and hydrogen peroxide that we have already mentioned. We have found that in 1 M $HClO_4$ at ambient temperature Pu(III) is not significantly oxidized by 0.01–0.02 M H_2O_2 in the course of 10–20 min, while the reaction between 0.004 M Pu(III) and 0.004 M peroxymonosulfate proceeds with an initial half-time on the order of 1 h.

Other sources of error were formation of gas bubbles and $CsClO_4$ precipitate in the light path. These usually manifested themselves as obvious irregularities in the signal during the reaction, and signals dis-

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Table I. Reaction of Pu(III) with XeF_2[a]

init concn, M		
$10^3[Pu^{3+}]_0$	$10^3[XeF_2]_0$[b]	$10^{-3}k^2$,[c] M^{-1} s^{-1}
1.9 °C		
5.00	1.80	1.11 ± 0.02
5.00	3.5–3.6	1.22 ± 0.02
10.0	3.8–3.9	1.08 ± 0.05
10.0	6.0–6.1	1.19 ± 0.04
		mean: 1.15 ± 0.07
14.6 °C		
5.00	1.82	2.01 ± 0.25
5.00	3.7–3.9	2.01 ± 0.11
10.0	3.2–3.5	2.07 ± 0.38
10.0	7.3–7.5	2.11 ± 0.32
		mean: 2.05 ± 0.05
24.2 °C		
9.99	5.1–6.9	4.68 ± 0.96

[a] In 1 M $HClO_4$. Each entry is the mean of four to six runs from the same stock solutions. [b] Variation reflects decay of reagent while standing in reservoir and drive syringe. [c] Uncertainties are twice the standard deviations of the means.

Table II. Reaction of Pu(III) with SO_4F^-[a]

init concn, M		
$10^3[Pu^{3+}]_0$	$10^3[SO_4F^-]_0$[b]	k_2,[c] M^{-1} s^{-1}
2.4 °C		
5.08	2.00	133 ± 7
5.08	3.5–3.9	113 ± 6
10.2	3.2–3.5	120 ± 3
10.2	6.3–6.8	127 ± 2
		mean: 123 ± 9
13.3 °C		
5.08	1.6–1.8	193 ± 10
5.08	3.8–4.1	206 ± 10
10.2	3.0–3.1	205 ± 11
10.2	7.5–8.2	197 ± 36
		mean: 200 ± 6
24.2 °C		
4.99	1.6–1.8	384 ± 38
4.99	3.5–4.3	347 ± 56
9.99	3.0–3.3	355 ± 76
9.99	6.3–7.0	339 ± 53
		mean: 356 ± 20

[a] In 1 M $HClO_4$. Each entry is the mean of three to five runs from the same stock solutions. [b] Variation reflects decay of reagent while standing in reservoir and drive syringe. [c] Uncertainties are twice the standard deviations of the means.

playing such irregularities were discarded.

Results

Qualitative Observations and Stoichiometry. In test-tube experiments, both XeF_2 and SO_4F^- oxidized Pu(III) to Pu(IV) within the time of mixing and analysis (1–2 min). Even when present in large excess, fluoroxysulfate did not oxidize plutonium beyond the +4 oxidation state. An excess of xenon difluoride, on the other hand, did oxidize the Pu(IV) all the way to the hexavalent state, but the reaction was quite slow. In the reaction of xenon difluoride with an excess of Pu(III), no significant amount (less than 1%) of Pu(VI) was seen 1–2 min after mixing.

Two experiments in which 0.009 M Pu(III) reacted with 0.0015 M $CsSO_4F$ in 1 M $HClO_4$ indicated the consumption of 2.02 and 1.99 mol of Pu(III)/mol of SO_4F^-. A similar experiment with Pu(III) and XeF_2 indicated a stoichiometry of 2.0. Stoichiometries of approximately 2 were also estimated for both reactions from the net decrease in absorbance in stopped-flow experiments in which the Pu(III) was present in excess.

Kinetic Results. The kinetic measurements are summarized in Tables I and II. Entries are averages of multiple runs taken from the same stock solutions. Within each group the initial Pu(III) concentration was constant, but because of the instability

of the XeF_2 and SO_4F^- stock solutions, the initial concentration of oxidant varied somewhat. The rate constants are those calculated from the bimolecular rate law

$$-d[Pu(III)]/dt = k_2[Pu(III)][OX]$$

where [OX] is either $[XeF_2]$ or $[SO_4F^-]$. Activation parameters were calculated from a least-squares analysis of the variation of $\ln k_2/T$ with $1/T$. For the XeF_2 reaction $\Delta H^* = 39.5 \pm 8.6$ kJ/mol and $\Delta S^* = -48.3 \pm 29$ J/(mol K); for the SO_4F^- reaction $\Delta H^* = 30.8 \pm 2.3$ kJ/mol and $\Delta S^* = -98.5 \pm 7.8$ J/(mol K). Uncertainties are standard deviations, and ΔS^* is calculated in terms of the activated complex $[Pu^{III}SO_4F^-]^*$. The poor precision of the parameters for the XeF_2 reaction probably reflects inaccuracies in the data at the highest temperature.

Discussion

Since the oxidation of Pu(III) by XeF_2 has a greater thermodynamic driving force than has the oxidation by fluoroxysulfate, it is perhaps not surprising that the former is roughly 1 order of magnitude faster than the latter. Despite the large uncertainties in the activation parameters for the XeF_2 reaction, it appears that its greater rate stems entirely from its less negative entropy of activation, since it actually has, if anything, the higher activation enthalpy.

A reaction with 2:1 stoichiometry that follows a bimolecular rate law poses some interesting mechanistic questions. One possible mechanism would entail a two-electron oxidation of Pu(III) to Pu(V), followed by reaction of Pu(V) with Pu(III) to yield Pu(IV). However, the Pu(V)–Pu(III) reaction has a bimolecular rate constant of only 4.4×10^{-2} M^{-1} s^{-1} in 1 M HClO₄ at 25 °C,[19] making it relatively slow even on the time scale of our stoichiometric measurements. Hence, such a mechanism would be inconsistent with the observed stoichiometry. Furthermore, the reaction

$$Pu(V) + Pu(IV) \rightleftharpoons Pu(VI) + Pu(III)$$
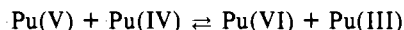
has a bimolecular rate constant of 37 M^{-1} s^{-1} in 1 M HClO₄ at 25 °C, and an equilibrium constant of about 13.[20] This equilibrium would therefore be established on the time scale of our test-tube measurements, so that any significant partial contribution from a two-electron oxidation would lead to the formation of observable quantities of Pu(VI). As we have already noted, no such formation of Pu(VI) was seen.

We can therefore rule out any substantial direct oxidation of Pu(III) to ordinary Pu(V) by either XeF_2 or SO_4F^-. In a study of the reaction of Pu(III) with XeO_3, Cleveland[21] has tried to resolve a similar dilemma by suggesting the formation of a metastable form of Pu(V) that would react rapidly with Pu(III). Rather than invoke such a *deus ex machina*, however, we prefer to consider one-electron-oxidation paths. In their studies of the reactions of fluoroxysulfate with a number of aqueous reductants, Thompson and Appelman[10] have suggested a fluorine atom transfer mechanism:
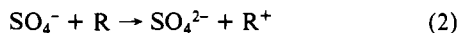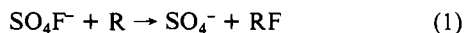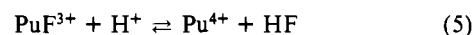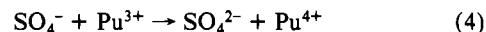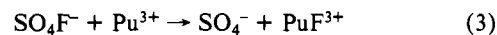
$$SO_4F^- + R \rightarrow SO_4^- + RF \tag{1}$$

$$SO_4^- + R \rightarrow SO_4^{2-} + R^+ \tag{2}$$

They obtained positive evidence for such a mechanism from the observation that the reaction of fluoroxysulfate with chromium(II) produced an approximately equimolar mixture of hexaaquochromium(III) and fluorochromium(III). Such a mechanism would be entirely consistent with our observations:

$$SO_4F^- + Pu^{3+} \rightarrow SO_4^- + PuF^{3+} \tag{3}$$

$$SO_4^- + Pu^{3+} \rightarrow SO_4^{2-} + Pu^{4+} \tag{4}$$

$$PuF^{3+} + H^+ \rightleftharpoons Pu^{4+} + HF \tag{5}$$

We may propose a similar mechanism for the reaction of Pu(III) with XeF_2:[22]

$$XeF_2 + Pu^{3+} \rightarrow XeF + PuF^{3+} \tag{6}$$

$$XeF + H_2O \rightarrow Xe + HF + OH \tag{7}$$

$$OH + Pu^{3+} \rightarrow OH^- + Pu^{4+} \tag{8}$$

$$PuF^{3+} + H^+ \rightleftharpoons Pu^{4+} + HF \tag{9}$$

$$OH^- + H^+ \rightleftharpoons H_2O \tag{10}$$

The reaction of OH with Pu^{3+} has recently been shown to have a rate constant of 2×10^9 M^{-1} s^{-1}.[23] Our results, of course, provide no information regarding the dependence of the plutonium reactions on hydrogen ion concentration.

We conclude, therefore, that despite the fact that both XeF_2 and fluoroxysulfate appear formally to be two-electron oxidants, both of them probably oxidize Pu(III) by one-electron mechanisms. A sequence of one-electron steps has recently been suggested for the oxidation of uranium(IV) by XeF_2,[8a] and in fact, such mechanisms may be the dominant mode by which both of these oxidants interact with aqueous reductants.

Very few rapid reactions of Pu^{3+} appear to have been studied in any great detail. Of reactions as fast as or faster than those studied here, i.e., with bimolecular rate constants in excess of 300 M^{-1} s^{-1} at 25 °C, quantitative kinetic data are available only for oxidations by the free radicals OH and Cl_2^- ($k_2 = 2 \times 10^9$ and 5×10^7 M^{-1} s^{-1}, respectively)[23,24] and for oxidation by the dichromate ion ($k_2 = 2.4 \times 10^4$ M^{-1} s^{-1}).[13] The last is particularly noteworthy, inasmuch as it constitutes rapid oxidation of plutonium(III) in a noncomplexing medium by a stable reagent of rather modest thermodynamic oxidizing power. It is evident that factors other than thermodynamic driving force are of primary importance in determining the rates of these reactions.

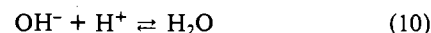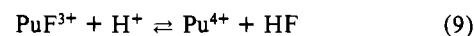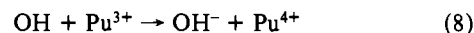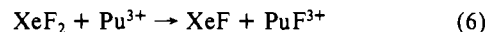(19) Lavallee, C.; Newton, T. W. *Inorg. Chem.* **1972**, *11*, 2616.
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(22) This mechanism was suggested to us by Dr. Ulrik Kläning, of Aarhus University, Aarhus, Denmark. It is supported by unpublished observations in which we have found that XeF₂, like SO₄F⁻, oxidizes Cr²⁺ to an approximately 1:1 mixture of CrF²⁺ and Cr³⁺. This is consistent with a reaction scheme analogous to reactions 6–10, in which the initial attack of XeF₂ on Cr²⁺ produces CrF²⁺, while the subsequent reaction of OH with Cr²⁺ produces Cr(H₂O)₆³⁺. If the postulated intermediate XeF were to react directly with Cr²⁺ instead of with water, we might expect it to produce instead a second 1 mol of CrF²⁺.
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