occurred. No oxygen was observed as a product but the solution contained an oxidizing agent capable of liberating iodine in the proportion of 6.01 equiv/mole of $XeF_6 \cdot GeF_4$ consumed (theoretical, 6.00).

The 1:1 complex did not melt in glass under an atmosphere of nitrogen up to a temperature of 135°. The substance sublimed readily at temperatures above 50°. At 110° a yellow vapor (presumably XeF_6) could be seen above the solid. The yellow color increased in intensity as the sample was heated to 135°. The heating was discontinued at this point because there was considerable attack on the glass.

X-Ray Powder Patterns.—The X-ray powder photographs were taken using samples contained in 0.2-mm Lindemann glass capillaries which were filled as previously described[1] and loaded into a 114.6-mm diameter Debye–Scherrer powder camera. Nickel-filtered copper radiation (λ 1.5418 A) was used, and exposures of 4–6 hr were made.

The *d* spacings found for $2XeF_6 \cdot GeF_4$ and $XeF_4 \cdot GeF_4$ are given in Tables I and II, respectively. The visually estimated relative intensity of each measured line is listed as strong (s), medium (m), or weak (w).

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR $2XeF_6 \cdot GeF_4$

d, A	Intens	*d*, A	Intens	*d*, A	Intens
7.6	w	2.45	w	1.731	w
4.65	w	2.40	w	1.711	w
4.55	s	2.29	m	1.668	m
4.32	w	2.23	w	1.633	w
4.22	w	2.18	w	1.585	w
4.01	w	2.13	w	1.554	w
3.93	w	2.09	m	1.531	w
3.83	w	2.03	w	1.498	w
3.54	w	2.01	m	1.473	w
3.32	m	1.98	w	1.431	w
3.15	w	1.96	w	1.409	w
2.94	w	1.91	w	1.388	w
2.85	w	1.89	w	1.364	w
2.72	w	1.87	w	1.306	w
2.64	m	1.799	m	1.273	w
2.60	w	1.768	w		
2.54	w	1.743	m		

TABLE II

X-RAY POWDER DIFFRACTION DATA FOR $XeF_6 \cdot GeF_4$

d, A	Intens	*d*, A	Intens	*d*, A	Intens
6.4	m	2.08	w	1.365	w
5.23	w	2.01	w	1.343	w
5.08	m	1.98	w	1.324	w
4.86	s	1.90	w	1.308	w
4.76	s	1.86	w	1.291	w
3.74	s	1.84	w	1.274	w
3.56	m	1.82	w	1.261	w
3.46	w	1.786	m	1.232	w
3.31	w	1.735	w	1.215	w
3.21	w	1.707	w	1.196	w
3.12	s	1.678	w	1.173	w
2.97	w	1.646	w	1.158	w
2.88	w	1.627	w	1.144	w
2.82	w	1.610	s	1.118	w
2.75	w	1.594	w	1.041	w
2.62	w	1.561	w	0.890	w
2.57	w	1.511	w	0.867	w
2.52	w	1.489	w	0.837	w
2.43	w	1.473	w	0.828	w
2.30	m	1.442	w	0.822	w
2.23	m	1.413	w	0.7941	w
2.17	w	1.396	w	0.7892	w
2.13	w	1.379	w	0.7800	w

Powder patterns were taken at some random compositions corresponding to XeF_6 to GeF_4 molar ratios between 2.0 and 1.0. These powder patterns showed only those lines attributable to $2XeF_6 \cdot GeF_4$ and $XeF_6 \cdot GeF_4$ suggesting that there are no other compounds in this molar ratio range.

Attempted Reaction of XeF_6 with SiF_4.—All attempts to prepare a complex between XeF_6 and SiF_4 were unsuccessful. Three preparations were attempted on a millimole scale at different temperatures. In all of the cases about equimolar amounts of XeF_6 and SiF_4 were used. After allowing the reactants to stand for several hours, the mixtures were pumped at −78°. Complete and rapid removal of the SiF_4 was taken as evidence that no reaction had occurred. Reactions were tried at 67, 22, and −78°. The low-temperature reaction was attempted by slowly cooling the reactants to −78° over a 30-min period and then allowing the reactants to stand 16 hr at that temperature. In every case all of the SiF_4 was removed in 3–5 min on pumping at −78°.

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Kinetics of the Reaction between Plutonium(III) and Xenon Trioxide

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The kinetics of the reaction between Pu(III) and XeO_3, according to the equation $6Pu(III) + XeO_3 + 6H^+ \rightarrow 6Pu(IV) + Xe + 3H_2O$, have been studied in perchlorate media by following the rate of disappearance of Pu(III) spectrophotometrically at 600 mμ. The rate law for the reaction is: $-d[Pu(III)]/dt = k[Pu(III)][XeO_3]$. The reaction rate is independent of acidity in the 0.5–2 *M* range. From the variation of the reaction rate with temperature, the following thermodynamic quantities of activation at 25° were calculated: $\Delta H^{\ddagger} = 15.3 \pm 2.1$ kcal/mole; $\Delta F^{\ddagger} = 20.2 \pm 0.1$ kcal/mole; $\Delta S^{\ddagger} = -16.0 \pm 6.9$ eu. The mechanism of the reaction appears to involve either successive one-electron changes or a two-electron change to form a Pu(V) species other than PuO_2^+, which then reacts with Pu(III) to form Pu(IV).

The preparation and identification of xenon trioxide by Koch and Williamson[1] indicated that this compound is a powerful new oxidizing agent with a six-electron change. The xenon–xenon(VI) potential has been estimated to be −1.8 v in acid solution,[2] placing xenon

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(1) S. M. Williamson and C. W. Koch, *Science*, **139**, 1046 (1963).

(2) E. H. Appelman and J. G. Malm, *J. Am. Chem. Soc.*, **86**, 2141 (1964).

trioxide between cerium(IV) ($E^\circ = -1.61$ v[3]) and ozone ($E^\circ = -2.07$ v[4]) in oxidizing power. It has an advantage over cerium(IV) since its reduced form, xenon, is a relatively insoluble gas that does not contaminate the solution. Compared to ozone, xenon trioxide is more convenient to use. Furthermore, aqueous solutions may be stored for months without measurable decomposition.[2] Aside from the work of Koch and Williamson[5] on the oxidation of bromide and iodide, there have been no reports of the kinetics of xenon trioxide reactions previous to the studies described in this paper.

In an earlier communication, the reaction of plutonium(III) with xenon trioxide was shown to be first order in each reactant.[6] The reaction follows the overall equation

$$6\text{Pu(III)} + \text{XeO}_3 + 6\text{H}^+ \longrightarrow 6\text{Pu(IV)} + \text{Xe} + 3\text{H}_2\text{O} \quad (1)$$

although in some cases there is apparent deviation from this stoichiometry, due to formation of plutonyl(VI). This paper presents a more complete report on the kinetics of the reaction and its thermodynamic quantities of activation, and a discussion of possible reaction mechanisms.

Experimental Section

Reagents.—The plutonium(III) solutions used in this study were prepared by dissolution of weighed samples of plutonium metal in concentrated perchloric acid at room temperature and dilution to the desired concentration. (A separate experiment indicated that after dissolution and dilution, the solutions contained approximately 0.001 M chloride. The effect of chloride on the reaction was not evaluated.) The solutions were used immediately after preparation to minimize oxidation of the plutonium by products of α radiolysis of the solutions. Essentially all the plutonium was present as the trivalent ion, as evidenced by the spectra of the solutions and by the close agreement between the extrapolated initial plutonium(III) concentrations calculated from the spectrophotometric data and the known amounts of plutonium present in the solutions.

The xenon trioxide solution, obtained from the Chemistry Division of Argonne National Laboratory, had been passed through a zirconium phosphate–zirconium oxide bed to remove fluoride. It was standardized by reduction with excess potassium iodide and titration of the iodine liberated with sodium thiosulfate.

Lithium perchlorate was used to maintain an essentially constant ionic strength of approximately 2 M. This compound was obtained from the G. Frederick Smith Chemical Co. and was recrystallized six times before use.

Procedure.—All reactions were conducted in a 1-cm spectrophotometer cell equipped with a water jacket through which was passed water (500 ml/min flow rate) from a constant-temperature bath at the desired temperature. The exact temperatures inside the cell were established by runs under similar conditions in which a thermocouple was immersed in the solution. The reactions were followed spectrophotometrically by periodic measurements of the plutonium(III) peak at 600 mμ [plutonium(III) and plutonium(IV) molar extinction coefficients 38 and 2 M^{-1} cm^{-1}, respectively[7]] and the plutonium(IV) peak at 470 mμ [plutonium(III) and plutonium(IV) molar extinction coefficients 3 and 55 M^{-1} cm^{-1}, respectively[7]] with a Cary Model 14 recording spectrophotometer.

A computer program was developed[8] for calculating corrected values of the plutonium(III) and xenon trioxide concentrations from the initial concentrations and the light absorption at 600 mμ or at 470 mμ.

Xenon trioxide concentrations were calculated from the plutonium(III) concentrations (in the case of the 600 mμ data) and from the plutonium(IV) concentrations (470 mμ data) assuming the stoichiometry given in eq 1.

In these calculations it was assumed that plutonium(IV) is the sole oxidation product and that therefore the sum of the plutonium(III) and plutonium(IV) concentrations was constant. This assumption was not valid, however, particularly at low acidities. Although the agreement between the values calculated from data at the two wavelengths is fair in 2 M acid, it is poor in 0.5 M acid, the values from data at 470 mμ being consistently lower. Calculations indicated that in 2 M acid the sum of the plutonium(III) and plutonium(IV) concentrations remained essentially constant, while in the more dilute acid approximately 10% of the plutonium(IV) was oxidized to plutonyl(VI). Because of this reaction, the values of A_{470} would not be an accurate indication of the quantities of plutonium(III) oxidized and would give low values for the rate of disappearance of plutonium(III). In contrast, the results computed from the 600 mμ data contain only minor inaccuracies, since plutonium(IV) has only a small absorbance at 600 mμ. The error resulting from the assumption that the sum of the plutonium(III) and plutonium(IV) concentrations is constant was found to be negligible; calculations using an alternate approach that did not require this assumption indicated an error in the plutonium(III) concentrations of less than 0.5% in 2 M and 1 M acid and no more than 1% in 0.5 M acid. Because of the availability of a computer program based on the absence of side reactions, the 600 mμ data were used in calculating plutonium(III) concentrations, and the resulting minor error was disregarded in subsequent calculations.

Another error in the 0.5 M acid runs resulted from failure to allow for the depletion of xenon trioxide resulting from the partial oxidation of plutonium(IV), but this error is also minor. Since they are more accurate, only the 600 mμ data are reported.

Results

The Rate Law.—The results obtained by means of the above relations were substituted into the equation

$$k_2t = 6/(6[\text{XeO}_3]_0 - [\text{Pu(III)}]_0) \ln \{[\text{Pu(III)}]_0[\text{XeO}_3]/[\text{XeO}_3]_0[\text{Pu(III)}]\} \quad (2)$$

which is the integrated second-order rate equation for a reaction of this stoichiometry. Plots of the right-hand side of this equation *vs.* time were good straight lines, confirming that the rate is first order in each reactant

$$-d[\text{Pu(III)}]/dt = k[\text{Pu(III)}][\text{XeO}_3]$$

Table I contains the rate constants obtained under various conditions. The values of k were determined by the least-squares method, and the uncertainties given are standard deviations. It will be noted that k remains approximately constant through a fourfold initial concentration range in each reactant and is independent of acidity in the concentration range investigated.

Temperature Dependence.—The temperature dependence was determined from second-order rate constants obtained at various temperatures as shown in Table I. A plot of log k *vs.* $1/T$ gave a good straight

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(3) W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1952, p 294.

(4) Reference 3, p 46.

(5) C. W. Koch and S. M. Williamson, "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, pp 181–184.

(6) J. M. Cleveland, *J. Am. Chem. Soc.*, **87**, 1816 (1965).

(7) D. Cohen, *J. Inorg. Nucl. Chem.*, **18**, 207 (1961).

(8) G. J. Werkema, "Fortran II Program for Reduction of Spectrophotometric Reaction Kinetics Data," U. S. Atomic Energy Commission Report RFP-629, Nov 17, 1965.

TABLE I[a]

RATE CONSTANTS FOR THE REACTION 6Pu(III) + Xe(VI) → 6Pu(IV) + Xe

$[Pu(III)]_0$, *M*	$[XeO_3]_0$, *M*	% completion	$k \times 10^3$, M^{-1} sec^{-1}
$[H^+] = 2.0 \pm 0.1$ *M*; *I* = 2 *M*; 30.0 ± 0.2°			
0.0117	0.00097	50	18.8 ± 0.15
0.0117	0.00097	28	17.0 ± 0.16
0.0119	0.00097	48	15.9 ± 0.11
0.0122	0.00097	51	18.4 ± 0.14
0.0229	0.00097	54	20.4 ± 0.39
0.0229	0.00097	50	18.5 ± 0.15
0.0226	0.00194	47	16.9 ± 0.15
0.0233	0.00194	50	17.6 ± 0.05
0.0234	0.00194	53	18.2 ± 0.04
0.0459	0.00194	66	17.7 ± 0.12
0.0462	0.00194	74	20.4 ± 0.12
0.0451	0.00388	63	17.2 ± 0.06
0.0459	0.00388	72	17.4 ± 0.04
0.0459	0.00388	67	18.0 ± 0.02
0.0464	0.00388	56	17.5 ± 0.03
			Mean 18.1 ± 1.2
$[H^+] = 1.0 \pm 0.1$ *M*; *I* = 2 *M*; 30.0 ± 0.2°			
0.0468	0.00388	70	17.8 ± 0.40
0.0478	0.00388	65	20.2 ± 0.06
			Mean 19.1 ± 1.2
$[H^+] = 0.5 \pm 0.1$ *M*; *I* = 2 *M*; 30.0 ± 0.2°			
0.0434	0.00388	66	16.2 ± 0.20
0.0489	0.00388	73	17.8 ± 0.19
0.0508	0.00388	77	19.9 ± 0.16
			Mean 18.0 ± 1.5
$[H^+] = 2.0 \pm 0.1$ *M*; *I* = 2 *M*; 15.6 ± 0.2°			
0.0479	0.00388	57	4.61 ± 0.01
0.0486	0.00388	57	4.43 ± 0.01
0.0487	0.00388	58	4.64 ± 0.01
			Mean 4.57 ± 0.09
$[H^+] = 2.0 \pm 0.1$ *M*; *I* = 2 *M*; 44.3 ± 0.3°			
0.0223	0.00194	59	56.0 ± 0.26
0.0224	0.00194	55	58.2 ± 0.34
0.0428	0.00388	65	54.0 ± 0.27
0.0443	0.00388	72	56.0 ± 0.28
			Mean 56.0 ± 1.5

[a] Two runs, one in 2 *M* $HClO_4$, with *k* = 12.2, and one in 1 *M* $HClO_4$, with *k* = 10.2, are omitted from this table and were not used in subsequent calculations. The reason for their deviation is not known.

line whose slope and intercept were determined by the least-squares method.

From the slope of this plot thermodynamic values for the net activation process

$$Pu^{3+} + XeO_3 = (Pu\text{–}XeO_3^{3+})^{\ddagger} \qquad (3)$$

were calculated according to absolute reaction rate theory.[9] The values obtained at 30° were: $\Delta H^{\ddagger} = 15.3 \pm 2.1$ kcal/mole, $\Delta F^{\ddagger} = 20.2 \pm 0.1$ kcal/mole, and $\Delta S^{\ddagger} = -16.0 \pm 6.9$ eu. (The uncertainties were calculated as follows: Extreme high and low values of log *k* (based on standard deviations of *k* of 0.0012 at 15.6 and 30.0° and 0.0015 at 44.3°) were included on the log *k vs.* $1/T$ plot. Using these extreme points, lines were drawn with maximum and minimum slopes, and these limiting slopes were then used to calculate the uncertainties given above. The standard deviation used for the 15.6° data is larger than that given in Table I, but it is felt to be more realistic.)

Discussion

The net equation for the reaction involves a loss of one electron by plutonium(III), and it is possible that the mechanism merely consists of steps of the type

$$Pu(III) + Xe(VI) \longrightarrow Pu(IV) + Xe(V) \qquad (4)$$

with the lower-valent xenon species being reduced by plutonium(III) in successive one-electron steps until xenon gas is the final reduction product. However, from the known chemistry of xenon compounds there are reasons to question this simple one-electron-change mechanism.

No odd-valent compounds of xenon have been reported, and it is probable that the formation of odd-valent xenon species, even as transient intermediates in solution, would be hindered. Preliminary experiments on the oxidation of chromium(II) by xenon trioxide revealed that chromium(III) dimer is the principal product,[10] indicating a preference for a two-electron-change mechanism involving chromium(IV) as an intermediate.[11] Furthermore, studies of the kinetics of oxidation of neptunyl(V) by xenon trioxide indicate that this reaction—which would be expected to proceed by a one-electron change—is extremely slow.[12] Nevertheless, the one-electron-change mechanism cannot be ruled out.

A possible two-electron-change mechanism for the reaction can be formulated as follows

$$Pu^{3+} + Xe(VI) \xrightarrow{k} PuO_2^{+} + Xe(IV) \qquad (5)$$

followed by

$$PuO_2^{+} + Pu^{3+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2Pu^{4+} \qquad (6)$$

[The Xe(IV) formed in reaction 5 would presumably be reduced by successive two-electron changes to xenon gas, the final reduction product.] In competition with reaction 6, however, would be another reaction

$$PuO_2^{+} + Pu^{4+} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} PuO_2^{2+} + Pu^{3+} \qquad (7)$$

which would become increasingly important as the plutonium(IV) concentration increased. The value of k_1 has been reported as 5.8×10^{-2} M^{-1} sec^{-1} in 0.5 *M*

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(9) S. Glasstone, K. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p 199.

(10) R. C. Thompson, Argonne National Laboratory, personal communication, 1966.

(11) M. Ardon and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3197 (1959).

(12) J. M. Cleveland and G. J. Werkema, unpublished results.

hydrochloric acid at room temperature.[13] Reaction 7 is much more rapid; in 1.0 *M* perchloric acid at 25°, k_3 is approximately 37 M^{-1} sec^{-1} and the equilibrium constant, *K*, is approximately 13.[14] The greater rate of reaction 7 may best be illustrated by comparing the plutonyl(V) half-times in the two reactions; in reaction 6, assuming a representative plutonium(III) concentration of 0.04 *M*

$$t_{1/2}(PuO_2^+) = \frac{0.693}{0.058 \times 0.04} \simeq 300 \text{ sec}$$

while for reaction 7, assuming a plutonium(IV) concentration of 0.004 *M* [*i.e.*, only one-tenth of the plutonium(III) has been oxidized to plutonium(IV)]

$$t_{1/2}(PuO_2^+) = \frac{0.693}{37 \times 0.004} \simeq 5 \text{ sec}$$

and the half-time would become progressively shorter as the plutonium(IV) concentration increased. Although the conditions in reactions 6 and 7 differed, this comparison suggests that if reaction occurred by the two-electron-change mechanism, the principal oxidation product should be plutonyl(VI), rather than the plutonium(IV) actually observed. On the other hand, the known chemistry of xenon trioxide suggests that the two-electron-change mechanism would be preferred. This contradiction may be resolved by postulating that the initial plutonium(V) species produced in reaction 5 is not the usual PuO_2^+, but is another species, such as PuO^{3+} or $PuOXeO_2^{3+}$, that reacts with plutonium(III) much more rapidly than it does with plutonium(IV)

$$Pu^{3+} + XeO_3 \longrightarrow PuO^{3+} \quad (\text{or } PuOXeO_2^{3+}) \qquad (8)$$

$$PuO^{3+} + Pu^{3+} \longrightarrow 2Pu^{4+} \quad (\text{relatively rapid}) \qquad (9)$$

$$PuO^{3+} + Pu^{4+} \longrightarrow Pu^{3+} + PuO_2^{2+} \quad (\text{relatively slow}) \qquad (10)$$

Such a mechanism does not seem unreasonable if it is recalled that the formation of oxygenated species such as PuO_2^+ is slow (hence the relatively low rate of most reactions involving the formation or decomposition of such species) and apparently involves more than a single step. It seems plausible that the first step could be the formation of a monoxygenated species, such as PuO^{3+}, or of an intermediate having the same composition as the activated complex, $PuOXeO_2^{3+}$. Either of these postulated intermediates would have a charge of +3 and would therefore experience less electrostatic repulsion in reacting with plutonium(III) than with plutonium(IV), suggesting a preference for reaction 9 compared to reaction 10. On the other hand, reactions 6 and 7 involve a plutonyl(V) ion with only a single charge, and electrostatic effects are therefore less pronounced.

In summary, it appears that the reaction mechanism involves either a one-electron-change to form plutonium(IV) directly or a two-electron-change to form a plutonium(V) species other than the plutonyl(V) ion, which then reacts with plutonium(III). A mechanism involving plutonyl(V) is unlikely since the principal product would be plutonyl(VI) rather than the observed plutonium(IV).

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(13) R. E. Connick, *J. Am. Chem. Soc.*, **71**, 1528 (1949).

(14) S. W. Rabideau and R. J. Kline, *J. Phys. Chem.*, **62**, 617 (1958).

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The Reaction of Xenon Difluoride with Water and with Xenon Trioxide[1]

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In 0.01 *M* $HClO_4$ xenon difluoride oxidizes water with a first-order rate constant of 4.2 × 10^{-4} sec^{-1} at 25°, and with $\Delta H^{\ddagger} = 19.6$ kcal/mole and $\Delta S^{\ddagger} = -8.1$ eu. The reaction is catalyzed by bases and by substances with affinity for fluoride ion. Intermediates in the reaction oxidize benzenesulfonic acid and reduce XeO_3. The reduction of XeO_3 has been studied in detail. The number of XeO_3 molecules consumed per molecule of XeF_2 varies from zero to 1, depending on the initial ratio of concentrations. Mechanisms are proposed invoking XeO and XeO_2 as intermediates.

In previous papers[2,3] we have shown that xenon difluoride dissolves in water as molecular XeF_2, which then oxidizes the solvent at a measurable rate, according to the reaction

$$XeF_2 + H_2O \xrightarrow{k_1} Xe + 0.5O_2 + 2HF \qquad (1)$$

We have also observed[4] that xenon trioxide introduced into an XeF_2 solution is consumed in the course of reac-

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(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) E. H. Appelman and J. G. Malm, *J. Am. Chem. Soc.*, **86**, 2297 (1964).

(3) E. H. Appelman, *Inorg. Chem.*, **6**, 1268 (1967).

(4) E. H. Appelman and J. G. Malm, "Preparative Inorganic Reactions," Vol. 2, W. L. Jolly, Ed., Interscience Publishers, Inc., New York, N. Y., 1965, p 344.