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Kinetics of the Reaction between Plutonium(III) and Chromium(VI) in Aqueous Perchlorate Solutions[1]

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The oxidation of Pu(III) to Pu(IV) by Cr(VI) was studied in aqueous perchlorate solutions from 0.10 to 2.0 *M* in $HClO_4$. To a good approximation the initial rates are given by $k[\mathrm{Pu(III)}][\mathrm{Cr(VI)}][\mathrm{H}^+]^2$, but k is increased slightly by increasing Cr(VI) and decreased markedly by Pu(IV). The reaction induces the oxidation of I^- by Cr(VI) with a limiting induction factor of 2 equiv of I^- oxidized per mole of Pu(IV) formed. The proposed mechanism involves the reversible formation of Cr(V) and is similar to that for the analogous oxidation of Fe(II) by Cr(VI). A small negative temperature coefficient was observed in 0.10 *M* $HClO_4$–0.90 *M* $LiClO_4$ solutions and the activation parameters for the first rate determining step are $\Delta F^* = 11.81 \pm 0.03$ kcal/mol, $\Delta H^* = -0.75 \pm 0.75$ kcal/mol, and $\Delta S^* = -42 \pm 2.6$ cal/(mol deg).

Introduction

Chromium(VI) is a convenient, useful oxidizing agent which is particularly interesting because two intermediate oxidation states are possible on the way to Cr(III), the usual final product. The kinetics of the reduction of Cr(VI) by many reducing agents have been reviewed recently.[2,3] Plutonium(III) was chosen for the present study in order to extend our knowledge of plutonium chemistry and of one-electron reductions of Cr(VI). Previous work on the oxidation of actinide ions by Cr(VI) was limited to U(IV),[4] Pu(IV),[5,6] and Np(V).[7]

Even though Cr(VI) is strong enough to oxidize Pu(III) all the way to Pu(VI), the observed stoichiometry is given by the equation:

$$3\mathrm{Pu}^{3+} + \mathrm{HCrO_4}^- + 7\mathrm{H}^+ = 3\mathrm{Pu}^{4+} + \mathrm{Cr}^{3+} + 4\mathrm{H_2O} \tag{1}$$

The kinetics of the oxidation of Fe(II) and Pu(III) are often similar and the work reported here shows that this similarity extends to the reduction of Cr(VI). For both reducing agents the rate is predominantly second power in the hydrogen ion concentration. Also the rates are inhibited by the products Fe(III) or Pu(IV), consistent with a reversible formation of Cr(V) in the first step. This suggestion is supported by the observation that the Pu(III) reaction, as well as the Fe(II) one, causes an induced oxidation of iodide ion with a limiting stoichiometric ratio of 2 equiv of I^- oxidized per 1 equiv of Pu(IV) (or Fe(III)) formed.

Experimental Section

Reagents. Solutions of Pu(III) in $HClO_4$ were prepared and analyzed as previously described.[8] Pu(III)–Pu(IV) mixtures were prepared by adding appropriate amounts of standardized Cr(VI) to stirred solutions of Pu(III). Doubly vacuum distilled $HClO_4$ from the G. F. Smith Chemical Co. was diluted and standardized using HgO. Solutions of $K_2Cr_2O_7$ and of KI were prepared from Mallinckrodt Analytical Reagent grade materials. $LiClO_4$ was prepared by neutralizing reagent grade Li_2CO_3 with reagent grade $HClO_4$ and recrystallizing three times. These $LiClO_4$ solutions were standardized by drying in air to constant weight at 170°.

Procedures. Reaction rates were determined spectrophotometrically using either the Gibbs–Durrum Stopped Flow apparatus or using thermostated, rapidly stirred 10 cm cells[9] in the Cary Model 14 recording spectrophotometer. For most of the runs a wavelength of 360 nm was used although a few runs were followed at other nearby wavelengths. Excess Pu(III) was used and this was determined after the stirred cell runs by spectrophotometric titrations with standardized Ce(IV). These titrations were made after adding H_2SO_4 to the solutions so that the rate of oxidation of Cr(III) by the Ce(IV) was negligibly slow. For the stopped flow runs, the separate reactant solutions were analyzed before the runs.

The formation of the Pu(IV)–Cr(VI) complex was studied spectrophotometrically using the Cary instrument. Solutions containing Pu(IV) and Cr(VI) were made by adding excess Cr(VI) to Pu(III) in 1 *M* $HClO_4$; the excess was determined by adding standardized Fe(II) and back titrating with Ce(IV) in 0.5 *M* H_2SO_4. These solutions were diluted appropriately and their absorbances were determined at several wavelengths near 360 nm. The solutions were thermostated in the cell compartment of the spectrophotometer.

The induced oxidation of I^- by the Pu(III)–Cr(VI) reaction was studied at 25°. Relatively small, known amounts of $HCrO_4^-$ were injected into known mixtures of Pu(III), I^-, $HClO_4$, and $LiClO_4$ in the thermostated stirred absorption cells. The I_2–I_3^- formed caused easily measurable absorbance increases at 440 or 465 nm. The absorbance values were extrapolated to the time of mixing to allow for the slow reaction between Pu(IV) and I^-. The average extinction coefficients of the I_2–I_3^- mixtures depend slightly on the free I^- concentrations and were determined in parallel experiments in which standardized Ce(IV) solutions were added to known I^- solutions. All solutions were swept with argon to eliminate the possible reactions with oxygen in the air.

Calculations. The absorbance, D_t, at a particular time, of a reacting solution is given by

$$D_t = D_0 + b\{([\mathrm{Cr(VI)}]_0 f_c\epsilon_1 - [\mathrm{Pu(IV)}]_0 f_p\epsilon_2) - x(\epsilon_3 - f_p\epsilon_2 - f_c\epsilon_1/3)\} \tag{2}$$

where D_0 is the sum of the absorbances of the initial reactants without the formation of the $\mathrm{PuCrO_4}^{2+}$ complex, b is the optical path length, $[\mathrm{Cr(V)}]_0$ is the initial stoichiometric concentration of Cr(VI), f_c is the fraction of the Cr(VI) which is complexed by Pu(IV), $[\mathrm{Pu(IV)}]_0$ is the initial stoichiometric concentration of Pu(IV), f_p is the fraction of the Pu(IV) which is complexed by the Cr(VI), $\epsilon_1 = \epsilon_{\mathrm{complex}} - \epsilon_{\mathrm{HCrO_4^-}}$, $\epsilon_2 = \epsilon_{\mathrm{Pu^{4+}}}$, $\epsilon_3 = \epsilon_{\mathrm{HCrO_4^-}}/3 + \epsilon_{\mathrm{Pu^{3+}}} - \epsilon_{\mathrm{Pu^{4+}}} - \epsilon_{\mathrm{Cr^{3+}}}/3$, and x is the extent of reaction $[\mathrm{Pu(III)}]_0 - [\mathrm{Pu(III)}]_t$.

The stoichiometric concentrations of Pu(III), Pu(IV), and Cr(VI) were calculated as a function of time using an appropriate rate law and f_c and f_p were calculated from [Pu(IV)], [Cr(VI)], and Q, the association quotient for Pu(IV)–Cr(VI) complex. These calculations were made numerically as part of a nonlinear least-squares program which determined the values for the rate constants and other selected parameters which minimized the sum of the squares of the differences between the observed and calculated absorbance values. For data from the stopped flow apparatus, the program was modified to minimize the sum of the squares of the differences between the observed and calculated transmission values.

For most of the runs the data were not consistent with a simple second-order rate law, so the following procedure was used to find a satisfactory rate law and to determine the rate constants. First, an empirical modification of the second-order rate law was used to find approximate initial values for the apparent second-order rate constants. Next, these rate constants were plotted against the concentrations of the various reactants and products to suggest possible forms for the actual rate law. Finally, these rate laws were used with the absorbance versus time data as described above to find the best values for the rate constants for the individual rate runs. If consistent values were found, the rate law was considered satisfactory.

The induction factor, F_i, for the induced oxidation of I^- is defined as the number of equivalents of I^- oxidized for each equivalent of Pu(IV) formed. This factor was calculated from the observed quantities using the expression

$$F_i = (1 - 3\Delta\epsilon/\epsilon')/(1.5\epsilon_{I_2}/\epsilon' - 1) \tag{3}$$

Table I. Determination of the Association Quotient for $PuCrO_4^{2+a}$

[Pu-(IV)], $M \times 10^4$	[Cr-(VI)], $M \times 10^5$	Absorbance values^b					
		350 nm		360 nm		370 nm	
		Obsd	Calcd^c	Obsd	Calcd^c	Obsd	Calcd^c
0.00	3.06	0.488	0.486	0.440	0.437	0.343	0.343
0.00	3.39	0.540	0.540	0.480	0.485	0.380	0.381
5.07	0.00	0.048	0.048	0.043	0.043	0.084	0.084
5.12	0.00	0.048	0.048	0.045	0.043	0.084	0.084
3.13	2.93	0.545	0.545	0.528	0.524	0.477	0.475
3.11	2.89	0.538	0.537	0.518	0.516	0.471	0.468
6.22	2.65	0.557	0.560	0.556	0.558	0.552	0.553
6.26	1.98	0.426	0.434	0.426	0.431	0.436	0.441
9.09	2.35	0.562	0.554	0.571	0.564	0.602	0.597
9.32	3.10	0.706	0.706	0.718	0.722	0.741	0.744

[a] Conditions: 1.8°, 0.10 M $HClO_4$–0.90 M $LiClO_4$. [b] Optical path, $b = 10.38$ cm. [c] Calculated using the values in Table II and the equations: absorbance $= b\{[\mathrm{Pu(IV)}]\epsilon_{\mathrm{Pu}^{4+}} + [\mathrm{Cr(VI)}]\epsilon_{\mathrm{HCrO_4}^-} + x\Delta\epsilon\}$, $x = [\mathrm{PuCrO_4}^{2+}] = Q([\mathrm{Pu(IV)}] - x)\cdot([\mathrm{Cr(VI)}] - x)/[\mathrm{H}^+]$, and $\Delta\epsilon = \epsilon_{\mathrm{PuCrO_4}^{2+}} - \epsilon_{\mathrm{Pu}^{4+}} - \epsilon_{\mathrm{HCrO_4}^-}$.

where $\Delta\epsilon = \epsilon_{\mathrm{Pu(IV)}} - \epsilon_{\mathrm{Pu(III)}}$, ϵ_{I_2} is the effective extinction coefficient of the I_2–I_3^- mixture at the prevailing I^- concentration, and ϵ' is an apparent extinction coefficient defined as the observed absorbance change per centimeter of path divided by the concentration of the injected Cr(VI), corrected for the Cr(III) formed:

$$\epsilon' = \Delta D/(b[\mathrm{Cr(VI)}]) - \epsilon_{\mathrm{Cr(III)}}$$

Experimental Results

Stoichiometry. Although Cr(VI) is strong enough to oxidize Pu(III) to Pu(VI), the rate of oxidation of Pu(IV) is quite low;[5,6] thus the predominant net reaction is given by eq 1. In support of this equation it was found that even with a 50% excess of Cr(VI) negligible amounts (<0.06%) of Pu(VI) formed in solutions 7×10^{-4} M in Pu and 0.1 M in $HClO_4$. The rate of disproportionation of the product, Pu^{4+}, is proportional to $[Pu^{4+}]^2[H^+]^{-3}$,[10] so that at relatively high concentrations of Pu^{4+} and low concentrations of H^+ appreciable amounts of PuO_2^{2+} are formed by the disproportionation reaction:

$$3Pu^{4+} + 2H_2O = 2Pu^{3+} + PuO_2^{2+} + 4H^+ \qquad (4)$$

Where appropriate, a correction for this reaction was applied in treating the rate data.

An additional complication arises from the fact that Pu^{4+} and $HCrO_4^-$ react to form a moderately stable complex[6] analogous to the $NpCrO_4^{2+}$ and $ThCrO_4^{2+}$ complexes previously described.[11] In the rate runs in which Pu^{4+} was initially present the absorbance in the region near 360 nm extrapolated to the time of mixing was found to be significantly greater than the sum of the absorbances of the initial components of the mixture. In order to correct the observed absorbances for the complex, values for the association quotient, $Q = [PuCrO_4^-][H^+]/([Pu^{4+}][HCrO_4^-])$, and the extinction coefficient for the complex were needed. These were obtained spectrophotometrically with sufficient accuracy for our purpose. Absorbance as a function of concentration of Pu(IV)–Cr(VI) mixtures was determined at three wavelengths. The values for Q and for the extinction coefficients which best reproduced the data were determined using a nonlinear least-squares program. The results of such a determination at 1.8° in 0.10 M $HClO_4$–0.90 M $LiClO_4$ solutions are summarized in Table I. The association quotient, Q, was found to be 42 ± 7; the appropriate extinction coefficient differences for the three wavelengths are given in Table II, along with the results from similar determinations made under different conditions.

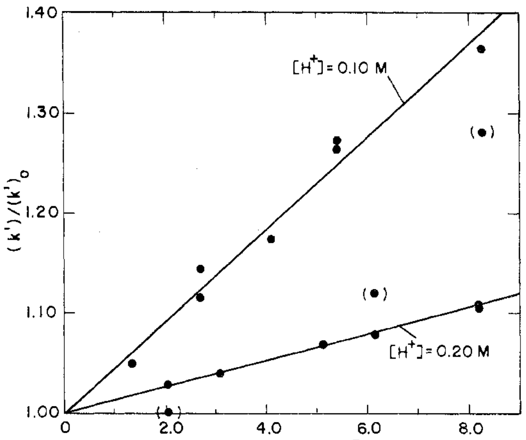

Figure 1. Effect of Cr(VI) on the initial apparent second-order rate constant. Ordinate is the ratio of the observed rate constant to that in the hypothetical absence of Cr(VI). Points in parentheses are apparently spurious.

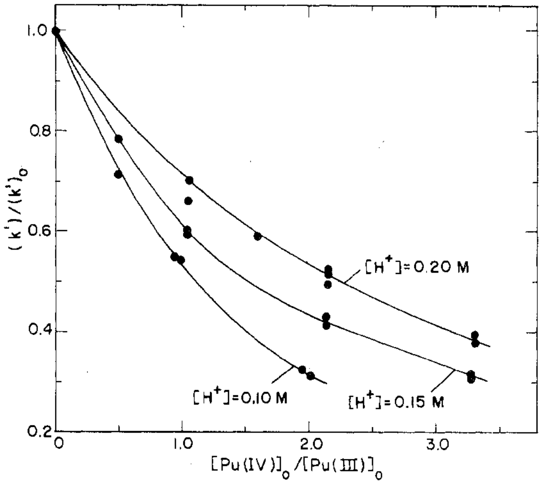

Figure 2. Effect of Pu(IV) on the initial apparent second-order rate constant. Ordinate is the ratio of the observed rate constant to that in the absence of added Pu(IV).

Rate Law. Reaction 1 is nearly first order in each reactant, so an apparent second-order rate constant can be defined by the expression $k' = (-d[\mathrm{Cr(VI)}]/dt)/([\mathrm{Cr(VI)}][\mathrm{Pu(III)}])$. However, we observed that the apparent second-order rate constant is decreased either by decreasing the initial Cr(VI) concentration or by increasing the initial Pu(IV) concentration. The concentrations of Pu(III) or Cr(III) are without significant effect on k. Some of these results, obtained at 25° and unit ionic strength, are illustrated in Figures 1 and 2. These dependences, together with the accepted mechanism for the

Table II. Association Quotients and Extinction Coefficients for $PuCrO_4^{2+}$

Temp, °C	$[HClO_4]$, M	$[LiClO_4]$, M	Q^a	$\Delta\epsilon$, M^{-1} cm^{-1} ^{b}		
				350 nm	360 nm	370 nm
1.8	0.1	0.1	150 ± 7	1080 ± 40	1670 ± 50	2050 ± 60
1.8	0.1	0.9	42 ± 7	1400 ± 180	2240 ± 280	2710 ± 332
25	0.1	0.9	147 ± 26	512 ± 85	1015 ± 115	1360 ± 140

[a] $Q = [PuCrO_4^{2+}][H^+]/[Pu^{4+}][HCrO_4^-]$. [b] $\Delta\epsilon = \epsilon_{\mathrm{PuCrO_4}^{2+}} - \epsilon_{\mathrm{Pu}^{4+}} - \epsilon_{\mathrm{HCrO_4}^-}$.

Table III. Effect of Cr(VI) on the Rate of Reaction 1[a]

0.10 M $HClO_4$			0.20 M $HClO_4$		
$[Cr(VI)]_0$, 10^5 M	$(k_1')_0$,[b] M^{-1} sec^{-1}	k_1',[c] M^{-1} sec^{-1}	$[Cr(VI)]_0$, 10^5 M	$(k_1')_0$,[b] M^{-1} sec^{-1}	k_1',[d] M^{-1} sec^{-1}
1.35	127	122	2.05	474	450
2.71	138	118	2.05	460	435
2.71	135	121	3.08	480	446
4.06	142	119	5.13	493	444
5.41	154	118	6.16	497	448
5.41	153	117	6.16	517	461
8.12	165	122	8.21	510	439
8.12	155	117	8.21	511	440

[a] Conditions: 25°, 1.00 M $(H,Li)ClO_4$, $Q = 147$. [b] Initial apparent second-order rate constant. [c] Calculated using $\alpha = 7.9 \times 10^3$ M^{-1} and $\beta = 0.967$. [d] Calculated using $\alpha = 6.0 \times 10^3$ M^{-1} and $\beta = 0.475$.

Table IV. Effect of Pu(IV) on the Rate of Reaction 1[a]

$HClO_4$, M	[Pu(IV)], 10^4 M	No. of determinations	$(k_1')_0$,[b] M^{-1} sec^{-1}	k_1'-(calcd),[c] M^{-1} sec^{-1}	k_1'-(calcd),[d] M^{-1} sec^{-1}
0.100	0.00	3	139	117	120
	1.05	1	99	120	121
	2.10	2	75.5	125	127
	4.25	2	44	110	114
0.150	0.00	5	303	263	271
	1.06	1	238	274	269
	1.42	2	182	264	267
	2.84	2	128	270	276
	4.26	2	92	261	272
0.200	0.00	6	483	432	448
	1.43	2	428	442	456
	2.13	1	284	447	460
	2.85	4	241	439	453
	4.28	3	184	419	440

[a] Conditions: 25°, 1.00 M $(H,Li)ClO_4$. [b] Apparent initial second-order rate constant. [c] Calculated from the absorbance versus time data using $\alpha = 7.9 \times 10^3$, 6.96×10^3, and 6.03×10^3 M^{-1} and $\beta = 0.947$, 0.675, and 0.478 in the 0.10, 0.15, and 0.20 M $HClO_4$ solutions, respectively. [d] Calculated from the absorbance versus time data under the assumption that $PuCrO_4^{2+}$ and $HCrO_4^-$ react with Pu^{3+} with equal rate constants, using $\alpha = 5.64 \times 10^3$, 4.51×10^3, and 3.38×10^3 M^{-1} and $\beta = 1.13$, 0.809, and 0.532 in the 0.10, 0.15, and 0.20 M $HClO_4$ solutions, respectively.

Table V. Hydrogen Ion Dependence of k_1 in Equation 5[a]

[Pu(III)], 10^4 M	[Cr(VI)], 10^5 M	$[HClO_4]$, M	$10^{-3}k_1$,[b] M^{-1} sec^{-1}	$10^{-4}k_1/[H^+]^2$, M^{-3} sec^{-1}
10.1	1.46	0.30	2.03	2.25
12.2	1.35	0.30	2.07	2.30
17.7	1.37	0.30	2.04	2.26
2.92	1.50	0.60	8.00	2.22
3.01	1.67	1.00	23.1	2.31
3.01	3.33	1.00	23.4	2.34
3.01	5.83	1.00	22.3	2.23
3.01	8.33	1.00	23.2	2.32
2.92	1.50	1.20	32.8	2.28
2.92	1.50	1.40	48.0	2.45
2.92	1.50	2.00	92.8	2.32
3.04	1.48	2.00	93.0	2.32
3.04	2.97	2.00	93.5	2.34
3.04	7.40	2.00	92.2	2.31

[a] Conditions: 2.00 M $(H,Li)ClO_4$, 25°, stopped flow apparatus. [b] Calculated assuming $\alpha = 0$, $\beta = 0.10/[H^+]$, and $Q = 114$.

Table VI. Hydrogen Ion Dependence for k_1 in Equation 5[a]

[Pu(III)], 10^4 M	[Cr(VI)], 10^5 M	$[HClO_4]$, M	$10^{-3}k_1$,[b] M^{-1} sec^{-1}	$10^{-4}k_1/[H^+]^2$, M^{-3} sec^{-1}	$10^{-3}k_1$,[d] M^{-1} sec^{-1}
1.99	2.99	0.100	0.110	11.0	0.109
1.99	2.99	0.200	0.393	9.8	0.389
1.99	2.99	0.217	0.434	9.2	0.454
1.99	2.99	0.267	0.652	9.1	0.673
5.93	3.00	0.350	1.16[c]	9.5	1.13
2.47	3.00	0.500	2.26[c]	9.1	2.26
5.93	3.00	0.500	2.33[c]	9.3	2.26

[a] Conditions: 0.50 M $(H,Li)ClO_4$, 25°, stirred cell apparatus, unless otherwise indicated. [b] Calculated from the absorbance versus time data assuming $\alpha = 0$, $\beta = 0.10/[H^+]$, and $Q = 199$. [c] Stopped flow apparatus used. [d] Calculated using $10^{-3}k_1 = 0.232\,[H^+] + 8.58\,[H^+]^2$ M^{-1} sec^{-1}.

analogous Fe(II) reaction,[3] suggest a trial rate law in the following form:

$$-d[Pu(III)]/dt = \frac{3k_1[Pu(III)][Cr(VI)](1-f_c)[1+\alpha[Cr(VI)](1-f_c)]}{1+\beta[Pu(IV)](1-f_p)/[Pu(III)]} \tag{5}$$

where k_1, α, and β are rate parameters; f_c and f_p are fractions complexed as defined in connection with eq 2. This rate law was integrated numerically as described above and found to be in agreement with the absorbance versus time data for the individual Cr(VI) dependence runs. The most consistent values for the rate constants, k_1, were obtained using values of $7.9 \pm 0.9 \times 10^3$ and $6.0 \pm 1.5 \times 10^3$ M^{-1} for the parameter α for the 0.10 and 0.20 M $HClO_4$ solutions, respectively. The results of these calculations are summarized in Table III.

Runs with varying initial Pu(IV) concentrations were made at 25° and $\mu = 1.00$ M in 0.10, 0.15, and 0.20 M $HClO_4$. Values for k_1 were calculated using the values for α given above or obtained by interpolation. The initial concentrations of Cr(VI) were low enough so that k_1 did not depend strongly on the value chosen. Again the rate law was found to be in agreement with the absorbance versus time data. The values for β which give the least variation in k_1 are 0.95 ± 0.20, 0.68 ± 0.05, and 0.48 ± 0.02 in 0.1, 0.15, and 0.20 M $HClO_4$ solutions, respectively. The results of these calculations are summarized in Table IV.

Hydrogen Ion Dependence. The main series of runs to determine the hydrogen ion dependence of k_1 was made at 25° in 2 M $(H,Li)ClO_4$ solutions. The initial concentrations of Pu(IV) and of Cr(VI) were low enough so that the H^+ dependences of α and β were relatively unimportant. The results, summarized in Table V, show that k_1 increases very rapidly with $[H^+]$, but that $k_1/[H^+]^2$ is essentially constant. The k_1 values in Table III which were calculated allowing for the effect of the initial concentrations of Cr(VI) cover only a factor of 2 in $[H^+]$, but they also indicate that the rates depend on $[H^+]^2$. Results obtained in 0.5 M $(H,Li)ClO_4$ are summarized in Table VI; these are noteworthy because the data obtained using the stirred cell are in substantial agreement with those obtained using stopped flow.

Temperature Dependence. Rates were measured at temperatures between 1.8 and 35.3° in 0.1 M $HClO_4$–0.9 M $LiClO_4$ solutions. Second-order rate constants were calculated from the absorbance versus time data using eq 5 and the appropriate values for β and Q. The initial concentration of Cr(VI) was the same for all the temperatures (3.2×10^{-5} M) and the small $[Cr(VI)]^2$ term was ignored. At 35° in particular, appreciable concentrations of Pu(VI) were detected, due to the disproportionation of Pu(IV), the rate of which is given by[10]

$$d[Pu(VI)]/dt = k_d[Pu(IV)]^2 - k_r[Pu(III)]^2[Pu(VI)]/[Pu(IV)] \tag{6}$$

where k_d and k_r are the rate constants for the forward and reverse reactions, respectively. Correction for the dispro-

Table VII. Temperature Dependence of k_1 in Equation 5[a]

Temp, °C	$10^3 k_d$, M^{-1} sec^{-1}	$10^4 k_r$, M^{-1} sec^{-1}	Q	β	k_1,[b] M^{-1} sec^{-1}	k_1,[c] M^{-1} sec^{-1}
1.8	0.4	9.6	42	0.21	163, 164	157
8.0	1.2	6.6	60	0.32	152	151
9.8	1.7	5.9	66	0.37	141	150
15.4	4.3	4.2	89	0.53	136	145
20.7	10	3.1	117	0.75	139	141
25.3	20	2.4	147	1.0	140[d]	138
35.3	97	1.4	237	1.8	132, 134	131

[a] Conditions: 0.10 M $HClO_4$–0.90 M $LiClO_4$, 3.2×10^{-5} M [Cr(VI)], 1.8×10^{-4} M [Pu(III)]. [b] Calculated from the absorbance versus time data using the listed values for k_d, k_r, Q, and β under the assumption that α in eq 5 is zero. [c] Calculated using the Eyring equation with $\Delta S^* = -44.6$ cal/(mol deg) and $\Delta H^* = -1.48$ kcal/mol. [d] Average of eight values.

portionation reaction was applied at all temperatures using values for k_d and k_r determined from the published data.[10] The corrections were significant only at 35°. The results of the temperature dependence studies are summarized in Table VII.

The apparent values for k_1 decrease by about 16% between 2 and 35°. This might indicate a small negative activation energy, but might also be due to the fact that α in eq 3 was ignored, or to errors in the values assumed for Q and β. It is clear, however, that the temperature dependence for k_1 is quite small.

Induced Oxidation of Iodide Ion. The results of determinataions of the induction factor for the induced oxidation of iodide ion are summarized in Table VIII. Plots of the reciprocals of the induction factors, as defined above, versus the concentration ratio, [Pu(III)]/[I^-], gave smooth curves with intercepts close to 0.5. This shows that the limiting value of the induction factor at high I^- concentrations is probably 2 and the overall stoichiometry under these conditions is

$$\mathrm{Pu(III)} + 2\mathrm{I}^- + \mathrm{Cr(VI)} = \mathrm{Pu(IV)} + \mathrm{I}_2 + \mathrm{Cr(III)} \qquad (7)$$

The I_3^- ion also forms, but at concentrations less than those of I_2(aq). The direct oxidation of I^- by Cr(VI) is not insignificant, particularly at acid concentrations near 1 M. This probably accounts for the value greater than 2 in the table. Published data[12] give apparent second-order rate constants for the disappearance of Cr(VI) of 5 and 190 M^{-1} sec^{-1} in 0.3 and 1.0 M $HClO_4$ at 25°. Since these values apply to an ionic strength of 0.13 M, an additional determination in 1 M $HClO_4$ was made. The initial concentrations were 5.1×10^{-5} M Cr(VI) and (6–9) $\times 10^{-4}$ M I^-, and the apparent second-order rate constant was found to be 68 ± 1 M^{-1} sec^{-1}. This result is in satisfactory agreement with the previous ones when the difference in ionic strength is taken into consideration.

In order to compare the Fe(II) and Pu(III) reactions, the Fe(II) induction of the oxidation of I^- was studied briefly in perchlorate solutions. The previous work was done in chloride solutions with acid concentrations ≤0.04 M.[13] In agreement with this earlier work, limiting induction factors of two were found. The concentration ratios, [I^-]/[Fe(II)], required to make $F_i = 1.0$ were 0.17_1 in 0.30 M $HClO_4$–0.70 M $LiClO_4$ solutions and 0.37_6 and 0.17_4 in 0.05 M and 0.20 M $HClO_4$ solutions, respectively.

Discussion

One conceivable set of reactions which leads to the overall reaction includes a two-electron oxidation of Pu(III) to Pu(V) followed by the reduction of the Pu(V) to Pu(IV) by Pu(III). However, the rate constant for the oxidation of Pu(V) by Cr(VI) is about 10^3 greater than that for the reduction of Pu(V) by Pu(III).[6,8] Thus the observed stoichiometry rules out such a two-electron step.

Table VIII. Induction Factors for the Induced Oxidation of Iodide Ion[a]

[H^+], M	[Pu(III)], 10^4 M[b]	[I^-], 10^4 M[b]	F_i Obsd	F_i Calcd[c]
0.30	7.66	5.85	0.64	0.64
	7.85	18.2	1.32	1.29
	7.86	21.3	1.39	1.39
	7.91	30.6	1.68	1.59
	9.66	5.90	0.53	0.54
	9.82	12.0	0.96	0.92
	9.91	24.4	1.36	1.37
1.00	2.47	2.39	1.28	1.24
	3.73	5.54	1.58	1.52
	3.77	8.59	1.86	1.72
	3.78	14.8	1.94	1.91
	3.80	30.2	2.13	2.08
	5.42	5.37	1.35	1.34
	5.50	11.3	1.82	1.73
	7.77	5.63	1.10	1.20
	7.92	30.3	1.98	1.96
	10.63	5.46	0.97	1.02
	10.73	11.35	1.40	1.50

[a] Equivalents of I^- per equivalent of Pu(III) oxidized. Conditions: 25°, 7×10^{-5} M Cr(VI), $\mu = 1.0$ M ($LiClO_4$). [b] Average concentration during the run. [c] Calculated using eq 12 with k_0/k_1, k_3/k_I, and a equal to 5.3×10^{-3}, 0.244, and 860 M^{-1} in 1 M H^+ and 1.6×10^{-3}, 0.633, and 260 M^{-1} in 0.3 M H^+, respectively.

The most plausible reaction scheme consistent with rate law 3 is analogous to the ones proposed for other one-electron reducing agents such as Fe(II) and Np(V).[3] Written without regard to hydrogen ions it is:

$$\mathrm{Pu(III)} + \mathrm{Cr(VI)} = \mathrm{Pu(IV)} + \mathrm{Cr(V)} \qquad k_1, k_2 \qquad (8a)$$

$$\mathrm{Pu(III)} + 2\mathrm{Cr(VI)} = \mathrm{Pu(IV)} + \mathrm{Cr(V)} + \mathrm{Cr(VI)} \qquad k_{12}, k_{22} \qquad (8b)$$

$$\mathrm{Pu(III)} + \mathrm{Cr(V)} = \mathrm{Pu(IV)} + \mathrm{Cr(IV)} \qquad k_3 \qquad (8c)$$

$$\mathrm{Pu(III)} + \mathrm{Cr(V)} + \mathrm{Cr(VI)} = \mathrm{Pu(IV)} + \mathrm{Cr(IV)} + \mathrm{Cr(VI)} \qquad k_{32} \qquad (8d)$$

$$\mathrm{Pu(III)} + \mathrm{Cr(IV)} = \mathrm{Pu(IV)} + \mathrm{Cr(III)} \qquad \text{rapid} \qquad (8e)$$

$$\mathrm{Pu(IV)} + \mathrm{Cr(VI)} = \mathrm{Pu(IV)}\text{–}\mathrm{Cr(VI)} \qquad Q\text{, rapid reversible equilibrium} \qquad (8f)$$

In this scheme reactions 8b and 8d are not meant to imply termolecular processes, but merely to show that two chromium species are required for the formation of the activated complexes. The implication of this is discussed below. The usual steady-state approximation in the concentration of the Cr(V) intermediate leads to the rate law:

$$-\mathrm{d}[\mathrm{Pu(III)}]/\mathrm{d}t = \frac{3k_1[\mathrm{Pu(III)}][\mathrm{Cr(VI)}](1-f_c)(1+(k_{12}/k_1)[\mathrm{Cr(VI)}](1-f_c))}{1+\dfrac{k_2[\mathrm{Pu(IV)}](1-f_p)(1+(k_{22}/k_2)[\mathrm{Cr(VI)}](1-f_c))}{k_3[\mathrm{Pu(III)}](1+(k_{32}/k_3)[\mathrm{Cr(VI)}](1-f_c))}} \qquad (9)$$

where f_c and f_p are the fractions of Cr(VI) and Pu(IV) that are complexed (as defined previously). If $k_{22}/k_2 = k_{32}/k_3$, eq 9 reduces to the form of eq 5 and we can identify k_{12}/k_1 with α and k_2/k_3 with β. Equation 9 is in agreement with the observations even if the rate ratios above are only approximately equal. Some calculations were made in which k_{32}/k_3 was made 65% greater than k_{22}/k_2 and it was found that the fit of the absorbance versus time data was not changed significantly. However, attempts to explain the Cr(VI) dependence in terms of the k_{32}/k_3 term alone ($k_{12}/k_1 = k_{22}/k_2$) led to distinctly poorer fits of the data. Microscopic reversibility requires that $k_{12}/k_1 = k_{22}/k_2$, so that $k_{32}/k_3 \approx \alpha$. Thus reactions 8a and 8c appear to be catalyzed by Cr(VI) and apparently both $Cr_2O_7^{2-}$ and its Cr(V)–Cr(VI) analog are reactive species. Participation of the latter in the Fe(II) reaction was suggested previously.[14,15]

Equation 5 is based on the assumption that the Cr(VI) which is complexed by Pu(IV) is nonreactive. Although this appears reasonable, it is not certain. For this reason some calculations were made for which it was assumed that $PuCrO_4^{2+}$ and $HCrO_4^-$ react with Pu^{3+} with equal rate constants. This assumption leads to the rate law:

$$-\mathrm{d}[\mathrm{Pu(III)}]/\mathrm{d}t = \frac{3k_1[\mathrm{Pu(III)}][\mathrm{Cr(VI)}](1+\alpha[\mathrm{Cr(VI)}](1-f_c))}{1+\beta[\mathrm{Pu(IV)}](1-f_p)(1+Q[\mathrm{Pu(IV)}]/[\mathrm{H^+}])/[\mathrm{Pu(III)}]} \qquad (5')$$

The use of this rate law gives essentially the same values for k_1 but somewhat larger values for β. The results of these calculations are summarized in the last column of Table IV.

Thus a precise determination of k_2/k_3 is impossible because of uncertainty in the reactivity of Cr(VI) complexed by Pu(IV). Qualitatively, however, k_2/k_3 is close to unity in 0.1 *M* acid and is inversely proportional to the hydrogen ion concentration. The analogous ratio for the Fe(II)–Cr(VI) reaction shows the same hydrogen ion dependence.[16]

The hydrogen ion dependence data in Table V show that at 25° in 2 *M* (H,Li)ClO_4 solutions the rate is predominantly second order in $[H^+]$. The acid dissociation quotient for H_2CrO_4 at unit ionic strength has been reported to be 4 *M*[17] (or perhaps 6 *M*[18]). This quotient should be a little larger in 2 *M* solutions, so $HCrO_4^-$, the principal chromium species, would be expected to decrease from about 0.95 to 0.75 of the stoichiometric Cr(VI) concentration on going from 0.3 to 2.0 *M* $[H^+]$. The fact that $k_1/[H^+]^2$ remains essentially constant over this range is consistent with either of two limiting assumptions: (1) the dissociation quotient is fairly small as reported and that $HCrO_4^-$ and H_2CrO_4 both react with Pu^{3+} and $2H^+$ with nearly equal rate constants; or (2) H_2CrO_4 is nonreactive but that the small effect of $[H^+]$ on the spectrum of Cr(VI) is a medium effect and is not due primarily to the formation of H_2CrO_4, as previously supposed, and that the dissociation quotient is at least 15 *M*.

The data for low acid concentrations, in Table VI, show that $k_1/[H^+]^2$ probably increases with decreasing $[H^+]$. This suggests that a term first order in $[H^+]$ is significant and it was found that the expression $k_1' = (0.23[H^+] + 8.58[H^+]^2) \times 10^3\ M^{-1}\ sec^{-1}$ fits the data with a root-mean-square deviation of 2.9%. This same functional form is shown also by the analogous Fe(II)–Cr(VI) reaction.[16]

These results show that the most important net activation process for reaction 8a is

$$Pu^{3+} + HCrO_4^- + 2H^+ = [Pu{\cdot}HCrO_4{\cdot}2H^{4+}]^* \qquad (10)$$

where the composition but not the structure of the activated complex is implied. The facts that four ions are involved in the net activation process and that ΔH^* for the process is zero or negative (see below) strongly suggest that at least one pre-equilibrium step precedes the actual rate-determining step.

The data in Tables V and VI show that in 0.5 *M* $HClO_4$ solutions, increasing the ionic strength from 0.5 to 2.0 *M* increases the apparent second-order rate constant by a factor of about 2.5. This increase is consistent with the Δz^2 for net activation process 10.

The data in Table VII show that the rate apparently decreases with an increase in temperature, consistent with an activation enthalpy of −1.5 kcal/mol with a statistical uncertainty of 0.2 kcal/mol. The actual uncertainty is probably larger than this due to possible errors in Q and β. It is unlikely, however, that ΔH^* is significantly larger than zero. Thus for the principal net activation process, given in eq 10, $\Delta F^* = 11.81$ kcal/mol, $\Delta H^* = -0.75 \pm 0.75$ kcal/mol, and $\Delta S^* = -42 \pm 2.6$ cal/(mol deg) for unit ionic strength. The value for the formal ionic entropy of the activated complex is $S^*_{complex} = -60 \pm 2.6$, based on $S°_{Pu^{3+}} = -45$, $S°_{HCrO_4^-} = 44$ (all in units of cal/(mol deg)), and the convention of minimum hydration.[19]

Table IX. Reduction of Cr(VI) and Comparison of Fe(II) and Pu(III) as Reducing Agents

	Fe(II)	Pu(III)
Reduction potential, V	0.739^a	0.982^b
k for self-exchange, $[H^+]^0$ path, $M^{-1}\ sec^{-1}$	9 ± 1^c	120 ± 60^d
k_1, principal path,^{e} $M^{-1}\ sec^{-1}$	$5 \times 10^5[H^+]^{2f}$	$1.15 \times 10^4[H^+]^{2g}$
$k_2/k_3{}^e$	$2 \times 10^{-3}[H^+]^{-1f}$	$0.1\ [H^+]^{-1g}$
k_3/k_I, in 0.30 *M* $HClO_4{}^e$	0.057^g	$0.63^{g,h}$
ΔH^*, kcal/mol	$0^{f,i}$	$-0.75 \pm 0.75^{g,j}$
ΔS^*, cal/(mol deg)	−32	-42 ± 2.6^g
$S^*_{complex}$, cal/(mol deg)	−36	-60 ± 2.6^g

[a] For the Fe(III)–Fe(II) couple, ref 21. [b] For the Pu(IV)–Pu(III) couple, ref 22. [c] Data from ref 23 with the assumption that k doubles on going from $\mu = 0.55$ to 1.0 *M*. [d] Data from ref 24 recalculated to find the parameters which best reproduce the hydrogen ion and temperature dependence data simultaneously. [e] In 1.00 *M* (H,Li)ClO_4 solutions. [f] Data from ref 16 extrapolated to $\mu = 1.0$ *M*. [g] This work. [h] The value is 0.24 in 1 *M* $HClO_4$. [i] For $Fe^{2+} + HCrO_4^- + 2H^+ = [*]^{3+} + H_2O$. [j] For $Pu^{3+} + HCrO_4^- + 2H^+ = [*]^{4+} + H_2O$.

The value for the ionic entropy of the activated complex, obtained in this way, falls at the upper end of the range of values for other 4+ charged activated complexes which, however, all involve reactions between cations.[20]

For the analogous oxidation of Fe(II) by $HCrO_4^-$ the activation energy is also essentially zero. The rate constant was reported to be almost identical (0.5% greater) at 15 and 25° for solutions of the same composition.[16] The data, extrapolated to $\mu = 1.0$ *M*, give $\Delta F^* = 9.7$ kcal/mol, $\Delta S^* = -32$ cal/(mol deg), and $S^*_{complex} = -36$ cal/(mol deg).

The formation of I_2 when Cr(VI) is reduced by Pu(III) in the presence of I^- indicates that the reactions

$$I^- + Cr(V) = I(I) + Cr(III) \qquad k_I \qquad (8g)$$

$$I^- + I(I) = I_2 \qquad \text{rapid} \qquad (8h)$$

probably compete with reactions 8c and 8d above. Under conditions where $[Cr(VI)] \ll [Pu(III)]$ and where 8d can be ignored, the induction factor is given by:

$$(F_i)^{-1} = 0.5 + 1.5(k_2/k_I)[\mathrm{Pu(III)}]/[I^-] \qquad (11)$$

Plots of $(F_i)^{-1}$ vs. $[Pu(III)]/[I^-]$ had intercepts reasonably close to 0.5 as required by the equation; however, they showed upward curvature indicating that additional reactions are important also. The direct reaction between Cr(VI) and I^- should be included as mentioned above, and it is also plausible to include the catalysis of step 8g by I^- since such a term is present in the rate law for the Cr(VI)–I^- reaction.[12] When terms for these reactions are included eq 11 becomes

$$(F_i)^{-1} = (0.5 + G)/(1 + 1.5(k_0/k_1)[I^-]/[\mathrm{Pu(III)}] + (k_0/k_1)G) \qquad (12)$$

where $G = 1.5(k_3/k_I)[Pu(III)]/[I^-]/(1 + a[I^-])$, k_0 is the rate constant for the direct reaction, and a is the catalytic constant. This equation reproduces the experimental F_i values fairly well, as indicated in the last column of Table VIII. The best values for k_0/k_1, k_3/k_I, and a were found to be 5.3×10^{-3}, 0.244, and 860 M^{-1} in 1 *M* H^+ and 1.6×10^{-3}, 0.633, and 260 M^{-1} in 0.3 *M* H^+, respectively.

The results which have been presented here show that the Fe(II) and Pu(III) reactions with Cr(VI) have similar mechanisms but somewhat different rate parameters. Values for the various rate constants are summarized in Table IX. The rate constant for the first step in the reaction, k_1, is larger for Fe(II) than for Pu(III); this is not surprising since Fe(II) is the stronger reducing agent. The Marcus theory,[25] although derived for outer-sphere reactions, has often been successful in predicting the relative rates of similar reactions which are not necessarily outer-sphere. The appropriate equation for the present case is

$$k_{\mathrm{Fe}}/k_{\mathrm{Pu}} = ((k_{\mathrm{Fe}}/k_{\mathrm{Pu}})_x Q_{\mathrm{r}})^{1/2} \tag{13}$$

where the subscript x indicates the self-exchange rate constants and Q_{r} is the equilibrium quotient for the reaction $\mathrm{Fe}^{2+} + \mathrm{Pu}^{4+} = \mathrm{Fe}^{3+} + \mathrm{Pu}^{3+}$. The ratio $(k_{\mathrm{Fe}}/k_{\mathrm{Pu}})_x$ is probably about 10^{-1}, from the data in Table IX, and Q_{r} is 1.28×10^4 based on the reduction potentials.[22,23] Thus the predicted ratio of k_1 values is about 30, in remarkably good agreement with the observed ratio of about 43. This agreement, however, should not be taken as evidence for a common outer-sphere mechanism.

The ratio of the rate constants for the reductions of Fe(II) and of Pu(III) with Cr(V) can be estimated from the data in two ways. First, it is easy to show that

$$(k_3)_{\mathrm{Fe}}/(k_3)_{\mathrm{Pu}} = [(k_1)_{\mathrm{Fe}}/(k_1)_{\mathrm{Pu}}][(k_2/k_3)_{\mathrm{Pu}}/(k_2/k_3)_{\mathrm{Fe}}]/Q_{\mathrm{r}} = 0.17$$

using the appropriate values from Table IX. Also, since it is reasonable to assume that k_{I} for the reaction 8g will be the same for either Fe^{2+} or Pu^{3+}

$$(k_3)_{\mathrm{Fe}}/(k_3)_{\mathrm{Pu}} = (k_3/k_{\mathrm{I}})_{\mathrm{Fe}}/(k_3/k_{\mathrm{I}})_{\mathrm{Pu}} = 0.09$$

In view of the uncertainties in the various quantities involved in these calculations, the agreement, within a factor of 2, is probably satisfactory. It is quite clear that the observed ratio of k_3 values is far less than what was observed or predicted for the k_1 values, and that different factors influence the relative rates in the two cases. The results suggest that electron transfer is rate determining for the reduction of Cr(VI) but that precursor complex formation (or product complex decomposition) is rate determining for Cr(V). Reasons for believing that the Fe(II)–Cr(V) reaction is inner-sphere have been discussed previously.[26]

The Cr(VI)–Cr(V) reduction potential has not been measured but various estimates have been proposed; the most recent one suggests that it lies between 0.5 and 0.65 V.[27] However, since Cr(VI) readily oxidizes Pu(III) to Pu(IV), an upper limit of 0.65 V appears too low. Our kinetic data strongly suggest that the lower limit is about 0.72 V. This is based on the limiting assumption that the fastest reaction in the scheme is diffusion controlled. In 1 *M* $\mathrm{HClO_4}$ reaction 8g has the largest apparent second-order rate constant. The actual second-order rate constant in terms of the bimolecular reactants will be even larger because these species are minor ones. Thus k_{I} must be less than the diffusion controlled limit which is about $1.4 \times 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$ for 2+ and 1− charged species in solutions with $\mu = 1\ M$. The equilibrium constant for reaction 8a is given by

$$Q_{\mathrm{a}} = k_1/k_2 = (k_1/k_{\mathrm{I}})(k_3/k_{\mathrm{I}})^{-1}(k_2/k_3)^{-1}$$

so Q_{a} is greater than $1.15 \times 10^4/(1.4 \times 10^{10} \times 0.24 \times 0.10) = 3.4 \times 10^{-5}\ M^{-2}$. This corresponds to $E° > -0.26$ V and a Cr(VI)–Cr(V) reduction potential of greater than 0.72 V.

An upper limit for the Cr(VI)–Cr(V) reduction potential of about 1.0 V appears to be consistent with the kinetic data since potentials greater than this lead to unrealistically large steady-state concentrations of Cr(V). The assumption of 1.00 V leads to an equilibrium quotient of 2 for reaction 8a and since $k_2/k_3 = 0.1$ in 1 *M* $\mathrm{HClO_4}$, k_1/k_3 would be 0.2. At low concentrations of Cr(VI) where reactions 8b and 8d can be ignored, the steady-state concentration of Cr(V) is given by the expression $k_1[\mathrm{Pu(III)}][\mathrm{Cr(VI)}]/(k_2[\mathrm{Pu(IV)}] + k_3[\mathrm{Pu(III)}])$, so at low concentrations of Pu(IV), $[\mathrm{Cr(V)}]_{\mathrm{ss}}/[\mathrm{Cr(VI)}]$ would be about 0.2. This is consistent with our observations because an approach to a steady-state concentration of Cr(V) as large as 20% of that of Cr(VI) would perturb the kinetics in the early stages of reaction.

Registry No. Pu(III), 22541-70-4; Cr(VI), 18540-29-9; I^-, 20461-54-5.

References and Notes

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