CONTRIBUTION FROM LOS ALAMOS SCIENTIFIC LABORATORY,
UNIVERSITY OF CALIFORNIA, LOS ALAMOS, NEW MEXICO 87544

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

BY CAROLYN LAVALLEE[2] AND T. W. NEWTON*

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The reaction Pu(III) + Cr(III)·Pu(V) = 2Pu(IV) + Cr(III) was studied in acid perchlorate solutions from 0.05 to 2.0 M $HClO_4$ and from 1.7 to 44.5°. The rate law in 2 M (H, Li)ClO_4 solutions is $d[Pu(IV)]/dt = 2k'[Pu(III)][Cr(III)\cdot Pu(V)]\cdot[H^+]^0$. The rate constant k' is 122 M^{-1} sec^{-1} and the activation parameters are $\Delta F^* = 14.61$ kcal/mol, $\Delta H^* = 4.58 \pm 0.07$ kcal/mol, and $\Delta S^* = -33.6 \pm 0.2$ cal/(mol deg) at 25° in 2 M $HClO_4$. Rates in $NaClO_4$ solutions are lower than in $LiClO_4$ solutions, apparently due to a medium effect. The ionic strength dependences up to 3.86 M $LiClO_4$ and up to 5.54 M $NaClO_4$ are consistent with the extended form of the Debye–Hückel equation with a distance of closest approach of 11 Å. A moderate, essentially linear [Cl^-] dependence was found. The results are compared with the analogous reduction of uncomplexed Pu(V).

I. Introduction

The oxidation of Pu(IV) by Cr(VI) in dilute acid solutions produces a Cr(III) complex in which PuO_2^+ and H_2O are the ligands.[3] Studies of the kinetics of this complex are important because they will provide information on the effect of a highly charged metal ion on the reactivity of PuO_2^+. Preliminary experiments, reported previously,[3] have shown that the presence of Cr^{3+} greatly reduces the rates of oxidation of PuO_2^+ but enhances the rates of its reduction. This paper describes a detailed study of the reaction between Pu(III) and the complex

$$Pu^{3+} + Cr\cdot PuO_2^{4+} + 4H^+ = 2Pu^{4+} + Cr^{3+} + 2H_2O \quad (1)$$

Interest in the effect of the high ionic charges on the hydrogen ion dependence, the value of ΔS^*, and the ionic strength dependence provide further reason for studying this reaction.

The analogous reaction of uncomplexed PuO_2^+

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

had previously been studied only at room temperature in 0.5 M HCl.[4] We have now measured its temperature coefficient and determined ΔH^* and ΔS^* for comparison with those for reaction 1.

II. Experimental Section

Reagents.—Solutions of Pu(III) in $HClO_4$ were prepared by dissolving pure plutonium metal in concentrated $HClO_4$ followed by dilution with water and reduction over zinc amalgam. The solutions were analyzed by spectrophotometric titration to Pu(IV) with Ce(IV) in 0.5 M H_2SO_4 solutions. Ultrahigh-purity plutonium metal[5] was found to give kinetic results within 1% of those using ordinary plutonium wire, so the latter was used for most of the rate determinations. The Cr(III)·Pu(V) complex was prepared by the oxidation of Pu(IV) with Cr(VI) and purified by ion exchange as previously described.[3] Less than 2% of the plutonium was found to be Pu(VI) by spectrophotometry at 830 nm. Solutions which were frozen and stored at −78° for periods up to 1 week gave kinetic results indistinguishable from those using fresh solutions of the complex.

Solutions of Pu(VI), $HClO_4$, $LiClO_4$, $NaClO_4$, and $La(ClO_4)_3$ were prepared and analyzed as before.[6] Double vacuum distilled $HClO_4$ from the G. F. Smith Chemical Co. was found to give essentially the same rates as B and A brand reagent grade acid from Allied Chemical Corp., treated as described.[6] Rates measured with perchlorate salts which had been given an additional recrystallization agreed with the others within 3%.

Procedure.—Reaction rates were determined spectrophotometrically with the Cary Model 14 spectrophotometer using 10-cm thermostated cells as previously described.[7] These absorption cells were either two chambered[8] or rapidly stirred.[7] The wavelength was 469.5 nm where the product, Pu(IV), is the principal absorbing species. The absorbance changes were usually quite small, so the sensitive slide wire (0–0.1 absorbance unit full scale) was used for nearly all the runs. The initial concentration of Pu(III) was calculated from the volume of stock solution added while that of the complex was determined by titration after the run was complete. The excess Pu(III) was titrated to Pu(IV) as described above.

For reaction 2, solutions of Pu(VI) were mixed with Pu(III) in the absorption cells and Pu(V) was formed by the rapid equilibrium reaction

$$Pu^{3+} + PuO_2^{2+} = Pu^{4+} + PuO_2^+ \quad (3)$$

Calculations.—Absorbance *vs.* time data for reaction 1 were fit to the integrated form of the second-order rate law using the Los Alamos nonlinear least-squares program.[9] For reaction 2 the kinetics are complicated by equilibrium 3 which is maintained during the course of the reaction. The concentrations *vs.* time are governed by a pair of simultaneous equations

$$\begin{aligned} d[Pu(IV)]/dt = {} & 2k_2[Pu(III)][Pu(V)] - \\ & 2k_{-2}[Pu(IV)]^2 + k_3[Pu(III)][Pu(VI)] - \\ & k_{-3}[Pu(IV)][Pu(V)] \\ d[Pu(VI)]/dt = {} & -k_3[Pu(III)][Pu(VI)] + \\ & k_{-3}[Pu(IV)][Pu(V)] \quad (4) \end{aligned}$$

The rate of the disproportionation of Pu(V) to give Pu(IV) and Pu(VI) is slow compared with reaction 2[10] and has been ignored. Best values for k_2 were determined by a least-squares method very similar to that used previously.[6] For both reactions the quantity minimized was $\Sigma(A_{obsd} - A_{calcd})^2$.

Least-squares programs were also used to fit the observed rate constants to the appropriate functions of [H^+], temperature, ionic strength, and [Cl^-]. In these cases the sum of squares of the relative errors was minimized. Estimates of the standard deviations of the various parameters determined from the data were also obtained.

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[1] Work done under the auspices of the U. S. Atomic Energy Commission.

[2] Graduate student summer employee.

[3] T. W. Newton and M. J. Burkhart, *Inorg. Chem.*, **10**, 2323 (1971).

[4] R. E. Connick, *J. Amer. Chem. Soc.*, **71**, 1528 (1949).

[5] We thank Dr. L. J. Mullins of this laboratory for providing this sample. Reported analyses showed 99.99% Pu with the greatest impurities being 11 ppm U, 6 ppm Am, and 2 ppm Fe.

[6] R. B. Fulton and T. W. Newton, *J. Phys. Chem.*, **74**, 1661 (1970).

[7] T. W. Newton and F. B. Baker, *ibid.*, **67**, 1425 (1963).

[8] T. W. Newton, *ibid.*, **62**, 943 (1958).

[9] R. H. Moore and R. K. Zeigler, Los Alamos Scientific Laboratory Report No. LA-2367, 1959, plus Addenda.

[10] S. W. Rabideau, *J. Amer. Chem. Soc.*, **79**, 6350 (1957).

III. Results

The stoichiometry of the reaction between Pu^{3+} and $Cr \cdot PuO_2^{4+}$ was studied using spectrophotometric titrations in 2.5 *M* $HClO_4$ and found to agree with eq 1 within 1%. Increments of Pu^{3+} were added and the complete disappearance of complex, determined at 566.5 nm, coincided with the maximum formation of Pu^{4+}, determined at 469.6 nm. Further, the amount of Pu^{3+} required corresponded to the initial amount of complex present, determined from the oxidation equivalents corrected for the Pu(VI) impurity, determined at 830.3 nm. This stoichiometry is not maintained in solutions of low acid and low ionic strength. Under these conditions the disproportionation of Pu(IV) (eq 5) becomes important. This was indicated by the observation that the Pu(IV) concentration first increases, then passes through a maximum, and finally decreases slowly. In order to estimate the effect of this behavior on the study of reaction 1, the rate of reaction 5 was determined separately in dilute $HClO_4$. The rate law was found to be $-d[Pu(IV)]/dt = 3k[Pu(IV)]^2$ in agreement with earlier results in 1 *M* $HClO_4$.[11] The apparent second-order rate constant, *k*, was found to be 0.15 M^{-1} sec^{-1} in 0.046 *M* $HClO_4$ at 25°. Under these conditions the rate constant for reaction 1 is about 2.2 M^{-1} sec^{-1}, so reaction 5 should be expected to compete with reaction 1, especially when the Cr(III)·Pu(V) is nearly consumed. The appropriate competitive-consecutive second-order system was solved numerically to generate a set of concentrations *vs.* time data. These were treated in the usual way to give a rate constant for reaction 1 ignoring reaction 5. The result was an apparent value for the rate constant which was 8% too high for a typical initial concentration ratio of [Pu(III)]/[Cr(III)·Pu(V)] = 14. The relative importance of reaction 5 decreases rapidly at higher acidities or ionic strengths, so the small corrections were ignored at all but the lowest acid concentrations.

$$3Pu^{4+} + 2H_2O = 2Pu^{3+} + PuO_2^{2+} + 4H^+ \qquad (5)$$

For reaction 1, all the individual rate runs were in accord with the rate law

$$d[Pu(IV)]/dt = 2k'[Pu(III)][Cr(III) \cdot Pu(V)] \qquad (6)$$

Values for *k′*, the apparent second-order rate constant, were determined by least-squares as described above. The uncertainty in the time at which the reaction actually started was treated as an adjustable parameter or, alternatively, the timing was assumed to be exact and the initial absorbance was made an adjustable parameter. Differences in the rate constants calculated in these two ways were insignificant, usually less than 1%. Results of a typical run are shown in Table I where observed and calculated absorbance values are given as a function of time.

The first power dependences indicated by eq 6 were confirmed in experiments in which the initial concentrations of Pu(III) and of Cr(III)·Pu(V) were varied by factors of 12.8 and 10.0, respectively. The observed rate constants, summarized in Table II, agree within the experimental error. The reaction products were found to be without significant effect on the rate at concentrations of Cr(III) equal to the initial concentration of Cr(III)·Pu(V) and at Pu(IV) concentrations twice as large.

TABLE I

TYPICAL RATE RUN[a]

Time,[b] sec	Absorbance		Time, sec	Absorbance	
	Obsd[c]	Calcd[d]		Obsd[c]	Calcd[d]
0.0	0.0237	(0.0237)	40.0	0.0707	0.0707
5.0	0.0333	0.0336	45.0	0.0739	0.0738
7.5	0.0380	0.0377	55.0	0.0790	0.0790
10.0	0.0416	0.0414	65.0	0.0832	0.0832
12.5	0.0449	0.0449	80.0	0.0884	0.0882
15.0	0.0479	0.0481	100.0	0.0930	0.0931
20.0	0.0539	0.0539	125.0	0.0970	0.0972
25.0	0.0590	0.0589	155.0	0.1003	0.1004
30.0	0.0634	0.0633	190.0	0.1030	0.1027
35.0	0.0670	0.0672	∞		0.1063

[a] Conditions: 9.35 × 10^{-5} *M* Cr(III)·Pu(V), 2.08 × 10^{-4} *M* Pu(III), 2.00 *M* $HClO_4$, 25.2°. [b] The effective time of the start of reaction was found to be −0.36 ± 0.9 sec. If the effective start is taken as zero, the calculated absorbance is 0.0244 ± 0.0002 and $k' = 117.6 \pm 0.9$ M^{-1} sec^{-1}. [c] Absorbance plus a small arbitrary base-line setting. [d] Calculated using the integrated form of the second-order rate law $k' = 118.1 \pm 0.8$ M^{-1} sec^{-1}.

TABLE II

EFFECT OF THE INITIAL CONCENTRATIONS OF REACTANTS ON THE APPARENT SECOND-ORDER RATE CONSTANT FOR REACTION 1[a]

[Cr(III)·Pu(V)], *M*	[Pu(III)], *M*	No. of detns	*k′* (av), M^{-1} sec^{-1}	Mean dev
0.56	0.65	2	46.1	2.6
0.56	1.3	2	43.1	0.2
0.54	6.2	2	43.6	0.7
0.70[b]	8.3	9	43.4	0.6
5.59[b]	8.3	8	43.3	1.8

[a] Conditions: 1.00 *M* $HClO_4$, 25.2°. [b] The Cr(III)·Pu(V) stock solutions were stored at −78° from 0.5 to 5 days with no apparent effect on *k′*.

The $[H^+]$ dependence was studied under a variety of conditions and the apparent second-order rate constants were found to be essentially independent of $[H^+]$ in $LiClO_4$ solutions. The results in 2.0 *M* $(H, Li)ClO_4$ solutions at 25.2° are summarized in Table III; *k′* was determined at eight different $[H^+]$ ranging from 0.05 to 2.0 *M*. The least-squares best straight line through the data is $k' = (118.96 \pm 0.60) + (0.074 \pm 0.432)[H^+]$ M^{-1} sec^{-1}. The indicated uncertainties are the standard deviations. The one for the $[H^+]$ dependent term is large enough to show that the term is not statistically significant. The equation reproduces the 35 experimental points with a root-mean-square deviation of 1.7% and a maximum deviation of

TABLE III

HYDROGEN ION DEPENDENCE IN $LiClO_4$ SOLUTIONS[a]

$[HClO_4]$, *M*	No. of detns	*k′* obsd,[b] M^{-1} sec^{-1}	Mean dev	*k′* calcd,[c] M^{-1} sec^{-1}
0.050	3	120.0	1.3	119.0
0.090	2	119.6	0.4	119.0
0.139	5	119.9	2.1	119.0
0.240	3	118.3	1.3	119.0
0.530	2	117.0	0.4	119.0
1.046	2	117.6	1.1	119.0
1.55	3	117.0	2.4	119.1
1.92	4	120.4	1.0	119.1
2.00	11	119.5	1.5	119.1

[a] Conditions: 2.00 *M* $(H, Li)ClO_4$, 25.2°. [b] Average observed second-order rate constant. [c] Calculated from the least-squares best straight line through the data, $k' = (118.96 \pm 0.60) + (0.0743 \pm 0.432)[H^+]$ M^{-1} sec^{-1}.

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(11) S. W. Rabideau, *J. Amer. Chem. Soc.*, **75**, 798 (1953).

3.6%. A similar set of measurements at 1.7° showed no trend with $[H^+]$. However, at 37 and 45°, k' increased 6 and 9%, respectively, when $[H^+]$ was increased from 0.5 to 2.0 M. Experiments in $LiClO_4$ solutions at lower ionic strengths showed small (4–10%) decreases with increasing $[H^+]$ at constant ionic strength.

In contrast to the results from $LiClO_4$ solutions, a rather large $[H^+]$ dependence was observed in $NaClO_4$ solutions, as shown in Table IV. At 25.2° and ionic strength equal to 2.0 M, k' increases almost linearly from 77 M^{-1} sec^{-1} in 0.046 M H^+ to 119.6 M^{-1} sec^{-1} in 1.92 M $HClO_4$. The data are in accord with the expression $k' = (72.9 \pm 1.3) + (22.0 \pm 1.4)[H^+]$. The 14 data points are reproduced with a root-mean-square deviation of 3.2% and a maximum deviation of 7.1%. An exponential function was found to fit the data slightly better; the equation $k' = (73.7 \pm 0.96) \cdot \exp((0.242 \pm 0.012)[H^+])$ reduces the root-mean-square deviation to 2.5%. Similar determinations at 1.7° lead to the parameters (32.94 ± 0.22) M^{-1} sec^{-1} and (0.281 ± 0.0065) M^{-1} and a root-mean-square deviation of 1.6% and a maximum deviation of 3.7%.

TABLE IV

HYDROGEN ION DEPENDENCE IN $NaClO_4$ SOLUTIONS[a]

$[HClO_4]$, M	k' obsd,[b] M^{-1} sec^{-1}	Mean dev	k' calcd I,[c] M^{-1} sec^{-1}	k' calcd II,[d] M^{-1} sec^{-1}
0.046	77.2	2.4	73.9	74.5
0.239	78.2	0.2	78.1	78.1
0.530	81.2	0.2	84.5	83.8
1.013	92.5	2.5	95.1	94.2
1.168	98.1	0.4	98.5	97.8
1.530	106.5	0.7	106.5	106.8
1.917	119.6	0.2	115.0	117.3

[a] Conditions: 2.00 M (H, Na)ClO_4, 25.2°. [b] Average of two determinations. [c] Calculated using $k' = (72.9 \pm 1.3) + (22.0 \pm 1.4)[H^+]$. [d] Calculated using $k' = (73.7 \pm 1.0) \cdot \exp((0.242 \pm 0.012)[H^+])$.

Values of k' were determined at five temperatures between 1.7 and 44.5° in 2.00 M $HClO_4$ solutions as shown in Table V. The temperature dependence is in agreement with the Eyring equation $k' = (k_BT/h) \cdot \exp(\Delta S^*/R - \Delta H^*/RT)$ with $\Delta S^* = -33.63 \pm 0.22$ cal/(mole deg) and $\Delta H^* = 4.58 \pm 0.07$ kcal/mol. The 33 k' values are repoduced with a root-mean-square deviation of 2.9% and a maximum deviation of 6.2%. These parameters and those obtained under other conditions are summarized in Table VI.

TABLE V

TEMPERATURE DEPENDENCE FOR REACTION 1[a]

Temp, °C	No. of detns	k' (av),[b] M^{-1} sec^{-1}	Mean dev	k' calcd,[c] M^{-1} sec^{-1}
1.7	6	59.3	0.5	58.0
12.8	2	85.0	2.2	83.6
25.2	17	119.7	1.4	122.0
36.1	4	167.0	3.6	166.1
44.5	4	218.3	2.0	207.8

[a] Conditions: 2.00 M $HClO_4$. [b] Average value of apparent second-order rate constant. [c] Calculated using the Eyring equation and the activation parameters in Table VI.

The ionic strength dependence was studied in $LiClO_4$ solutions at 1.7 and 25.2° and in $NaClO_4$ solutions at 25.2°. The results are summarized in Table VII. All of the data are in accord with the extended form of the Debye–Hückel equation, eq 7.

$$\log k' = \log k^0 + (A\Delta z^2\mu^{1/2})/(1 + B\mathring{a}\mu^{1/2}) + C\mu \quad (7)$$

Values for the three adjustable parameters, k^0, $\mathring{a}$, and C were determined by least squares and are given in Table VIII.

The effect of substituting $La(ClO_4)_3$ for $NaClO_4$ was investigated in a short series of experiments in 0.06 M $HClO_4$ at 25.2°. Apparent second-order rate constants were found to be significantly smaller in the lanthanum solutions. The ratio k'_{Na}/k'_{La} ranged linearly from 1.55 for $\mu = 2.0$ M to 1.40 at $\mu = 5.5$ M. In $NaClO_4$–$La(ClO_4)_3$ mixtures at an ionic strength of 2 M, the apparent second-order rate constant is given by $k' = (83.9 \pm 1.6) - (90.6 \pm 3)[La^{3+}]$ or by the equivalent expression $k' = (23.3 \pm 1.6) + (30.4 \pm 1.0)[ClO_4^-]$ M^{-1} sec^{-1}. At $\mu = 5.5$ M the apparent $[ClO_4^-]$ dependence is distinctly nonlinear with $k' = (285 \pm 4) + (0.932 \pm 0.044)[ClO_4^-]^3$.

The effect of chloride was studied in a series of experiments at 25.2° in 2.00 M H(ClO_4, Cl) summarized in Table IX. A moderate, approximately linear, in-

TABLE VI

ACTIVATION PARAMETERS FOR PROCESS 11[a]

Solution	No. of detns	ΔS^*, cal/(mol deg)	ΔH^*, kcal/mol	Rms dev,[b] %	Max dev, %
2.0 M $HClO_4$	33	−33.6 ± 0.2	4.58 ± 0.07	2.9	6.2
1.0 M $HClO_4$	10	−36.4 ± 0.16	4.35 ± 0.05	1.2	2.4
0.5 M $HClO_4$	12	−39.2 ± 0.4	3.98 ± 0.13	3.3	7.4
0.0 M $HClO_4$[c]		−44.6 ± 1.4	3.1 ± 0.42		
2.0 M $NaClO_4$[d]		−33.2 ± 0.4	5.0 ± 0.12		

[a] The parameters apply to the Eyring equation; the uncertainties are standard deviations. [b] Root-mean-square deviation between observed and calculated values. [c] Values for k' extrapolated to $\mu = 0$ at 1.7 and 25.2°. [d] Values for k' extrapolated to $[H^+] = 0$ at 1.7 and 25.2°.

TABLE VII

IONIC STRENGTH DEPENDENCE

Salt (deg)	Ionic strength, M	No. of detns	k' (av), M^{-1} sec^{-1}	Mean dev	k' calcd,[a] M^{-1} sec^{-1}
$LiClO_4$ (1.7)	0.059[b]	2	1.26	0.03	1.20
	0.252	2	5.31	0.36	5.17
	0.500	8	10.24	0.44	10.41
	1.32	2	31.6	0.7	31.26
	1.975	3	57.2	0.3	55.2
	2.24	2	70.6	0.8	67.7
	3.40	2	144.1	1.1	150.5
$LiClO_4$ (25.2)	0.060[b]	4	2.38	0.13	2.32
	0.108	2	4.28	0.01	4.20
	0.154	2	6.03	0.18	6.05
	0.225	6	8.90	0.44	8.93
	0.350	5	13.6	0.37	14.1
	0.50	14	20.6	1.27	20.4
	1.00	4	44.5	1.5	44.1
	1.45	2	72.8	2.3	70.8
	2.12	2	130.8	3.3	125.4
	2.80	4	211.7	6.5	207.4
	3.64	2	330.0	8.2	366.7
	3.86	2	456.2	9.1	423.1
$NaClO_4$ (25.2)	0.302[c]	2	11.8	0.1	11.6
	0.530	3	19.8	0.5	19.9
	1.08	2	39.6	0.03	40.1
	1.59	2	60.8	0.4	60.5
	2.00	4	79.2	2.6	79.2
	2.66	1	114.9		114.9
	3.58	2	182.4	0.3	180.6
	4.71	2	303.0	5.1	298.2
	5.54	2	416.3	13.1	421.7

[a] Calculated using the extended Debye–Hückel equation and the parameters listed in Table VIII. [b] No added salt. [c] 0.05 M $HClO_4$.

TABLE VIII

DEBYE–HÜCKEL PARAMETERS[a]

Solution	Temp, °C	No. of detns	$100k^0$, M^{-1} sec^{-1}	$\mathring{a}$, Å	C, M^{-1}	Rms dev,[b] %	Max dev, %
$LiClO_4$	1.7[c]	23	3.39 ± 0.19	10.90 ± 0.19	0.225 ± 0.009	5.0	8.9
$LiClO_4$	25.2[d]	49	5.79 ± 0.22[e]	11.00 ± 0.13	0.233 ± 0.006	5.9	14.6
$NaClO_4$	25.2[d]	20	5.79 ± 0.22[e]	10.95 ± 0.11	0.149 ± 0.004	2.7	5.8

[a] For the function $\log k' = \log k^0 + (A\Delta z^2\mu^{1/2})/(1 + B\mathring{a}\mu^{1/2}) + C\mu$, with k^0, $\mathring{a}$, and C determined by least-squares. [b] Root-mean-square deviation. [c] $A = 0.4900$, $B = 0.3244$. [d] $A = 0.5093$, $B = 0.3287$. [e] The $LiClO_4$ and $NaClO_4$ data were pooled and k^0 was constrained to be the same for both data sets.

TABLE IX

CHLORIDE ION DEPENDENCE[a]

[HCl], M	No. of detns	k' obsd[b] (av)	Mean dev	k' calcd[c]	k' calcd[d]
0.0	4	117.5	0.6	116.8	117.7
0.0332	4	154.0	2.2	153.2	152.3
0.0664	4	185.1	6.3	187.4	185.9
0.0996	3	217.5	9.6	219.5	218.3
0.1992	3	313.7	13.6	305.3	309.9

[a] Conditions: 2.00 M H(Cl, ClO_4), 25.2°. [b] Observed second-order rate constant, M^{-1} sec^{-1}. [c] Calculated using $k' = ((116.76 \pm 2.04) + (1251.5 \pm 36.1)[Cl^-])/(1 + [Cl^-])$. [d] Calculated using $k' = ((117.7 \pm 1.9) + (1119.7 \pm 32.8)[Cl^-])/(1 + 0.5[Cl^-])$.

crease in k' was observed between 0 and 0.2 M Cl^-. A satisfactory equation is

$$k' = (a + b[Cl^-])/(1 + 0.5[Cl^-]) \tag{8}$$

The parameters a and b were found to be 117.7 ± 1.9 M^{-1} sec^{-1} and 1120 ± 33 M^{-2} sec^{-2}; these reproduce the 18 experimental values with a root-mean-square deviation of 3.6% and a maximum deviation of 7.7%. If the denominator in eq 8 is taken to be $(1 + [Cl^-])$ rather than $(1 + 0.5[Cl^-])$, the best value for b is increased by 12% and the fit of the data to the function is slightly poorer (3.8 and 8.6%). The choice of either of these denominator terms is discussed in section IV.

The Pu^{3+}–PuO_2^+ Reaction.—Previous work[4] in 0.5 M HCl at room temperature showed the rate law for reaction 2 to be

$$-d[Pu(IV)]/dt = k_2[Pu(III)][Pu(V)][H^+]^n \tag{9}$$

where $k_2 = 0.058$ M^{-1} sec^{-1} but n was not determined. Rabideau[11] studied the disproportionation of Pu(IV), reaction 5, and found the equilibrium quotient, Q_5, to be 8.4×10^{-3} M^4 and to show the expected fourth power hydrogen ion dependence. The rate depends on $[Pu^{4+}]^2$ and $[H^+]^{-3}$ and the rate-determining step is the reverse of reaction 2. These results show that $n = 1$ in rate law 9.

We have assumed that the rate law is satisfactorily established and have determined the temperature coefficient in 1 M $HClO_4$. At 25° the initial concentration ranges were (9.65–22.8) × 10^{-3} M Pu(III) and (1.01–1.98) × 10^{-3} M Pu(VI). Eight determinations gave an average value for the rate constant of 0.0444 M^{-2} sec^{-1} with a mean deviation of 2.6%. A similar series of eight determinations at 50° gave 0.137 M^{-2} sec^{-1} with a mean deviation of 2.7%. These values lead to $\Delta H^* = 8.0 \pm 0.3$ kcal/mol and $\Delta S^* = -38 \pm 1$ cal/(mol deg).

In calculating these rate constants from the absorbance *vs.* time data k_2, the initial absorbance, and the largest absorptivity change (effectively the absorbance at infinite time) were determined by least squares. The other rate constants are known with sufficient precision from previous work. At both temperatures the absorptivity change, $\Delta\epsilon = 2\epsilon_{Pu(IV)} - \epsilon_{Pu(III)} - \epsilon_{Pu(V)}$, agreed with values calculated from directly measured absorptivities within the experimental error.

At 50°, the rate of the reverse of reaction 2 is relatively important and hence the value chosen for the equilibrium quotient for reaction 5 affects the calculated values of both k_1 and $\Delta\epsilon$. Published values for ΔH and ΔS[12] lead to $\Delta F_{323°} = -0.01$ kcal/mol or $Q_5 = 1.02$ M^4. However, a value of 1.53 M^4 was found to fit the 50° data a little better; this leads to $\Delta F_{323°} = -0.27$ kcal/mol, which agrees with the previous value within the experimental error.

IV. Interpretation and Discussion

Hydrogen Ion Dependence.—The observed hydrogen ion dependence indicates a rate law of the form

$$d[Pu(IV)]/dt = 2[Pu^{3+}][Cr\cdot PuO_2^{4+}](k_0 + k_1[H^+]) \tag{10}$$

with $k_1/k_0 = 0.3$ M^{-1} in $NaClO_4$ solutions but with $k_1/k_0 = 0$ in $LiClO_4$ solutions. These results suggest that a path for reaction is available in $NaClO_4$ solutions which is not available in $LiClO_4$. This seems quite unlikely and an alternate explanation may be based on a medium effect in which the pertinent activity coefficient quotient decreases by more than 37% when 2 M Na^+ is substituted for 2 M H^+ or 2 M Li^+. Such medium effects are often consistent with Harned's rule and the exponential function, mentioned previously, which is in accord with the $NaClO_4$ data. Previously reported effects of substituting Na^+ for Li^+ at constant ionic strength indicated that the ratio k_{Li}/k_{Na} increases with increasing Δz^2. As examples, the activation processes for both the $U^{3+} + Co(NH_3)_4(H_2O)_2^{3+}$ [13] and the $V^{2+} + Np^{4+}$ [14] reactions have $\Delta z^2 = 18$ and show k_{Li}/k_{Na} ratios of 1.37 and 1.29, respectively. Similarly, for the $Np^{3+} + UO_2^{2+}$ [15] and the $Pu^{3+} + NpO_2^{2+}$ [6] reactions $\Delta z^2 = 12$ and the ratios are 1.20 and 1.25, respectively. It thus appears that the large value $k_{Li}/k_{Na} = 1.60$ observed for the present reaction, for which $\Delta z^2 = 24$, is not inconsistent with previously observed values.

The effect of substituting $La(ClO_4)_3$ for $NaClO_4$ at constant ionic strength is ambiguous in that it may be explained either as a medium effect or as a specific perchlorate effect. The fact that $k_{Li}/k_{Na} \gtrsim k_{Na}/k_{La}$ indicates that even though the rate is linear in $[ClO_4^-]$ an explanation based on a general medium effect is plausible. Similar effects were observed for the Pu^{3+}–

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NpO_2^{2+} reaction[6] where again $k_{Li}/k_{Na} \gtrsim k_{Na}/k_{La}$. In contrast, however, $k_{Na}/k_{La} = 1.0$ for the V^{2+}–Np^{4+} reaction.[14]

It is concluded that

$$Pu^{3+} + Cr \cdot PuO_2^{4+} = [Cr \cdot PuO_2 \cdot Pu^{7+}]^* \quad (11)$$

is probably the only important net activation process although participation of ClO_4^- in the activated complex cannot be ruled out.

Ionic Strength Dependence.—Although the observed second-order rate constant increases by a factor of nearly 200 between 0.06 and 3.86 *M*, this large ionic strength effect is completely in accord with the extended form of the Debye–Hückel equation. The large effect is to be expected because of the high charges on the ions involved; Δz^2 for the predominant net activation process, eq 11, is 24. At 25.2° the $LiClO_4$ and $NaClO_4$ data sets both give essentially the same value for k^0, at zero ionic strength, so the two sets were pooled and k^0 (but neither $\mathring{a}$ nor *C*) was constrained to be the same for both data sets. The values for the Debye–Hückel parameters given in Table VIII show that the significant difference between $LiClO_4$ and $NaClO_4$ solutions is due primarily to differences in *C*, the linear parameter. The values found for $\mathring{a}$, all near 11 Å, are slightly larger than those observed for other reactions of actinide ions, where the range is from 8.3 to 9.9 Å for $LiClO_4$ solutions and to 10.7 Å for $NaClO_4$ solutions.

Chloride Ion Dependence.—A quantitative interpretation of the chloride ion dependence required a rate law written in terms of species actually present in the solution, such as: $d[Pu(IV)]/dt = 2[Pu^{3+}][Cr \cdot PuO_2^{4+}](a + b[Cl^-] + c[Cl^-]^2 + \ldots)$. The observed second-order rate constant, defined by eq 3 in terms of the stoichiometric concentrations, is given by

$$k' = (a + b[Cl^-] + c[Cl^-]^2 + \ldots)/(1 + \beta[Cl^-])(1 + \beta'[Cl^-]) \quad (12)$$

where β is the association quotient for $PuCl^{2+}$ and β' is the association quotient for the chloride complex of $Cr \cdot PuO_2^{4+}$. The value for $PuCl^{2+}$ is probably smaller than one[16] and that for the Cr–Pu complex is probably much smaller. The reasonable assumption that $\beta + \beta' = 0.5$ leads to eq 8 if *c* is zero. This equation, or a similar one with $(1 + [Cl^-])$ in the denominator, is in agreement with the data, so it is concluded that the *c* and higher terms in eq 12 are unimportant and that activated complexes with no more than one Cl are important in the concentration range studied. The ratio *b/a* is about 10, a value small enough to indicate that the Cl probably does not occupy a bridging position in the activated complex.[17]

Activation Parameters.—The temperature dependence of reaction 1 was determined under a variety of conditions; from these data ΔS^* and ΔH^* were determined using the Eyring equation. The results are summarized in Table VI. It is seen that ΔH^* as well as ΔS^* increases between 0 and 2 *M* $HClO_4$. Also, the lower rate in 2 *M* $NaClO_4$ compared with 2 *M* $LiClO_4$ depends almost entirely on the difference in ΔH^*.

It is interesting to compare the reduction of $Cr \cdot PuO_2^{4+}$ with the reduction of some dicobalt complexes. The ΔS^* value for reaction 1 is about 6 cal/(mol deg) larger than for the reaction of Cr^{2+} or Eu^{2+} with $((NH_3)_5CoO)_2^{5+}$ [18] or for the reaction of Cr^{2+}, V^{2+},[19] or Fe^{2+} [20] with $((NH_3)_5CoO)_2^{5+}$, in spite of the higher Δz^2 for the plutonium reaction. This observation is consistent with the idea that the plutonium activated complex is more extended than the cobalt ones so that a lower density of positive charge results. In this connection it is pertinent to note that oxygen-18 tracer experiments on an analogous reaction, the reduction of $CrUO_2^{4+}$ by Cr^{2+}, indicate an activated complex of the form $[Cr \cdot OUO \cdot Cr^{6+}]^*$.[21] If, however, the plutonium reaction is inner-sphere but the cobalt reactions are outer-sphere, an alternative explanation would be required.

The effect of Cr^{3+} on the reduction of PuO_2^+ can be determined by comparing reaction 1 with reaction 2, for which the net activation process is

$$Pu^{3+} + PuO_2^+ + H^+ = [Pu \cdot PuO_2 \cdot H^{5+}]^* \quad (13)$$

Our values for ΔH^* and ΔS^* for this process are 8.0 ± 0.3 kcal/mol and −38 ± 1 cal/(mol deg), respectively. Net activation process 11 cannot be directly compared with eq 13; instead the formal process

$$Pu^{3+} + PuO_2^+ + Cr^{3+} = [Cr \cdot PuO_2 \cdot Pu^{7+}]^* \quad (14)$$

should be considered. This requires ΔH and ΔS values for the equilibrium $Cr^{3+} + PuO_2^+ = Cr \cdot PuO_2^{4+}$. Sullivan[22] has studied the analogous neptunium equilibrium and reported $\Delta H = -3.3 \pm 0.6$ kcal/mol and $\Delta S = -9 \pm 2$ cal/(mol deg) for an ionic strength of 8 *M*. From these data we estimate $\Delta H = -3 \pm 2$ kcal/mol and $\Delta S = -14 \pm 5$ cal/(mol deg) for the association of $Cr \cdot PuO_2^{4+}$ at unit ionic strength.[23] These estimates lead to $\Delta H^* = 1.35 \pm 2$ kcal/mol and $\Delta S^* = -50 \pm 5$ cal/(mol deg) for net activation process 14.

Comparing the activation parameters for processes 13 and 14 shows that the higher charges involved in the latter tend to reduce its rate in that ΔS^* is about 12 cal/(mol deg) more negative. However, this effect is greatly overbalanced by the much smaller ΔH^* value and the net result is that substituting Cr^{3+} for H^+ apparently weakens the Pu–O bond, decreases ΔF^* at 25° by about 3 kcal, and increases the rate by a factor greater than 100.

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CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY,
THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO 43210

Studies on the Formation and Hydrolysis of Osmate(VI) Esters

BY L. R. SUBBARAMAN, JIJIE SUBBARAMAN, AND E. J. BEHRMAN*

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3-Cyclohexenecarboxylic acid reacts with osmium tetraoxide in aqueous buffer solutions in the presence of a variety of pyridines to form osmate(VI) esters of the general formula $(RO)_2OsO_2L_2$, where L represents the monodentate ligand. The compounds appear to be octahedral osmyl complexes with a trans O═Os═O group. The general kinetic equation describing the formation of the esters is rate $= k_0[OsO_4][S] + k_1\beta_1[OsO_4][S][L] + k_2\beta_2[OsO_4][S][L]^2$ where S is the substrate, 3-cyclohexenecarboxylic acid, and β_1 and β_2 are the overall stability constants for the osmium tetraoxide–ligand system. The hydrolysis of the uncomplexed ester produces the expected diol and osmium-containing products whose nature is pH dependent. In strong alkali, the osmate(VI) ion is the sole product. At pH 9.5, the initially produced Os(VI) species is oxidized by oxygen to osmium tetraoxide. In water or acid, 1 mol of the initially produced Os(VI) species dismutes to $^1/_3$ mol of OsO_4 and $^2/_3$ mol of Os(V), the latter perhaps present as a dimeric oxide. On long standing, both of these products, when present together, are reduced by water to osmium dioxide, $OsO_2 \cdot 2H_2O$. The hydrolysis is pH dependent and is catalyzed by both acid and alkali. $H_2{}^{18}O$ experiments show that the hydrolysis proceeds exclusively with osmium–oxygen bond cleavage.

Our studies[1] on the reaction of osmium tetraoxide–pyridine complexes with nucleic acid components left unanswered a number of fundamental questions about the reaction of olefins with osmium tetraoxide and with osmium tetraoxide complexes. In this paper, we examine the kinetics of the reactions between a single olefin, 3-cyclohexenecarboxylic acid (CCA), and osmium tetraoxide in aqueous solutions in the presence and absence of pyridine and some of its derivatives. We also report some observations on the hydrolysis of the uncomplexed osmate ester.

Results and Discussion

Properties of the Osmate(VI) Esters.—Table I gives analytical data for a number of osmate esters. The analyses correspond well with the general formula $(RO)_2OsO_2L_2$, where L represents a monodentate ligand. Table I also gives iodometric titration data which show 1 mol of I_2 produced per mole of ester corresponding to reduction of hexavalent osmium to Os(IV).[2]

Ir Spectra.—Griffith has suggested that the bis(pyridine) osmate esters are osmyl compounds,[3] that is, of octahedral geometry with a trans O═Os═O arrangement. He has assigned a strong band between 800 and 850 cm^{-1} to the asymmetric stretch of the osmyl group.[4] This band is present in the bis(pyridine) ester of CCA (830 ± 5 cm^{-1}, KBr) unshifted by deuteration and absent in both CCA and its *cis*-diol.

Nmr Spectra.—The nmr spectra of the esters showed chemical shifts which were qualitatively similar to those reported previously for the thymine and uracil esters.[1] The spectra of the bis(pyridine), the bis(3-picoline), bis(4-picoline), bis(3-chloropyridine), and the 2,2′-dipyridyl osmate esters of CCA in DMSO-d_6 at 35° all showed an upfield shift for the 3 and 4 protons of about 1.20 ppm as compared with the olefinic protons in CCA. The pyridine and substituted pyridine protons all showed a downfield shift of about 0.1–0.3 ppm. For the case of the 2,2′-dipyridyl ester, the pyridine protons were shifted downfield by about 0.5 ppm. Integration of these spectra confirmed the stoichiometry of Table I. We note, in addition, that the lack of any large chemical shift or line-broadening suggests that the osmate esters are diamagnetic, as expected. This was confirmed by measurement of the magnetic susceptibilities by the Faraday method.[5] Both the osmate ester of CCA and its bis(pyridine) adduct were diamagnetic.

Kinetics of Formation of the Osmate Esters.—We have analyzed our kinetic results according to the three-term equation suggested by our previous work[1]

$$\text{rate} = k_0[OsO_4][S] + k_1\beta_1[OsO_4][S][L] + k_2\beta_2[OsO_4][S][L]^2 \quad (1)$$

where S is the substrate and β_1 and β_2 are the successive stability constants for the osmium tetraoxide–ligand system.[1] Values for k_0 were obtained by studying the reaction in the absence of ligands. Table II gives these results for the temperature range 40–15° together with an extrapolated rate constant for 8°. The hydrolysis of the ester is sufficiently slow so as to give no interference under the conditions we have used; at 25°, the half-time for hydrolysis was of the order of 100 min while that for formation was of the order of 3 min.

Evaluation of k_0 allows evaluation of k_1 and k_2. From eq 1, with limiting osmium tetraoxide concentration, we can write for k_ψ, the pseudo-first-order rate constant

$$k_\psi = k_0[S] + k_1\beta_1[S][L] + k_2\beta_2[S][L]^2 \quad (2)$$

and hence

$$(k_\psi - k_0[S])/[L] = k_1\beta_1[S] + k_2\beta_2[S][L] \quad (3)$$

Accordingly, plots of $(k_\psi - k_0[S])/[L]$ *vs.* [L] should give straight lines with slopes equal to $k_2\beta_2[S]$ and intercepts equal to $k_1\beta_1[S]$. Plots of this kind are shown in Figure 1 for the ligands pyridine, 3-picoline, and 4-picoline. If a ligand forms no bis complex or if β_2 is sufficiently small, then

$$\text{rate} = k_0[S][OsO_4] + k_1\beta_1[S][OsO_4][L] \quad (4)$$

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