contribution ($\Delta H_c^‡$) and another constant contribution, from, for example, a diffusion process, the observed values of $\Delta H^‡$ are predicted to decrease with increasing ionic strength. In summary then, the effects of increasing ionic strength on the activation parameters of a reaction controlled by Coulombic factors are predicted to result in increasingly less negative values of both $\Delta S^‡$ and $\Delta H^‡$, whereas experimentally the values of $\Delta S^‡$ are found to be constant and those of $\Delta H^‡$ to become less positive.

The possibility that the mechanism of the two reactions under study involves a combination of ionic diffusion and electron tunneling can also be considered, particularly since the enthalpies of activation of fast electron-transfer reactions (Table IV) are at least comparable to the activation energies for the diffusion of ions in liquids, normally quoted to be in the range 3–4 kcal mol^{-1}.[31] On this basis, the values of $\Delta H^‡$ could be attributed largely to a diffusion process, while the uniformly highly negative $\Delta S^‡$ values could be interpreted as reflecting a transmission coefficient having a value much less than unity. A similar electron tunneling mechanism for a homonuclear electron-exchange reaction has been examined in detail elsewhere,[32] but the application of these concepts to the heteronuclear reactions presently under consideration is exceedingly difficult, so that this interpretation cannot easily be verified or discounted.

In conclusion it may be noted again that the apparent absence of any ionic strength effect on the value of $\Delta S^‡$ in the present reactions is rather perplexing and the results suggest that the mechanisms of these at first sight simple reactions may, in fact, be very much more complicated. Similar studies on the effects of ionic strength on the activation parameters of other reactions may be of value in the interpretation of the unusual effects observed in this study.

Registry No. U(III), 22578-81-0; Fe(III), 20074-52-6; V(II), 15121-26-3; Cl$^-$, 16887-00-6.

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Kinetics of the Neptunium(IV)–Plutonium(VI) and the Neptunium(IV)–Neptunium(VI) Reactions in Aqueous Perchlorate Solutions[1]

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Received May 19, 1976 AIC60377N

The oxidation of Np(IV) by Pu(VI) was studied at four temperatures from 30 to 45 °C in 1 M (H,Li)ClO_4 solutions with [H^+] between 0.04 and 0.6 M. Calculations were made to allow for the complications due to further reaction of Pu(V) and other products. The rate law for the predominant reaction is $-d[\text{Np(IV)}]/dt = k[Np^{4+}][PuO_2^{2+}]$, where k depends on [H^+]: $k = a[H^+]^{-2} + b[H^+]^{-3}$ or, alternatively, $k^{-1} = (c[H^+]^{-2})^{-1} + (d[H^+]^{-3})^{-1}$. ΔH^* values associated with a, b, c, and d are 31.1 ± 0.9, 40.1 ± 2.0, 33.5 ± 0.8, and 37.3 ± 2.5 kcal/mol, respectively. The corresponding ΔS^* values are 30 ± 3, 53 ± 6, 39 ± 3, and 50 ± 8 cal/(mol deg). Sulfate was found to inhibit the reaction. The oxidation of Np(IV) by Np(VI) was studied at 25 and 35 °C in 1 M (H,Li)ClO_4 solutions with [H^+] between 0.04 and 0.5 M. Except for the details of the hydrogen ion dependence the results were in agreement with the previous work of Hindman et al.[4,5]

Introduction

The oxidation of Np(IV) by Pu(VI), reaction 1, is typical

$$Np^{4+} + PuO_2^{2+} + 2H_2O = NpO_2^+ + PuO_2^+ + 4H^+ \qquad (1)$$

of a class of actinide oxidation–reduction reactions. Kinetic studies have been made on eight reactions of this type, among the ions of uranium, neptunium, plutonium, and americium. Four of the reactions, the disproportionations of UO_2^+, PuO_2^+, and AmO_2^+ and the NpO_2^+–AmO_2^+ reaction, occur in the direction opposite to that of (1). For the forward direction, the free energy values ($\Delta G°$) range from −12.3 to +12.5

kcal/mol and the rate laws consist of terms of the form $k \cdot [An^{4+}][AnO_2^{2+}][H^+]^n$. The hydrogen ion dependences range from −1 to −3 and show a distinct trend with $\Delta G°$. The U^{4+}–PuO_2^{2+} reaction appears to be unique in this class in that its hydrogen ion dependence is consistent with consecutive rate-determining steps rather than the more usual parallel rate-determining steps.

Reaction 1 was studied previously[3] in a set of preliminary experiments covering a short range of hydrogen ion concentrations, from 0.14 to 0.37 M. The present work was undertaken in order to provide a more complete study over a wider range of acid concentrations and to determine more precise values for the activation parameters. In addition, the previous work[4–6] on the Np(IV)–Np(VI) reaction was extended to lower acid concentrations. For both reactions it was of interest to seek possible evidence for consecutive rate-determining steps analogous to that found for the U(IV)–Pu(VI) reaction.[7]

The plutonium(V) ion, one of the products of reaction 1, is unstable with respect to its disproportionation

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

Although this reaction is relatively slow, it has been pointed out[3] that it and reactions 3–6 must be considered in an ad-

$$Pu^{4+} + Np^{4+} + 2H_2O = Pu^{3+} + NpO_2^{+} + 4H^+ \qquad (3)$$

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

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

$$PuO_2^{+} + Np^{4+} = Pu^{4+} + NpO_2^{+} \qquad (6)$$

equate description of the kinetic behavior when Np(IV) and Pu(VI) are mixed. As reaction 1 proceeds and Pu(V) builds up, these reactions complicate the interpretation of the results but fortunately rate constants have been published for all but reaction 6.

Experimental Section

Reagents. Solutions of Pu(VI) were prepared from ultrahigh-purity electrolytic plutonium metal[8] as described previously.[9] The Pu(VI) concentrations were determined by treating an aliquot with excess standard Fe(II) followed by spectrophotometric titrations at 380 nm with standard Ce(IV) in 0.5 M H_2SO_4; Ce(IV) persists as soon as all Pu(III) is converted to Pu(IV). The perchloric acid concentrations were calculated from the total perchlorate concentrations determined by the use of an ion-exchange column in the acid form. Solutions of $LiClO_4$ and Np(VI) were prepared and standardized as before.[9] Neptunium(IV) solutions were prepared by mixing carefully measured volumes of Np(III) and Np(VI) in a mole ratio of 2:1. The Np(III) was prepared by reduction on zinc amalgam and protected from the air by a blanket of argon. Doubly distilled $HClO_4$ from the G. F. Smith Chemical Co. was diluted and standardized using HgO. Stock solutions of Li_2SO_4 were prepared from reagent grade material supplied by the Matheson Coleman and Bell, and concentrations were determined by passing aliquots through cation-exchange columns in the acid form and titrating the effluents with standard NaOH. Doubly distilled water was used for preparing all solutions; the second distillation was made from alkaline permanganate in an all-Pyrex still. The concentration units used in this paper are moles per liter, M, at 25 °C.

Procedure. The kinetic measurements were made spectrophotometrically at 7233 Å, where Np(IV) is the principal absorbing species. The reaction vessels were thermostated, two-chambered absorption cells[7] of 5- and 10-cm length, used in a Cary recording spectrophotometer, Model 14. Absorbance vs. time was usually recorded until the reaction was at least 80% complete; final values were determined after at least 10 half-lives. Rate constants were calculated from the absorbance vs. time data using the integrated form of the required rate law. The Los Alamos Non Linear Squares Program[10] with appropriate subroutines was used for these calculations. The quantity minimized was the sum of squares of the differences between the observed and calculated absorbance values.

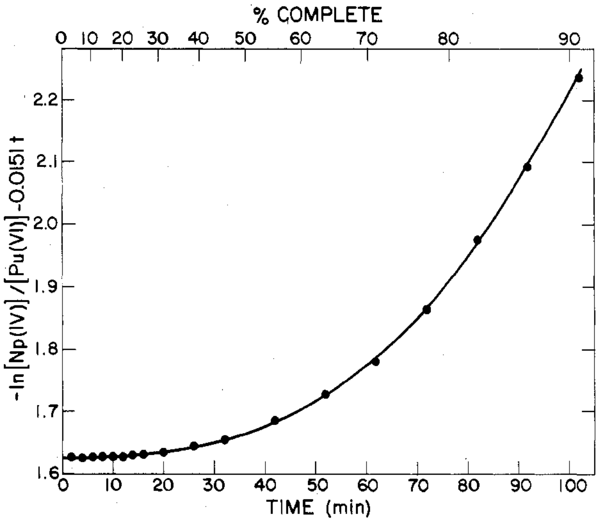

Figure 1. $\ln([Pu(VI)]/[Np(IV)]) - 0.015t$ vs. time; $[Pu(VI)]_0 = 5.13 \times 10^{-3}$ M, $[Np(IV)]_0 = 1.01 \times 10^{-3}$ M, $[HClO_4] = 0.20$ M, $[LiClO_4] = 0.77$ M, 35 °C.

Results and Discussion

Reaction 1 is expected to be first order in each of the actinide ion reactants, so we define an apparent second-order rate constant by

$$k' = -(d[Np(IV)]/dt)[Np(IV)]^{-1}\,[Pu(VI)]^{-1} \qquad (7)$$

However, in agreement with the previous results,[3] plots of ln ([Pu(VI)]/[Np(IV)]) were found to curve upward. Typical data are shown in Figure 1, where the limiting slope times the time was subtracted from the logarithm of the concentration ratio in order more clearly to show the curvature. This curvature has been explained[3] as the result of the additional reactions 2–6. Rather than using only the initial rates, we decided to include the complicating reactions in the kinetic treatment to see if quantitative agreement with the observed absorbance vs. time data could be obtained. In nearly all cases the agreement was within the experimental error for at least 80% of the reaction. For example, the solid line in Figure 1 was calculated from known values for the rate constants for reactions 2–5 and values for k_1 and k_6 were determined from the data. Since the use of initial rates may be subject to error, all the rate constants for reaction 1, with the exception of those for sulfate solutions, were determined using the complete calculation.

These calculations required the numerical solution of three simultaneous differential equations as part of the least-squares determination of k_1, the rate constant for reaction 1. The important details for this calculation are given in the Appendix. The values used for the rate constants for reactions 2–5 are given in Table VI. It was found that neither the calculated value for k_1 nor the agreement between the calculated and observed absorbance values depends strongly on the values assigned to k_2–k_5. This was shown by recalculating the data from typical runs in 0.4 and 0.05 M $HClO_4$ after increasing each of the rate constants in turn by a factor of 20; in no case was the calculated value for k_1 changed by more than 3%.

The calculated absorbance values did not agree with the observed ones unless reaction 6 was included in the scheme. Since values for k_6 were not previously available, they were determined from the data along with those for k_1. The values for k_6 obtained in this way cannot be very accurate but they do show a reasonable, approximately inverse square, hydrogen ion dependence. In solutions at 35 °C with ionic strength equal to 1.00 M the values were 5.3, 1.6, 0.3, and 0.07 M^{-1} min^{-1}

Table I. Hydrogen Ion Concentration and Temperature Dependence for Reaction 1[a]

Temp, °C	$[H^+]$, M	No. of detns	k'',[b] M min^{-1}	k'(obsd), M^{-1} min^{-1} Av	Md,[c] %	k'(calcd), M^{-1} min^{-1} Eq 8[d]	Eq 9[e]
30.0	0.040	4	0.091	47.5	1.9	47.8	42.9
	0.060	4	0.076	18.6	1.5	19.2	19.3
	0.097	4	0.073	7.2	7.7	6.7	7.2
	0.297	4	0.058	0.64	5.5	0.62	0.57
35.0	0.0502	4	0.210	68.8	0.8	71.2	67.0
	0.100	4	0.177	16.1	1.8	15.3	16.8
	0.201	4	0.149	3.5	7.3	3.4	3.6
	0.403	4	0.130	0.78	8.8	0.83	0.75
40.0	0.0464	4	0.557	200	1.0	207	181
	0.0976	4	0.458	42.1	2.0	38.5	42.4
	0.200	3	0.351	8.21	0.3	8.05	9.12
	0.361	1	0.290	2.1		2.31	2.33
	0.498	4	0.261	1.03	3.1	1.19	1.07
45.0	0.059	4	1.22	269	3.2	281	245
	0.109	4	1.01	72.8	4.6	70.4	78.7
	0.290	3	0.93	10.4	3.2	8.36	9.46
	0.603	3	0.69	1.84	7.5	1.80	1.63

[a] In 1.00 M (H,Li)ClO$_4$. [b] $k'' = k'[H^+]([H^+] + K_{Np})$; k_{Np} = 0.008, 0.0105, 0.0138, and 0.0179 M at the four temperatures. [c] Mean deviation from the mean. [d] $k'' = k_a + k_b[H^+]^{-1}$; ΔH_a^*, ΔS_a^*, ΔH_b^*, and ΔS_b^* are 31.1 kcal/mol, 30 cal/(mol deg), 40.1 kcal/mol, and 53 cal/(mol deg), respectively. [e] $(k'')^{-1} = k_c^{-1} + (k_d[H^+]^{-1})^{-1}$; ΔH_c^*, ΔS_c^*, ΔH_d^*, and ΔS_d^* are 30.5 kcal/mol, 39 cal/(mol deg), 37.3 kcal/mol, and 50 cal/(mol deg), respectively.

in 0.05, 0.10, 0.20, and 0.40 M HClO$_4$, respectively. A similar hydrogen ion dependence was reported for the analogous AmO_2^+–Np^{4+} reaction.[11]

The assumed first-order dependence on [Pu(VI)] was confirmed in a short series of runs in which the Pu(VI) concentration was varied from 2.6×10^{-3} to 2.3×10^{-2} M. The apparent second-order rate constant, calculated as described above, was the same within 3%. The Np(IV) concentration changed widely during the runs since Pu(VI) was in excess; thus the dependence assumed for it is adequately confirmed by the agreement between the observed and calculated absorbance values.

The hydrogen ion and temperature dependences for reaction 1 were determined in an extensive series of experiments in LiClO$_4$ solutions of unit ionic strength. Four temperatures from 30 to 45 °C were used and the hydrogen ion concentration was varied between 0.04 and 0.60 M. The data are summarized in Table I. The apparent second-order rate constants increase markedly with decreasing $[H^+]$ suggesting that the rate is inverse square in $[H^+]$. If it is assumed that the disappearance of Np(IV) is given by $-d[Np(IV)]/dt = k''[Np^{4+}][PuO_2^{2+}][H^+]^{-2}$, then since hydrolysis of Np(IV) but not of Pu(VI) is significant in the $[H^+]$ range covered, k'' will be given by $k'[H^+]([H^+] + K_{Np})$, where k' is the apparent second-order rate constant and K_{Np} is the first hydrolysis constant for Np(IV). The values for k'' decrease significantly with increasing $[H^+]$ as shown in the sixth column in Table I. Thus it is reasonable to postulate an equation of the form

$$k'' = k_a + k_b[H^+]^{-1} \qquad (8)$$

with the interpretation that k_a and k_b are the rate constants for parallel paths inverse square and inverse cube in $[H^+]$, respectively.

The hydrogen ion and temperature-dependence data were treated using eq 8 and the assumption that both k_a and k_b are given by the Eyring equation: $k = (k_BT/h)\exp(\Delta S^*/R - \Delta H^*/RT)$. A nonlinear least-squares procedure was used to find the values for ΔH_a^*, ΔS_a^*, ΔH_b^*, and ΔS_b^* which minimized the sum of the squares of the percent deviation between the observed and calculated k'' values. The results of this calculation are given in Table II along with the net activation processes for the two parallel paths.

Table II. Net Activation Processes and Activation Parameters

Net activation process	ΔG^*,[a] kcal/mol	ΔH^*, kcal/mol	ΔS^*, cal/(mol deg)	Rate law
$Np^{4+} + PuO_2^{2+} + H_2O$	22.17	31.1 ± 0.9	30 ± 3	(8)[b]
$= [*]^{4+} + 2H^+$	21.98	33.5 ± 0.8	39 ± 2.6	(9)[c]
$Np^{4+} + PuO_2^{2+} + 2H_2O$	24.35	40.1 ± 2.0	53 ± 6	(8)[b]
$= [*]^{3+} + 3H^+$	22.49	37.3 ± 2.5	50 ± 8	(9)[c]

[a] For 25 °C. [b] Consistent with parallel rate-determining steps, $k'' = k_a + k_b[H^+]^{-1}$, rms deviation is 8.4%. [c] Consistent with consecutive rate-determining steps, $(k'')^{-1} = k_c^{-1} + (k_d[H^+]^{-1})^{-1}$, rms deviation is 8.6%.

A rate law based on consecutive rate-determining steps, analogous to that found for the U(IV)–Pu(VI) reaction,[7] is

$$(k'')^{-1} = k_c^{-1} + (k_d[H^+]^{-1})^{-1} \qquad (9)$$

The use of this expression leads to values for the heats and entropies of activation, shown in Table II, which are somewhat different from those obtained using eq 8. For both calculations the root-mean-square difference between the observed and calculated values is about 8.5%. Since neither eq 8 nor 9 fits the data very well, a more complicated rate law based on both parallel and consecutive reactions was tried.[28] This rate was

$$k'' = [k_c^{-1} + (k_d[H^+]^{-1})^{-1}]^{-1} + k_b[H^+]^{-1} \qquad (9a)$$

Again the temperature dependences for the individual rate constants were assumed to be given by the Eyring equation and the best values for all six activation parameters were determined by least squares. The use of six rather than four parameters improved the fit slightly; the root-mean-square deviation was reduced from 8.5 to 7%. However the standard deviations for the individual parameters were very large, indicating that a reasonably unique set of six parameters does not exist. Thus it is concluded that a distinction among the two limiting mechanisms, parallel and consecutive, or a combination of the two, cannot be made on the basis of the data available.

It is of interest to compare the results summarized in Table I with the previously published ones. Rykov[3] reported five values for k' at 35 °C in solutions with μ = 2.0 M (NaClO$_4$) ranging from 213 M^{-1} min^{-1} in 0.141 M HClO$_4$ to 18.4 M^{-1} min^{-1} in 0.369 M HClO$_4$. Interpolating the data in Table I

Table III. Ionic Strength Dependence for Reaction 1[a]

Ionic strength,[b] M	k''(obsd), M min^{-1}	k''(calcd),[c] M min^{-1}
0.1290	0.360, 0.352	0.357
0.3014	0.278, 0.268	0.271
0.6461	0.202, 0.205	0.205
1.163	0.162, 0.154, 0.163	0.159
2.025	0.122, 0.132, 0.114	0.118

[a] Conditions: 0.100 M $HClO_4$, 35.0 °C. [b] Made up with $LiClO_4$. [c] Calculated using $k'' = k_a + k_b[H^+]^{-1}$, $\log k = \log k^\circ + \Delta z^2[0.5211\mu^{1/2}/(1 + B\mu^{1/2}) + C\mu]$, $k^\circ = 0.291 \pm 0.005$ M min^{-1}, $B = 2.81 \pm 0.44$ $M^{-1/2}$, and $C = 0.039 \pm 0.007$ M^{-1} by least squares, and $\Delta z^2{}_a = -2$, $\Delta z^2{}_b = -8$, and $(k_b/k_a)_{\mu=1} = 0.0319$ M.

for 35 °C gives 7.54 and 0.94 M^{-1} min^{-1} for the same two acid concentrations. The differences between the two sets of data are far too large to be explained on the basis of the different ionic strengths and media employed; in fact, the observed ionic strength dependence (see Table III) shows that the values for k' will be about three-fourths as large in solutions with μ = 2 M as compared with those with μ = 1 M.

Values for k' in solutions 0.220 M in $HClO_4$ (μ = 2 M) were reported[3] for four temperatures; they ranged from 17.8 M^{-1} min^{-1} at 30 °C to 220 M^{-1} min^{-1} at 45 °C. These data lead to an activation energy of 32.5 ± 4.4 kcal/mol. For comparison, values for k' in 0.220 M $HClO_4$ were found by interpolating in Table I. The four values found in this way lead to an activation energy of 34.3 ± 1.1 kcal/mol.

Although the two activation energies agree within the larger uncertainty, we cannot account for the very large discrepancy between the two sets of rate constants. Perhaps an efficient catalyst was present in the previous solutions.

The effect of ionic strength was studied in 0.100 M $HClO_4$ solutions at 35 °C by varying the $LiClO_4$ concentration. The rate constants for reaction 1 were determined from the absorbance vs. time data as described above. The effects of ionic strength on K_{Np} and on the rate constants for reactions 2–6 were included in the calculations. The data are summarized in Table III.

The ionic strength dependence for reaction 1 is consistent with an extended form of the Debye–Hückel equation in the sense that when eq 8 is assumed, both k_a and k_b can be represented by

$$\log k = \log k^\circ + \Delta z^2(0.5115\mu^{1/2}/(1 + B\mu^{1/2}) + C\mu) \qquad (10)$$

The values for parameters B and C were assumed to be the same for both rate constants, while the values for $(k_b/k_a)_{\mu=1}$, $\Delta z^2{}_a$, and $\Delta z^2{}_b$ were taken as 0.0319 M, −2, and −8, respectively, from the hydrogen ion dependence data at unit ionic strength. The values for the three adjustable parameters, B, C, and $k^\circ{}_a$, which minimized the sum of squares of the relative differences between the observed and calculated k'' values, were determined by the least-squares program. The values found in this way (given in Table III) reproduced the experimental values with a root-mean-square deviation of 3.9%.

The effect of sulfate ion on the rate of reaction 1 was determined in a short series of experiments at 35 °C with μ = 1.00 M ($LiClO_4$) and $[H^+]$ = 0.050 M. Since the effects of sulfate on the rates of reactions 2–6 are not known, the apparent initial apparent second-order rate constants were determined by fitting the data to the empirical function: $\log([Pu(VI)]/[Np(IV)]) = \alpha + \beta t + \gamma t^2$, where t is the time and β is the initial slope. Essentially the same results were obtained using a different empirical function based on the approximation that the rate law is $-d[Np(IV)]/dt = a'[Np(IV)][Pu(VI)] + b'[Np(IV)]$. For the same data the two methods gave essentially the same values for the initial second-order rate constant; the average difference was 0.9% and the maximum was 2.4%. The experimental results are summarized in Table IV. It is seen that increasing the total sulfate up to 0.008 M causes a small decrease in the overall rate.

Table IV. Effect of Sulfate on Reaction 1[a]

10^3[total sulfate], M	$10^3\cdot[SO_4^{2-}]$, M	D[b]	k'/k_0	
			Obsd	Calcd[c]
0.500	0.141	1.725	1.03	1.01
0.625	0.186	1.965	0.99	1.01
1.00	0.331	2.797	1.00	1.00
1.25	0.438	3.452	1.01	0.99
1.87	0.721	5.373	0.93	0.96
2.00	0.778	5.794	0.97	0.95_6
4.00	1.758	14.95	0.88	0.88
6.25	2.92	31.16	0.85	0.83
8.00	3.83	48.62	0.80	0.81

[a] Conditions: 35 °C, $[H^+] = 0.050$ M, $\mu = 1.0$ M, $[Np(IV)]_0 = 5.3 \times 10^{-4}$ M, $[Pu(VI)]_0 = (2.5–2.7) \times 10^{-3}$ M. [b] $D = (1 + K_1/K_a[SO_4^{2-}] + K_1K_2/K_a^2[SO_4^{2-}]^2)(1 + \beta_{21}[SO_4^{2-}] + \beta_{22}[SO_4^{2-}]^2)$. [c] Calculated using $k'/k_0 = (1 + 5.13 \times 10^3[SO_4^{2-}] + 8.1 \times 10^5\cdot[SO_4^{2-}]^2 + 1.2 \times 10^8[SO_4^{2-}]^3)/D$ with $K_a = 0.076$, $K_1 = 365$, $K_1\cdot K_2 = 5680$, $\beta_{21} = 110$, and $\beta_{22} = 990$.

The interpretation of this effect requires a consideration of the sulfate complexing of both reactants. This leads to a generalized expression for constant hydrogen ion concentrations of the form

$$k'/k_0 = \frac{1 + a[SO_4^{2-}] + b[SO_4^{2-}]^2 + c[SO_4^{2-}]^3 + \ldots}{(1 + \beta_{11}[SO_4^{2-}] + \beta_{12}[SO_4^{2-}]^2 + \ldots) \times (1 + \beta_{21}[SO_4^{2-}] + \beta_{22}[SO_4^{2-}]^2 + \ldots)} \qquad (11)$$

where k_0 is the rate constant in the absence of sulfate and β_{11}, β_{12}, β_{21}, and β_{22} are the association quotients for $NpSO_4^{2+}$, $Np(SO_4)_2$, PuO_2SO_4, and $PuO_2(SO_4)_2^{2-}$, respectively. Sullivan and Hindman[12] have studied the equilibria

$$Np^{4+} + HSO_4^- = NpSO_4^{2+} + H^+ \quad K_1 \qquad (12)$$

$$Np^{4+} + 2HSO_4^- = Np(SO_4)_2 + 2H^+ \quad K_2 \qquad (13)$$

in solutions with μ = 2.0 M from 10 to 35 °C. We have used their results and the Debye–Hückel equation with $\mathring{a}$ = 7.5 Å to estimate K_1 = 365 and K_1K_2 = 5680 for 35 °C and μ = 1.0 M. In order to use these data the equilibrium quotients β_{11} and β_{12} in eq 11 were replaced by K_1/K_a and K_1K_2/K_a^2, respectively, where K_a is the acid dissociation quotient for HSO_4^-. This was taken as 0.076 M at 35 °C and μ = 1.0 M from the data provided by Marshall and Jones.[13] Association quotients are not available for the plutonium complexes, but we estimate β_{21} = 110 M^{-1} and β_{22} = 990 M^{-2} based on the values for the corresponding uranium complexes.[14] The free sulfate concentrations, $[SO_4^{2-}]$, were calculated iteratively from the stoichiometric ones by subtracting the concentrations of HSO_4^-, $NpSO_4^{2+}$, and PuO_2SO_4 and twice the concentrations of $Np(SO_4)_2$ and $PuO_2(SO_4)_2^{2-}$, which in turn were calculated from the equilibrium quotients and $[SO_4^{2-}]$. The observed values of k'/k_0 were multiplied by the denominator terms in eq 11 and the parameters a, b, and c were determined by least squares and found to be (5.13 ± 0.14) × 10^3 M^{-1}, (8.1 ± 2.3) × 10^5 M^{-2}, and (1.2 ± 0.6) × 10^8 M^{-3}, respectively. These values must be considered as only approximate because they depend rather strongly on the values assumed for K_a and K_1. For example the largest effects are given by $\partial \ln a/\partial \ln K_a \simeq -1$, $\partial \ln b/\partial \ln K_a \simeq -2.3$, and $\partial \ln c/\partial \ln K_a \simeq -1.8$. K_2 does not affect a significantly but $\partial \ln b/\partial \ln K_2 \simeq 1.1$ and $\partial \ln c/\partial \ln K_2 \simeq 0.6$. β_{21} has small effects on b and c but β_{22} has essentially no effect on any of the parameters. A short series of experiments in 0.1 M acid (μ = 1.0 M) gave essentially the same value for a as those in 0.05

Table V. Rate Constants for the Np(IV)-Np(VI) Reaction[a]

Temp, °C	$[HClO_4]$, M	No. of detns	Av k',[d] M^{-1} min^{-1}	Mean dev	k'',[b] M min^{-1}	Calcd k',[c] M^{-1} min^{-1}
25.0	0.040	5	1558	47	2.87	1621
	0.050	5	1036	82	2.89	1073
	0.080	5	441	22	3.03	439
	0.101	5	294	6	3.17	281
	0.162	4	122	5	3.32	114
	0.200	7	77.5	0.9	3.21	75.8
	0.300	2	34.8	0.3	3.20	35.0
	0.500	7	13.2	0.2	3.34	13.5
35.0	0.040	5	5642	146	11.4	5801
	0.060	4	2740	16	11.6	2798
	0.091	4	1334	14	12.3	1301
	0.098	4	1169	26	12.4	1134
	0.297	4	150	7	13.7	145
	0.497	4	55.5	0.3	14.0	57.0

[a] $Np^{4+} + NpO_2^{2+} + 2H_2O = 2NpO_2^{+} + 4H^{+}$. Conditions: ionic strength 1.00 M ($LiClO_4$). [b] $k'' = k'[H^+]([H^+] + K_{Np})$; K_{Np} is the hydrolysis quotient for Np(IV), 0.006 M at 25 °C and 0.0105 M at 35 °C. [c] Calculated using $k'' = 2.945 + 0.95[H^+]$ at 25 °C and $k'' = 11.5 + 5.8[H^+]$ at 35 °C. [d] $k' = -(d[Np(IV)]/dt)[Np(IV)]^{-1}[Np(VI)]^{-1}$.

M acid; this indicates that the hydrogen ion dependence for the $[SO_4^{2-}]$ term is about the same as for the $[SO_4^{2-}]$-independent term.

It is interesting to note that the effect of sulfate on the oxidation of Np(IV) by Pu(VI) is far smaller than for oxidation by Np(VI). For the latter reaction the rate increased up to a factor of 5.6 as the free sulfate concentration was increased from zero to 1.8×10^{-3} M and then decreased at higher sulfate concentrations.[15] The parameter that corresponds to a in eq 11 has a value of about 1.9×10^4 M^{-1} at 25 °C and $\mu = 2$ M; we estimate its value at 35 °C and $\mu = 1$ M to be greater than 1.4×10^4 M^{-1}, significantly greater than the value for Pu(VI) (5×10^3 M^{-1}).

The parameter a is a measure of the tendency for the activated complex to associate with sulfate; it is the equilibrium quotient for the hypothetical process

$$[NpAnO_2]^* + SO_4^{2-} = [SO_4NpAnO_2]^* \qquad (14)$$

where An represents either Np or Pu. Since Np(IV) forms much stronger sulfate complexes than either NpO_2^{2+} or PuO_2^{2+}, the sulfate in the activated complex is probably associated with the Np that was originally in the IV state. Thus the relative values for a for the two reactions indicate that the Np that is being oxidized is more like Np(IV) when Np(VI) is the oxidizing agent than when Pu(VI) is. This conclusion can be rationalized by the fact that Np(VI) is a stronger oxidizing agent than Pu(VI) and by the hypothesis that for similar reactions the greater the driving force the more the activated complex will resemble the reactants.

The Np(IV)-Np(VI) Reaction

Previous work on the reaction

$$Np^{4+} + NpO_2^{2+} + 2H_2O = 2NpO_2^{+} + 4H^{+} \qquad (15)$$

was done in 2.0-2.2 M $(H,Na)ClO_4$ solutions[4-6] in the acid range from 0.23 to 1.99 M. We have used 1.0 M $(H,Li)ClO_4$ and extended the acid concentrations down to 0.04 M for comparison with our data for the analogous Np(IV)-Pu(VI) reaction.

In agreement with the earlier results, we find that the rate of the reaction is first order in each of the reactants, Np(IV) and Np(VI), and is predominantly inverse square in the hydrogen ion concentration. Our values for the rate constants were in satisfactory agreement with the previous ones[4] when similar concentrations were used. Six determinations at 25 °C in 0.47-0.49 M $HClO_4$ solutions ($\mu = 0.51$ M) gave an average value for $k'[H^+]^2$ of 3.72 ± 0.03 M min^{-1} compared with 3.48 ± 0.09 M min^{-1} obtained by extrapolating the previous data from an ionic strength of 0.55 M to 0.51 M.[16] As before, k' is the apparent second-order rate constant.

The main series of determinations was made at 25 and 35 °C in $LiClO_4$-$HClO_4$ solutions with an ionic strength of 1.00 M. The results in terms of k' are summarized in Table V. Assuming an inverse square hydrogen ion dependence and correcting for hydrolysis of Np(IV), it is convenient to define $k'' = k'[H^+]([H^+] + K_{Np})$, as before. Values for this quantity increase with increasing $[H^+]$ as shown in the sixth column of Table V. This suggests an expression of the form

$$k'' = k_e + k_f[H^+] \qquad (16)$$

This expression fits the data satisfactorily; the root-mean-square deviations between the observed and calculated values were 4.9% at 25 °C and 3.3% at 35 °C. The values for the rate constants k_e and k_f were determined by the least-squares program; they were 2.95 ± 0.04 M min^{-1} and 0.95 ± 0.16 min^{-1} at 25 °C and 11.5 ± 0.1 M min^{-1} and 5.8 ± 0.6 min^{-1} at 35 °C, respectively. A rate law based on consecutive, rather than parallel, rate-determining reactions was found to fit the data slightly, but not significantly, better than (16). The temperature coefficient of k_e between 25 and 35 °C leads to $\Delta H_e^* = 24.2 \pm 0.5$ kcal/mol, in satisfactory agreement with the value of 25.1 ± 0.6 kcal/mol we have calculated from the data in 1 M $HClO_4$-1 M $LiClO_4$ solutions.[4]

The previous results in 2.0 M[6] and in 2.2 M[5] $(H,Na)ClO_4$ solutions indicated a different hydrogen ion dependence for the minor term in the rate law. Those data were consistent with the expression

$$k'' = k_e + k_g[H^+]^{-1} \qquad (17)$$

The difference between (16) and (17) is probably due to the fact that the use of $NaClO_4$ and higher acid concentrations caused relatively large medium effects at constant ionic strength. $NaClO_4$ has been shown to give much larger medium effects than $LiClO_4$ in several other reactions.[17]

The observation that the minor term in the rate law for the Np(IV)-Np(VI) reaction is inverse first power rather than inverse third power in the hydrogen ion concentration improves the correlation between hydrogen ion dependence and $\Delta G°$ mentioned previously. The results for all eight reactions of this type are summarized in Table VI.

The data reported here for both the Np(IV)-Pu(VI) and the Np(IV)-Np(VI) reactions are consistent with either parallel or consecutive rate-determining reactions. Although we cannot reject the possibility of consecutive mechanisms, by comparison with the other actinide reactions of this type, it is likely that the usual parallel-path mechanism is correct. This leaves the U(IV)-Pu(VI) reaction as the only example

Table VI. Data for Actinide(IV)-Actinide(VI) Reactions[a]

Reactants	$\Delta G°$,[b] kcal/mol	Hydrogen ion dependence[c]	ΔG^*,[d] kcal/mol	Ref
U(IV)-Np(VI)	−12.3	*−1*	16.05	18
Np(IV)-Np(VI)	−9.2	−1, *−2*	19.3	4, this work
U(IV)-Pu(VI)	−7.2	*−1*, −2[e]	16.6	7
Am(IV)-Am(VI)[f]	−4.4	*−1*, −2	22	19
Np(IV)-Pu(VI)	−4.1	*−2*, −3	22.2	This work
Am(IV)-Np(VI)[f]	5	−2, *−3*	25	20
Pu(IV)-Pu(VI)[f]	5.8	*−3*	26.9	21
U(IV)-U(VI)[f]	12.5	*−3*	27.0	22

[a] $An^{4+} + AnO_2{}^{2+} + 2H_2O = AnO_2{}^{+} + AnO_2{}^{+} + 4H^+$. [b] For the overall reaction. [c] The dependence for the predominant path in 1 M acid is italicized. [d] Activation free energy for the predominant path. [e] The rate law indicates consecutive rather than parallel rate-determining reactions. [f] Calculated from data for the reverse reaction.

for which there is compelling evidence for consecutive rate-determining steps.

Appendix

Three overall reactions are required to describe the stoichiometry of reactions 1–6. A convenient set is

$$Np^{4+} + PuO_2{}^{2+} + 2H_2O = NpO_2{}^{+} + PuO_2{}^{+} + 4H^+$$

$$2PuO_2{}^{+} + 4H^+ = Pu^{4+} + PuO_2{}^{2+} + 2H_2O$$

$$3PuO_2{}^{+} + 4H^+ = Pu^{3+} + 2PuO_2{}^{2+} + 2H_2O$$

If x, y, and z are the concentrations of Np(V), Pu(IV), and Pu(III) formed, then as the three independent stoichiometric reactions proceed, the individual concentrations are given by $A = [\mathrm{Np(IV)}]_0 - x$, $B = [\mathrm{Pu(VI)}]_0 - x + y + 2z$, $C = [\mathrm{Np(V)}]_0 + x$, $D = [\mathrm{Pu(V)}]_0 + x - 2y - 3z$, $E = [\mathrm{Pu(IV)}]_0 + y$, $F = [\mathrm{Pu(III)}]_0 + z$, and $H = [\mathrm{H^+}]_0 + 4(x - y - z)$, where A, B, ..., H are the concentrations of Np(IV), Pu(VI), ..., and H^+, respectively. The rates of the individual reactions 1–6 are given by

$$R_1 = k_1AB/[H(H + K_{Np})]$$

$$R_2 = k_2D^2H - k_{-2}BE/[H^2(H + K_{Pu})]$$

$$R_3 = k_3AE/[H(H + K_{Np})(H + K_{Pu})]$$

$$R_4 = k_4DFH - k_{-4}E^2/[H(H + K_{Pu})^2]$$

$$R_5 = DE/[1 + K_{Pu}/H] - k_{-5}BF$$

$$R_6 = AD$$

The simultaneous differential equations which describe the system are

$$dx/dt = R_1 + R_3 + R_6$$

$$dy/dt = R_2 - R_3 + 2R_4 - R_5 + R_6$$

$$dz/dt = R_3 - R_4$$

where the R_i are functions of x, y, and z, the rate constants, and the initial concentrations as defined above. A subroutine using the Runge–Kutta method was used to solve these equations to give values for x, y, and z as functions of time. Absorbance values were calculated from x, y, and z and the molar absorptivities and compared with the observed values in the nonlinear least-squares routine. Appropriate changes in k_1 and the other adjustable parameters were made by the routine until the values which minimize the sum of squares of the differences between the observed and calculated absorbance values were found.

Table VII. Values for the Rate and Equilibrium Constants Used

Quantity	Value at 25 °C[a]	E_a, kcal/mol	Ref[b]
k_2	2.16×10^{-1}	19.6	21
k_{-2}	7.2×10^{-6}	39.7	21
k_3	1.5×10^{1}	34.5	23
k_4	2.64	8.6	17b
k_{-4}	1.74×10^{-3}	37.5	17b
k_5	2.24×10^{3}	14.2	24
k_{-5}	1.62×10^{2}	5.4	24
K_{Np}	6.0×10^{-3} [c]	10.3[d,e]	25
K_{Pu}	7.0×10^{-2} [c]	7.3[d]	26

[a] Units are M and min. [b] Based on data from the reference cited. [c] Hydrolysis constant, corrected to $\mu = 1.0$ M on the basis of data in ref 27. [d] Heat of hydrolysis. [e] Estimated under the assumption that ΔS is the same as for the hydrolysis of Pu(IV).

The values used for K_{Np}, K_{Pu}, and the various rate constants and their activation energies are summarized in Table VII.

Registry No. Np(IV), 22578-82-1; $PuO_2{}^{2+}$, 22853-00-5; $NpO_2{}^{2+}$, 18973-22-3; $SO_4{}^{2-}$, 14808-79-8.

References and Notes

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(2) Graduate Student, Summer Research Assistant.
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