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Kinetics of Reduction of Plutonium(VI) and Neptunium(VI) by Sulfide in Neutral and Alkaline Solutions

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The rate of reduction of plutonium(VI) and neptunium(VI) by bisulfide ion in neutral and mildly alkaline solutions has been investigated by the stopped-flow technique. The reduction of both of these ions to the pentavalent oxidation state appears to occur in an intramolecular reaction involving an unusual actinide(VI)–hydroxide–bisulfide complex. For plutonium the rate of reduction is 27.4 (±4.1) s^{-1} at 25 °C with $\Delta H^* = +33.2$ (±1.0) kJ/mol and $\Delta S^* = -106$ (±4) J/(mol K). The apparent stability constant for the transient complex is 4.66 (±0.94) × 10^3 M^{-1} at 25 °C with associated thermodynamic parameters of $\Delta H_c = +27.7$ (±0.4) kJ/mol and $\Delta S_c = +163$ (±2) J/(mol K). The corresponding rate and stability constants are determined for the neptunium system at 25 °C (k_3 = 139 (±30) s^{-1}, K_c = 1.31 (±0.32) × 10^3 M^{-1}), but equivalent parameters cannot be determined at reduced temperatures. The reaction rate is decreased by bicarbonate ion. At pH >10.5, a second reaction mechanism, also involving a sulfide complex, is indicated.

Introduction

Despite the ubiquitous presence of sulfide in the ecosphere and the importance of sulfide (and sulfur-containing organic compounds) in controlling the oxidation state of metal ions in solution, comparatively little is known about the effect of sulfide on the redox chemistry of the actinides. Early reports state only that plutonium is readily reduced by hydrogen sulfide in acidic solutions.[1] A more recent study of the reduction of neptunium(VI) by thioglycolic acid and coordinated thioglycolate species[2] reported that the oxidation of the sulfide-containing organic compounds by neptunium(VI) was a simple one-electron reaction with the organic product being a disulfide that is resistant to further oxidation. The coordinated species undergo further, more complex reactions to produce a variety of oxidized organic species.

Stability field diagrams based on equilibrium thermodynamic considerations predict that H_2S and HS^- are the stable soluble forms of sulfur at pH 6–10 and E_h between −0.1 and −0.4 V. Widely varying solubility limits are predicted on the basis of the species controlling solubility (e.g. native sulfur, pyrite). In addition, nonequilibrium processes can produce locally high concentrations in natural environments. For example, microbiological reduction of the amino acids cysteine and methionine produces H_2S as a product, as does the metabolic activity of sulfate-reducing bacteria. High sulfide concentrations are typically observed in pore waters of reducing sediments, in organic-rich/oxygen-poor waters, in association with salt domes and petroleum deposits, and in certain geologically active areas. As sulfide and sulfate-reducing bacteria are widely distributed in the environment and the oxidation state of actinide ions is relatively easily changed, this system has considerable relevance to the environmental chemistry of the actinides.

In this work we will discuss the results of a study of the kinetics of the reduction of neptunium(VI) and plutonium(VI) by sulfide under conditions approximating those found in natural waters.

Experimental Section

Reagents. Reagent grade sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$) was used without further purification. Stock solutions (0.1 M) of this reagent were prepared daily and standardized by titration with 0.1000 M lead perchlorate with end point detection via a sulfide-specific electrode. Titrations were performed in 1.00 M sodium hydroxide with a trace of ascorbic acid added as an antioxidant. Neptunium and plutonium solutions were prepared from Argonne National Laboratory stocks. Adjustment to the hexavalent oxidation state was achieved by ozonolysis of an acid neptunium (plutonium) perchlorate solution. The concentrations of the actinide stock solutions were determined spectrophotometrically. Sodium perchlorate, sodium bicarbonate, sodium sulfate, and Tris (tris(hydroxyethyl)amine) buffer were all reagent grade and were used without further purification. All solutions were prepared in triply distilled water.

Methods. Solutions were prepared immediately before use to minimize air oxidation of sulfide. The solutions were not degassed, as the air oxidation of bisulfide (HS^-) is relatively slow in the pH 7–11 range. It was observed in preparation of the solutions for the kinetic experiments that it was necessary to add the various reagents (Tris, $NaClO_4$, $HClO_4$, Na_2S) in such an order as to at all times prevent the solution from becoming acidic. Sulfide was rapidly air-oxidized in even slightly acidic solutions (pH <5), forming a yellowish suspension. This material was not identified but presumably is a polysulfide or colloidal sulfur. The kinetic experiments were conducted in the pH range 7–11. Adjustment of the pH was achieved by careful, measured addition of standardized perchloric acid. With the exception of one experiment, the ionic strength was adjusted to 0.1 M.

In both the neptunium and plutonium systems, experiments were run in which pH and total sulfide were varied independently, and for neptunium two experiments were run in which only the total metal ion concentration was changed. Experiments were run with sulfide in 2–60-fold excess. For the neptunium experiments, the pH range was from 7.0 to 11.5. The effect of added sodium bicarbonate and sodium sulfate on the reaction rate was investigated in this system. In the plutonium system the pH was restricted to the range 7.0–9.2. The effect of adding an anionic surfactant (sodium dodecyl sulfate, $CH_3(CH_2)_{11}OSO_3Na$) at the critical micellar concentration to the reaction mixture was studied in one set of experiments in the plutonium system. Experiments were performed at temperatures of 3.0, 14.0, and 25.0 °C to permit calculation of activation parameters.

Kinetic measurements were made on a Model D-110 Durrum[3] stopped-flow spectrophotometer equipped with a storage oscilloscope. Progress of the reaction was monitored at 400 nm, the position of a distinct shoulder in the spectra of the respective neptunium(VI) and plutonium(VI) hydroxides. Temperature was controlled to ±0.1 °C. Data acquisition was through a DEC VT1123 system with least-squares fitting of the absorbance–time data performed by a VAX computer. Four to six replicate injections were made for each set of conditions. The data were fit by a nonlinear least-squares adjustment of the absorbance–time traces, according to the first-order rate expression

$$A_t = A + (A_0 - A_\infty)e^{-kt} \qquad (1)$$

where A_0, A_∞, and k are treated as adjustable parameters.

Results and Discussion

Before we proceed with the discussion of the kinetic results, a brief summary of actinide chemistry in neutral and alkaline solutions and discussion of the expected redox chemistry of the system are useful. According to calculations of Allard et al.,[4] the speciation of both Np(VI) and Pu(VI) in the absence of competing complexes in the pH 7–10 range is dominated by the 1:2 acti-

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(1) Connick, R. E. In "The Actinide Elements"; McGraw-Hill: New York, 1954; Div. IV, Vol. 14A, NNES, pp 221–300.

(2) Weschler, C. J.; Sullivan, J. C.; Deutsch, E. *Inorg. Chem.* **1974**, *13*, 2360.

(3) The use of trade names is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.

(4) Allard, B.; Kipatsi, H.; Liljenzin, J. O. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1015.

0020-1669/86/1325-1169$01.50/0

nyl(VI) hydroxide complex ($AnO_2(OH)_2$). At pH >10 the dominant species is the 1:3 hydroxide. Polynuclear hydroxide species (2:2 and 3:5 complexes) are important only at lower pHs and relatively high actinide concentrations. Our calculations for the specific conditions of these experiments, using Allard's estimates of the stability constants for the 1:2 and 1:3 complexes (which have not been measured), indicate that at pH <8.5 $NpO_2(OH)_2$ is the dominant neptunium species and at higher pH $NpO_2(OH)_3^-$ is dominant. For Pu(VI) the corresponding crossover point occurs at about pH 9.5. Speciation of the product An(V) is dominated by AnO_2^+ at pH <9 and by $AnO_2(OH)_2^-$ at higher pHs.

The log of the first protonation constant for S^{2-} at 25 °C is reported at 13.8,[5] while that for the second protonation is 6.95. Therefore, the dominant species in the pH range 8–14 is HS^-. Sulfide exhibits a tendency to form polysulfur anions, including S_2^{2-}, S_3^{2-}, S_4^{2-}, and S_6^{2-}. Soluble sulfide complexes have been reported only for the alkali and alkaline-earth elements and for Sn(IV), Sb(III), and Hg(II). Other metals tend to form insoluble sulfide compounds. The potential for the reduction of sulfur to H_2S in aqueous, acidic solutions is +0.141 V, while in basic solutions the potential for reduction of sulfur to HS^- is −0.478 V.

It is instructive to examine the thermodynamic potential for neptunium(VI) and plutonium(VI) reduction as a function of the acidity. Allard et al.[4] have calculated the redox potentials for the various transformations of neptunium and plutonium as a function of pH, on the basis of the hydrolysis equilibria. In acidic solutions H_2S is thermodynamically capable of reduction of Pu(VI) to Pu(III), while neptunium reduction probably will stop at Np(IV). At pH 8 the calculated E_0 values for HS^- reduction of An(VI)/An(V) and An(VI)/An(IV) are +1.11 and +0.63 V for neptunium and +0.64 and +0.82 V for plutonium. Reduction of An(IV) to An(III) by HS^- at this pH is not favorable thermodynamically ($E_0 = -1.40$ V for neptunium and −0.56 V for plutonium).

As more complete reduction by sulfide is likely in acidic solutions, the normal procedure of acidifying the solution to identify the products spectrophotometrically was not feasible in these experiments. In the plutonium system the kinetic traces did show some evidence of complex reactions, with further reduction to Pu(IV) a possible explanation. In this system the initial rates of reaction (corresponding to about one-third to one-half of the total absorbance change) were fit by the first-order relation; these initial rates presumably correspond to the one-electron reduction of Pu(VI) to Pu(V). In the neptunium experiments no such complications were observed, suggesting one-electron reduction of Np(VI) to Np(V).

The spectra of the Np(VI) and Pu(VI) hydroxides were run in the 300–500 nm range prior to the kinetic study. The extinction coefficient of the hydroxide at the wavelength used for the kinetic runs (400 nm) was ~1100 M^{-1} cm^{-1} for neptunium and ~600 M^{-1} cm^{-1} for plutonium. In the initial kinetic runs in the stopped flow, a rapid increase in the absorbance was observed in the first 3 ms after mixing. The A_0 value derived in the fit of the rate data indicated that the starting absorbance was about twice that expected for the hydroxide complex, suggesting that formation of a new species on mixing of the An(VI)–hydroxide and the bisulfide solutions. The magnitude of the absorbance increase was directly dependent on the An(VI) concentration and largely independent of pH, total sulfide concentration (since sulfide was in 2–60-fold excess), and, in those experiments in which bicarbonate was present, total carbonate. If we assume that this new species is a An(VI)–bisulfide complex (probably a mixed-ligand hydroxide–bisulfide complex), that the complex is completely formed before any reduction occurs, and that it is a mononuclear complex, the calculated extinction coefficient at 400 nm is ~2000 M^{-1} cm^{-1} for neptunium and ~1000 M^{-1} cm^{-1} at 400 nm and ~600 M^{-1} cm^{-1} at 440 nm for plutonium. As the actinide cations normally are considered as hard-sphere ions, the formation of an apparently stable sulfide complex under these conditions is a fundamental departure from normal actinide solution behavior. This observation also indicates that the rate being measured is that of the disappearance of the complex and not explicitly the rate of reduction of the An(VI) ion.

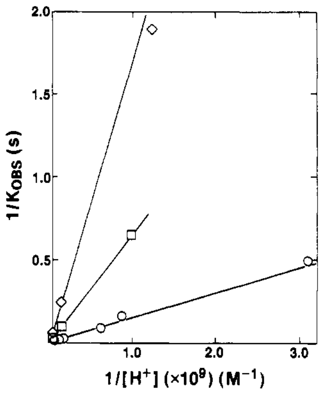

Figure 1. Weighted least-squares fits of $1/k_{obsd}$ vs. $1/[H^+]$ for the neptunium data: ○, 25 °C; □, 14 °C; ◇, 3 °C. At 25 °C: slope 1.49 (±0.15) × 10^{-10} M s; intercept 7.69 (±3.23) × 10^{-3} s; $[Na_2S] = 5.6 \times 10^{-3}$ M. At 14 °C: slope 6.41 (±0.05) × 10^{-10} M s; intercept 8.51 (±0.55) × 10^{-3} s; $[Na_2S] = 6.1 \times 10^{-3}$ M. At 3 °C: slope 1.64 (±0.18) × 10^{-9} M s; intercept 2.21 (±1.04) × 10^{-2} s; $[Na_2S] = 5.9 \times 10^{-3}$ M.

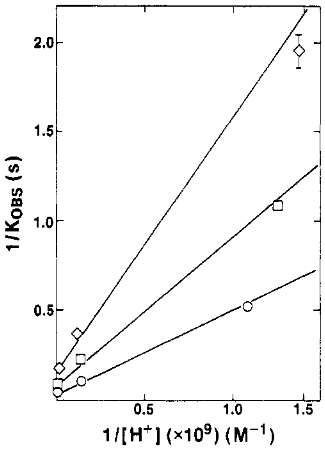

Figure 2. Weighted least-squares fits of $1/k_{obsd}$ vs. $1/[H^+]$ for the plutonium data: ○, 25 °C; □, 14 °C; ◇, 3 °C. At 25 °C: slope 4.64 (±0.36) × 10^{-10} M s; intercept 3.64 (±0.53) × 10^{-2} s; $[Na_2S] = 2.4 \times 10^{-3}$ M. At 14 °C: slope 8.28 (±0.86) × 10^{-10} M s; intercept 7.46 (±0.49) × 10^{-2} s; $[Na_2S] = 2.5 \times 10^{-3}$ M. At 3 °C: slope 1.42 (±0.24) × 10^{-9} M s; intercept 1.52 (±0.19) × 10^{-1} s; $[Na_2S] = 2.4 \times 10^{-3}$ M.

To verify that this postulated complex is not an artifact of the reduction reactions, a brief investigation of the corresponding U(VI)–sulfide system was performed. U(VI) is aptly suited to such an investigation as it is much more resistant to reduction than either Np(VI) or Pu(VI) but forms similar hydrolyzed species in alkaline, aqueous solutions. In a difference spectrum run at pH 5, a distinct maximum was observed at 320 nm ($\epsilon \sim 200$ M^{-1} cm^{-1}) in a solution containing 2.5 × 10^{-3} M U(VI) and 5.0 × 10^{-3} M total sulfide (the reference solution was 2.5 × 10^{-3} M U(VI) at the same pH). There was no obvious indication of U(VI) reduction (e.g. formation of a U(IV) precipitate) during the 1–2-h observation period.

While the reaction rate is proportional to the acidity in both of these systems, it does not exhibit a simple integral dependence in the pH 7–10 regime. Figures 1 and 2 are plots of the reciprocal of the observed rate constant vs. the reciprocal of hydrogen ion concentration at each temperature (and at constant total sulfide concentration) for the neptunium and plutonium systems, respectively. The linear fits indicate that the observed rate constant must be a function of the form

$$k_{obsd} = k[H^+]/(1 + a[H^+]) \tag{2}$$

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[5] Martell, A. E.; Smith, R. M. "Critical Stability Constants"; Plenum: New York, 1976; Vol. 4, p 76.

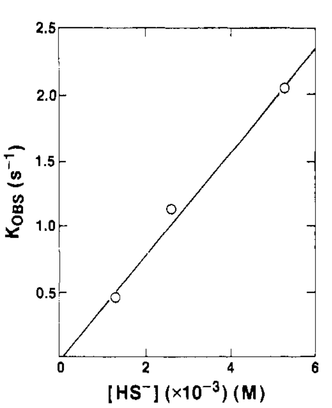

Figure 3. Pseudo-first-order rate constants (k_{obsd}) vs. [HS^-] for the Np(VI) system: pH ~ 9.5; T = 25.0 °C; I = 0.1 M; [H^+] = 3.02 (±0.21) × 10^{-10} M. Weighted least-squares fit: slope 392 (±27) M^{-1} s^{-1}; intercept −0.032 (±0.103) s^{-1}.

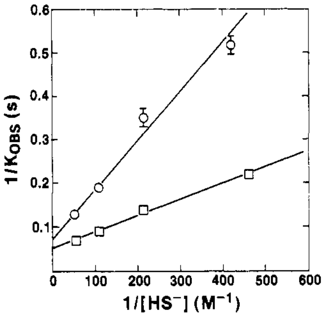

Figure 4. Weighted least-squares fits for $1/k_{obsd}$ vs. 1/[HS^-] for the plutonium data: ○, 25 °C; □, 14 °C. At 25 °C: $[H^+]_{av}$ = 7.87 (±0.82) × 10^{-10} M; slope 1.13 (±0.13) × 10^{-3} M s; intercept 7.03 (±1.12) × 10^{-2} s. At 14 °C: $[H^+]_{av}$ = 7.95 (±0.45) × 10^{-9} M; slope 4.20 (±0.23) × 10^{-4} M s; intercept 4.50 (±0.28) × 10^{-2} s.

In the neptunium system at 25 °C and pH ~9.5, the observed pseudo-first-order rate constants exhibit a simple direct dependence on [HS^-] with zero intercept (Figure 3). Corresponding data for the plutonium system at lower pHs and two temperatures indicate a more complex dependence on [HS^-]. Figure 4 is a plot of $1/k_{obsd}$ vs. 1/[HS^-] for the plutonium system at constant [H^+]. The linearity of the fits suggests an empirical rate law analogous to that observed for the hydrogen ion dependence.

Addition of 0.02 M sodium sulfate had no effect on the rate of disappearance of the Np(VI)–S complex. For the plutonium experiment with the surfactant, the empirical rate law predicts a pseudo-first-order rate constant of 11.8 s^{-1}, which is not appreciably different from the observed value of 11.04 s^{-1}. This result suggests that the sulfide complex is in true solution and is not a metastable colloidal species. As the SDS micelle is anionic, it also is suggestive evidence for an anionic or neutral plutonium–sulfide–hydroxide complex. For the experiments in which only the total neptunium concentration was changed, equivalent rate constants were observed, implying that the activated complex is not polynuclear.

Several mechanisms were considered that gave rate laws satisfying all or most of the above observations. All save one gave expressions too complex to solve or resulted in unreasonable values for the derived parameters. Assuming $AnO_2(OH)_2$ is the principal hexavalent actinide species present, the following series of reactions results in the simplest rate law consistent with experimental observation:

$$H^+ + HS^- \overset{K_a}{\rightleftharpoons} H_2S \qquad (3)$$

$$AnO_2(OH)_2 + H_2S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} AnO_2OHSH + H_2O \qquad (4)$$

$$AnO_2OHSH \xrightarrow{k_3} AnO_2^+ + OH^- + HS \qquad (5)$$

Under the conditions of these experiments, [H_2S] was generally equal to or greater than $[An(VI)]_t$ on mixing. The radical product HS probably combines with ambient HS^- to form the radicals $H_2S_2^-$ or HS_2^{2-}, which have been identified in pulse-radiolysis studies of the sulfide system.[6] This radical species absorbs strongly at the wavelength of observation, but its reported lifetime in aqueous solution is 1 μs, and hence it does not interfere with observation of the rate of Np(VI) or Pu(VI) reduction. It disappears from solution presumably by reaction with water to form a stable disulfide. The interpretation that the principal pathway for reduction of Np(VI) involves an intramolecular reaction is fortified by the observation that the absorbance–time traces under second-order conditions (2.2 × 10^{-3} or 4.3 × 10^{-3} M total sulfide, 1.25 × 10^{-3} M Np(VI) at 25 °C, pH 9.8) were fit by the first-order rate expression (eq 1).

If reaction 5 is assumed to be the slow step of the series of reactions, the rate of disappearance of the AnO_2OHSH complex is

$$-d[AnO_2OHSH]/dt = k_3[AnO_2OHSH] \qquad (6)$$

Applying the steady-state approximation to [AnO_2OHSH] and expressing [H_2S] in terms of total sulfide ([Na_2S]) and [H^+] result in the following expression for the rate law:

$$-d[AnO_2OHSH]/dt = \frac{(k_1k_3/(k_2 + k_3))K_a[AnO_2(OH)_2][H^+][Na_2S]}{1 + K_a[H^+]} \qquad (7)$$

If $k_2 \sim k_3$, only a composite rate constant ($k_1k_3/(k_2 + k_3)$) can be determined. However, two limiting conditions are possible that lead to more specific information.

(1). If $k_3 \gg k_2$ (that is, the rate of reduction of An(VI) is greater than the rate of decomposition of the complex), the rate law simplifies to

$$-d[AnO_2OHSH]/dt = \frac{k_1K_a[AnO_2(OH)_2][H^+][Na_2S]}{1 + K_a[H^+]} \qquad (8)$$

This result implies that the rate of formation of the intermediate complex is rate-determining. Experimental observation of a rapid rise in absorbance on mixing suggests that this condition does not occur.

(2). If $k_2 \gg k_3$, the rate law also can be simplified to

$$-d[AnO_2OHSH]/dt = \frac{(k_1/k_2)k_3K_a[AnO_2(OH)_2][H^+][Na_2S]}{1 + K_a[H^+]} \qquad (9)$$

Under these conditions, eq 4 represents a true preequilibrium and inclusion of [$AnO_2(OH)_2$] is no longer appropriate as the total actinide concentration will be represented by the sum of [$AnO_2(OH)_2$] and [AnO_2OHSH]. Defining $[An(VI)]_t$ = [$AnO_2(OH)_2$] + [AnO_2OHSH] and $k_1/k_2 = K_c$ and substituting for [$AnO_2(OH)_2$] in eq 9 result in the rate law given in eq 10.

$$-d[AnO_2OHSH]/dt = \frac{k_3K_cK_a[An(VI)]_t[H^+][Na_2S]}{1 + K_a[H^+] + K_cK_a[H^+][Na_2S]} \qquad (10)$$

In this limit both the rate of reduction of An(VI) in the complex and the stability constant of the AnO_2OHSH complex can be determined.

Complex dependence of k_{obsd} on both [Na_2S] and [H^+] was observed in the plutonium system, suggesting that the latter limiting condition may be appropriate. These data were fit to eq 11

$$k_{obsd} = \frac{k_3K_cK_a[H^+][Na_2S]}{1 + K_a[H^+] + K_cK_a[H^+][Na_2S]} \qquad (11)$$

at each temperature by using a multivariable weighted least-squares procedure with appropriate values for the protonation constant of HS^- (from ref 5). The parameters that fit this equation are given in Table I. The thermodynamic parameters were

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[6] Karmann, W.; Meissner, G.; Henglein, A. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1967**, *22B*, 273.

Table I. Rate Constants, Stability Constants, Activation Parameters, and Thermodynamic Parameters for the Plutonium System[a]

k_3, s^{-1}	$10^{-3}K_c$, M^{-1}	T, °C
27.4 (±4.1)	4.66 (±0.94)	25.0
15.6 (±1.1)	3.04 (±0.53)	14.0
8.6 (±1.0)	1.91 (±0.45)	3.0

$\Delta H^*(k_3) = +33.2\ (\pm 1.0)$ kJ/mol $\quad \Delta S^*(k_3) = -106\ (\pm 4)$ J/(mol K)

$\Delta H(K_c) = +27.7\ (\pm 0.5)$ kJ/mol $\quad \Delta S(K_c) = +163\ (\pm 2)$ J/(mol K)

[a] Values in parentheses correspond to one standard deviation error limit.

Table II. Rate Constants and Stability Constant for the Neptunium System[a]

k_3, s^{-1}	$10^{-3}K_c$, M^{-1}	T, °C
139 (±30)	1.31 (±0.32)	25.0

$10^{-4}k_1k_3/(k_2 + k_3)$, $M^{-1}\ s^{-1}$	T, °C
2.48 (±0.10)	14.0
0.705 (±0.035)	3.0

[a] Values in parentheses correspond to one standard deviation error limit.

calculated by a van't Hoff plot of the K_c values, while the activation parameters were calculated by applying the Eyring relationship to the k_3 values.

For the neptunium data at 14 and 3 °C, plots of k_{obsd} vs. $K_a[H^+][Na_2S]/(1 + K_a[H^+])$ ($\equiv[H_2S]$) were linear with zero intercept, as the simpler rate law expressed in eq 7 and 8 predicts. At 25 °C the simple form of the rate law gave large deviations at low pH. These data were fit by eq 11, implying that the same limiting condition that applies to the plutonium data also applies to the neptunium data at 25 °C. The results of the fitting procedure are given in Table II. For the 25 °C data, the rate of reduction of the neptunium complex is 5 times faster than that for the plutonium complex, while the apparent stability constant for the neptunium complex is a factor of 4 smaller.

If the limiting condition 1 is assumed for the neptunium results at 14 and 3 °C, the rate constant for formation of the complex at 25 °C can be calculated by extrapolation. A simple ln k_1 vs. $1/T$ plot predicts $k_1 = 7.9 \times 10^4\ M^{-1}\ s^{-1}$ at 25 °C, from which we calculate (since $K_c = k_1/k_2$) $k_2 = 60\ s^{-1}$. Because the rate law that fits the 25 °C data requires $k_2 \gg k_3$, we must conclude that the resolved values in the neptunium system at 14 and 3 °C are for the composite rate constant $k_1k_3/(k_2 + k_3)$ and not k_1.

In this case, back-calculation from the 14 and 3 °C data is not possible because of the complex temperature dependence of $k_1k_3/(k_2 + k_3)$ as illustrated by

$$k_1 = (kT/h)\exp(-\Delta H_1^*/RT + \Delta S_1^*/R) \qquad (12)$$

$$k_2 = (kT/h)\exp(-\Delta H_2^*/RT + \Delta S_2^*/R) \qquad (13)$$

$$k_3 = (kT/h)\exp(-\Delta H_3^*/RT + \Delta S_3^*/R) \qquad (14)$$

which yields

$$k_1k_3/(k_2 + k_3) = (kT/h)\exp(-\Delta H_1^*/RT + \Delta S_1^*/R)\exp(-\Delta H_3^*/RT + \Delta S_3^*/R)/\{\exp(-\Delta H_2^*/RT + \Delta S_2^*/R) + \exp(-\Delta H_3^*/RT + \Delta S_3^*/R)\} \qquad (15)$$

where k is the Boltzmann constant and h is Planck's constant. This equation contains six unknown quantities, and simple extrapolation of these results to 25 °C is not possible. Since the resolved rate constants at 14 and 3 °C are not compatible with the rate constants at 25 °C, no calculation of activation parameters is possible for the neptunium system.

In contrast to the experiments with SDS and with sulfate, increasing concentrations of sodium bicarbonate slow the rate of disappearance of the Np(VI)–S complex considerably, as is illustrated by the data in Table III. An increase in absorbance on mixing, comparable to that observed in the absence of bicarbonate, also occurred in these experiments. Both the initial absorbance (A_0) and the change in absorbance ($A_0 - A_\infty$) were independent of the bicarbonate concentration. These observations suggest that the rate-determining step is not altered by the presence of bicarbonate.

Table III. First-Order Rate Parameters for the Neptunium System as a Function of Bicarbonate Concentration[a]

k_1,[b] s^{-1}	$[NaHCO_3]$, M	k_1,[b] s^{-1}	$[NaHCO_3]$, M
37.10 (±0.97)	0.0	5.478 (±0.063)	0.005
25.00 (±0.20)	0.0004	0.8729 (±0.0064)	0.02
15.34 (±0.08)	0.001		

[a] Conditions: $T = 25$ °C, $I = 0.1$ M, $[Np]_t = 1.25 \times 10^{-4}$ M, $[Na_2S] = 5.6 \times 10^{-3}$ M, pH 8.11 (±0.02), [Tris] = 0.01 M. [b] Values in parentheses correspond to one standard deviation error limit.

The simplest mechanistic interpretation of these results is that preequilibria of the type

$$NpO_2(OH)_2 + HCO_3^- \overset{Q_1}{\rightleftharpoons} NpO_2OHCO_3^- + H_2O \qquad (16)$$

$$NpO_2(OH)_2 + 2HCO_3^- \overset{Q_2}{\rightleftharpoons} NpO_2(CO_3)_2^{2-} + 2H_2O \qquad (17)$$

compete with reaction 4 to inhibit formation of the Np(VI)–S complex. If this interpretation is correct, the mass balance expression must be modified to account for the equilibria represented in eq 16 and 17:

$$[Np(VI)]_t = [NpO_2(OH)_2] + [NpO_2OHSH] + [NpO_2OHCO_3^-] + [NpO_2(CO_3)_2^{2-}] \qquad (18)$$

Substituting for the relevant equilibria results in the expression for the observed rate constant

$$k_{obsd} = k_3K_cK_a[H^+][Na_2S]/\{1 + K_a[H^+] + K_cK_a[H^+] \times [Na_2S] + (1 + K_a[H^+])(Q_1[HCO_3^-] + Q_2[HCO_3^-]^2)\} \qquad (19)$$

Assuming k_3 and K_c are as determined in the absence of bicarbonate, the data in Table III were fit with appropriate weighting to derive the following values: $Q_1 = 1.7\ (\pm 0.1) \times 10^3\ M^{-1}$; $Q_2 = 5.6\ (\pm 1.3) \times 10^4\ M^{-2}$. The value for Q_1 is remarkably similar to that for K_c, implying that the bisulfide and carbonate complexes have comparable stability under these conditions. As the pH dependence of these reactions was not investigated, these parameters are correct only at the pH of the experiments (pH 8.1).

Maya[7] has recently reported stability constants for the formation of the complexes $(NpO_2)_2CO_3(OH)_3^-$, $NpO_2(CO_3)_2^{2-}$, and $NpO_2(CO_3)_3^{4-}$. The conditions of his experiments were similar to those in this work except for 1 order of magnitude greater total metal ion concentration and higher ionic strength. He did not observe a mononuclear 1:1 Np(VI)–carbonate (or hydroxy-carbonate) complex comparable to that proposed in eq 16. From his data and the estimate of the hydrolysis constants of Allard, we calculate for the reaction corresponding to eq 17 $\beta = 1.6 \times 10^7\ M^{-1}$, which is ~300 times greater than the value of Q_2 determined in these experiments. As this value is calculated by using an estimate of the hydrolysis constant, the apparent disagreement is not surprising. It also is possible that the assumption that the rate-determining step does not change is in error, as Maya's results indicate that carbonate complexing competes effectively with hydrolysis under these conditions.

Application of the previously derived rate law (eq 10) to the neptunium data at pH >10 (Table IV) predicts pseudo-first-order rate constants of 0.017–0.025 s^{-1}. That the observed rate constants are 3 orders of magnitude greater suggests that a different reaction mechanism may be operational under these conditions. The rapid increase in absorbance on mixing was observed in these experiments, but the normalized absorbance change ($(A_0 - A_\infty)/[Np(VI)]_t$) at 400 nm is 40% lower than was observed in the pH 8–10 range.

The data were fit by the empirical rate law

$$k_{obsd} = (a + b[H^+])[Na_2S] \qquad (20)$$

with values $a = 2.8\ (\pm 2.2) \times 10^3\ M^{-1}\ s^{-1}$ and $b = 3.0\ (\pm 0.5) \times$

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Inorg. Chem. **1986**, *25*, 1173–1182

Table IV. Rate Data for Neptunium(VI)–Sulfide Reaction at pH >10.5 and T = 25.0 °C

10^4[Np], M	10^3[Na$_2$S], M	k_1,[a] s^{-1}	pH	ionic strength, M
5.00	4.9	60.26 (±0.38)	11.53	0
5.00	4.9	60.92 (±0.45)	11.41	0.1
2.50	2.6	57.19 (±0.32)	11.18	0.1
2.50	2.4	58.28 (±1.42)	11.08	0.1
1.25	2.4	56.26 (±0.43)	11.23	0.1
1.25	1.2	53.74 (±0.64)	10.84	0.1

[a] Values in parentheses correspond to one standard deviation error limit.

10^{15} M^{-2} s^{-1}. The value for a is within 1.3 standard deviations of zero and so probably does not represent a real reaction pathway. As noted above, calculations indicate that the principal Np(VI)–hydroxide species in this pH regime is $NpO_2(OH)_3^-$. Since the $K_a[H^+]$ term in this pH range is much less than 1, [Na$_2$S] is equivalent to [HS$^-$] under these conditions. A rate law consistent with these observations can be derived from the mechanism

$$NpO_2(OH)_3^- + HS^- \overset{K_c'}{\rightleftharpoons} NpO_2(OH)_2SH^- + OH^- \quad (21)$$

$$NpO_2(OH)_2SH^- \xrightarrow{k_4} NpO_2(OH)_2^- + HS \quad (22)$$

The derived rate law is

$$-d[NpO_2(OH)_2SH^-]/dt = k_4K_c'/K_w[NpO_2(OH)_3^-][H^+][Na_2S] \quad (23)$$

where K_w is the ionization constant for water (1.66×10^{-14} M^{-2} at 0.1 M ionic strength). In this rate law, the empirical parameter b is equivalent to k_4K_c'/K_w, giving k_4K_c' = 49 (±8) s^{-1}. Because the dimensions of k_4K_c' are different from those of k_3K_c, the two parameters cannot be compared.

Conclusions

Both neptunium(VI) and plutonium(VI) are rapidly reduced by bisulfide ion in neutral to slightly alkaline solutions. The mechanism involves formation of a soluble sulfide complex followed by reduction of the hexavalent actinide ion in an intramolecular reaction. For plutonium, the rates of reaction are such that both the rate of the intramolecular reduction and the stability constant of the intermediate complex can be determined. The equivalent constants can be determined for neptunium at 25 °C but not at reduced temperatures. The rate of reduction of Np(VI) as a function of pH indicates two distinct reaction mechanisms at pH <10 and pH >10.5. The reaction rate is appreciably decreased but the reaction is not prevented by the presence of bicarbonate ions in the solution, implying that the postulated sulfide complex has considerable stability under these conditions. Further investigation of the nature of the sulfide complexes is planned.

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Registry No. Np, 7439-99-8; Pu, 7440-07-5; HS$^-$, 15035-72-0.

Supplementary Material Available: Tables containing the rate constants for all experiments for both plutonium and neptunium and the results of least-squares fits for several alternative mechanisms (22 pages). Ordering information is given on any current masthead page.

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Semiexhaustive Determination of Rate Parameters for Dissociative Axial Ligand Substitution in 24 Ferrous Dimethylglyoxime Complexes Involving 7 Different Axial Ligands

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Syntheses, visible spectra, and kinetic data are presented for 24 of 28 possible complexes Fe(DMGH)$_2$LT (L or T = methylimidazole (MeIm), pyridine (py), tributylphosphine (PBu$_3$), tributyl phosphite (P(OBu)$_3$), benzyl isocyanide (BzNC), tosylmethyl isocyanide (TMIC), and carbon monoxide). Axial ligand substitution reactions proceed via a dissociative mechanism in all cases. Dissociative rate constants spanning 8 orders of magnitude depend upon a leaving group order py > MeIm > P(OBu)$_3$ > PBu$_3$ ≥ CO > BzNC ≃ TMIC and a trans labilizing order py > MeIm > PBu$_3$ > P(OBu)$_3$ > BzNC ≥ TMIC > CO. The trans effect on MeIm and py dissociation correlates with the MLCT band in the visible spectrum, indicating that weakening of π bonding to the trans ligand constitutes a significant part of the barrier for dissociation. Relative rates of addition to the pentacoordinate intermediates cover about a factor of 10 and are independent of the trans ligand. The order of addition is similar to that found in hemes: MeIm ≃ BzNC ≃ TMIC > PBu$_3$ ≃ P(OBu)$_3$ > CO. Rates of dissociation of pyridines with substituents 4-CN, 3,4-Me$_2$, and 4-NMe$_2$ correlate with ligand basicity. Trans effects with increased donor strength of substituted pyridines are mildly accelerating for loss of σ donors and mildly decelerating for loss of CO. Relevance to other low-spin d^6 systems including hemes and Cr(0) complexes is discussed.

Introduction

Kinetic investigations of axial ligand substitution reactions of a variety of low-spin iron(II) complexes of the general form *trans*-FeN$_4$LT,[1] where N$_4$ is a planar tetradentate ligand such as bis(glyoxime),[2-4] porphyrin,[5,6] phthalocyanine,[7-9] or another macrocyclic ligand[10-14] and L and T monodentate ligands such

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[1] Abbreviations: FeN$_4$, used in place of Fe(DMGH)$_2$ to designate bis(dimethylglyoximato)iron except when comparisons with other tetradentate ligands might lead to ambiguity; MeIm, 1-methylimidazole; Im, imidazole; BzNC, benzyl isocyanide; TMIC, tosylmethyl isocyanide; py, pyridine, 4-CNPy, 4-cyanopyridine; 3,4-Me$_2$Py, 3,4-dimethylpyridine; 4-Me$_2$NPy, 4-(dimethylamino)pyridine; MLCT, metal to ligand charge transfer. Rate constants are designated by $k_{-L}{}^T$ for dissociation of the ligand L trans to T. The shortened forms N (MeIm), P (PBu$_3$), and PO (P(OBu)$_3$) are used as subscripts and superscripts.

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