

Contribution from Chemistry Division,
Argonne National Laboratory, Argonne, Illinois 60439**Kinetic Study of the Reduction of Neptunium(VI) and Plutonium(VI) by Iodide Ion in Aqueous Perchlorate Media¹**

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The title reactions proceed with the stoichiometry $2\text{AnO}_2^{2+} + 2\text{I}^- = 2\text{AnO}_2^+ + \text{I}_2$. The empirical form of the rate law for these reactions is first order in AnO_2^{2+} and I^- and independent of hydrogen ion concentration with a small Harned-type factor that arises from the replacement of LiClO_4 by NaI . At 25 °C and $\mu = 1.00$, the values for the apparent second-order rate constants are 530 ± 6 and $17.0 \pm 0.1 \text{ M}^{-1} \text{ s}^{-1}$ for NpO_2^{2+} and PuO_2^{2+} , respectively. The apparent activation parameters for the reduction of NpO_2^{2+} are $\Delta H^\ddagger = 12.2 \pm 0.3 \text{ kcal/mol}$ and $\Delta S^\ddagger = -6 \pm 1 \text{ eu}$ and for the reduction of PuO_2^{2+} are $\Delta H^\ddagger = 13.8 \pm 0.1 \text{ kcal/mol}$ and $\Delta S^\ddagger = -8.0 \pm 0.4 \text{ eu}$. The results are discussed in terms of and found to be consistent with the Marcus cross relations.

Introduction

In dilute perchloric acid solutions the dioxo cations of Np and Pu are linear O–An–O²⁺ species in the V and VI oxidation states.² While the formal reduction potentials of the respective V–VI couples vary from +1.14 to +0.92 V, the standard entropies of the AnO_2^{2+} ions are the same within the estimated error limits.³ In this report, we present the results obtained in a dynamic study of the reduction of the AnO_2^{2+} ions by iodide in aqueous perchloric acid–perchlorate media. Among the considerations that prompted this investigation was the determination of (a) whether the differences in ΔG^\ddagger for the title reactions can be quantitatively described by the Marcus equations⁴ and (b) whether there are any significant differences in the values of ΔS^\ddagger for these two reactions. In addition, the results add to the phenomenological description of the dynamics for the production of I_2 using 1–equiv oxidants.

Experimental Section

Lithium iodide and sodium iodide were each recrystallized three times from triply distilled water. The lithium iodide was placed in a vacuum desiccator which was pumped on for 2 h until no discoloration due to iodine was evident. Solutions were stored in brown glass bottles in the dark and were standardized against silver nitrate using either a potentiometric or an eosin end point.

Lithium perchlorate and perchloric acid were prepared and standardized as previously described.⁵ Iodine solutions were prepared from resublimed iodine and standardized against thiosulfate. Np(VI) solutions were prepared from two separate stock solutions of ²³⁷Np by evaporation of a Np(V) solution in perchloric acid almost to dryness, diluting with triply distilled water, and passing a stream of N_2 through the solution. A blank solution (containing no Np) gave no discernible reaction with I^- . The Np(VI) solutions were assayed spectrophotometrically, after reduction to Np(V) by NO_2^- ; ϵ at 980.5 nm is $403 \text{ M}^{-1} \text{ cm}^{-1}$.

The ²⁴²PuO₂ was dissolved in nitric acid, purified by a solvent extraction procedure,⁶ and fumed repeatedly with perchloric acid. Stock solutions of Pu(VI) were prepared using a procedure similar to that described for the preparation of Np(VI) solutions. The Pu solutions were assayed spectrophotometrically in 1 M perchloric acid at 831.1 nm, ϵ $555 \pm 5 \text{ M}^{-1} \text{ cm}^{-1}$.⁷ Hydrogen ion concentrations in the stock solutions of Np(VI) and Pu(VI), which were freshly prepared and analyzed daily, were estimated by diluting aliquots and measuring the pH in the range of 2–4 on an instrument calibrated against solutions of known perchloric acid concentration.

The kinetic studies were carried out on a Durrum stopped-flow spectrophotometer interfaced with a Xerox Sigma V computer. The wavelength monitored was 467 nm, the I_2 – I_3^- isobestic point, where iodine absorbs much more strongly than the reactants or other products. All kinetic data were collected with pseudo-first-order excess of iodide and hydrogen ion, at $\mu = 1.00 \text{ M}$ (LiClO_4).

The A_t , t data from individual kinetic experiments were treated with a nonlinear least-squares routine, fitted to the first-order rate equation

$$A_t = (A_0 - A_\infty) \exp(-k_{\text{obsd}}t) + A_\infty \quad (1)$$

where A_0 , A_∞ , and k_{obsd} are adjustable parameters. Each kinetic

experiment was monitored to at least 90% of completion; 800–950 A_t , t data pairs were collected for each experiment. A minimum of six determinations of k_{obsd} was made for each set of experimental constraints and we report \bar{k}_{obsd} , the mean of these determinations, and their standard deviations, σ_m .

Results

The stoichiometry of the Np(VI)– I^- reaction was verified by adding a known amount of Np(VI) to an excess of I^- in dilute HClO_4 and determining the iodine and Np(V) produced spectrophotometrically. The resulting ratios were found to be $\Delta[\text{Np(V)}]/\Delta[\text{I}_2] = 2.02 \pm 0.05$ and $\Delta[\text{Np(VI)}]/\Delta[\text{I}_2] = -1.98 \pm 0.04$, consistent with the reaction



Similarly the stoichiometry of the reaction between Pu(VI) and I^- was estimated by the amount of iodine produced from the reaction of $1.02 \times 10^{-3} \text{ M}$ Pu(VI) solution with a solution initially $1.48 \times 10^{-2} \text{ M}$ in I^- . Pu(V) was detected by the appearance of a weak band at 569 nm and no evidence of Pu(IV) or Pu(III) was detected at 473 or 600 nm, respectively. The ratio determined was $\Delta[\text{Pu(VI)}]/\Delta[\text{I}_2] = -1.89 \pm 0.05$. This ratio was not affected by the order of mixing and the absorbance of the I_2 produced was constant over a period of ca. 20 min. These results are consistent with the principal mode of iodine production



Np(VI)– I^- Kinetics. Equation 1 provided an adequate adjustment of the A_t , t data, and the calculated values of \bar{k}_{obsd} are summarized in Table I. These data provide a sufficient basis for the following statements: (a) the rate law is first order in Np(VI) and zero order in Np(V) and I_2 ; (b) the rate parameter is independent of the hydrogen ion concentration over the indicated range.

The dependence of \bar{k}_{obsd} on initial sodium iodide concentration was marginally greater than first order at each temperature. As is evident from the data presented, the replacement of sodium iodide by lithium iodide does not cause an experimentally detectable contribution to the dynamics of the system. The \bar{k}_{obsd} , $[\text{I}^-]$ data were adequately correlated either by a two-term polynomial

$$\bar{k}_{\text{obsd}} = k'[\text{I}^-] + k''[\text{I}^-]^2 \quad (4)$$

or by a first-order dependence plus a Harned-type correction term

$$\bar{k}_{\text{obsd}} = k[\text{I}^-] \exp\{a[\text{I}^-]\} \quad (5)$$

The data at each temperature were adjusted by the appropriate least-squares routines and the optimized parameters are presented in Table II.

The variation in the rate parameter with change in ionic strength, using lithium perchlorate, was studied at 25 °C, $[\text{H}^+] = 0.056 \text{ M}$, $[\text{I}^-]_0 = 3.64 \text{ mM}$, and $[\text{Np(VI)}]_0 = 0.19 \text{ mM}$. At

Table I. Rate Parameters for the Reaction of Np(VI) with I^{-a}

1.8 °C		13.15 °C		25.0 °C				34.85 °C	
[I ⁻], mM	$\bar{k}_{\text{obsd}}, \text{s}^{-1}$	[I ⁻], mM	$\bar{k}_{\text{obsd}}, \text{s}^{-1}$	[I ⁻], mM	$\bar{k}_{\text{obsd}}, \text{s}^{-1}$	[I ⁻], mM	$\bar{k}_{\text{obsd}}, \text{s}^{-1}$	[I ⁻], mM	$\bar{k}_{\text{obsd}}, \text{s}^{-1}$
18.9	1.86 ± 0.04	18.9	4.71 ± 0.09	3.64	1.98 ± 0.02 ^b	27.3	16.6 ± 0.1	3.78	4.71 ± 0.05
37.8	4.26 ± 0.07	45.1	13.5 ± 0.3	3.64	1.99 ± 0.03 ^c	36.4	22.6 ± 0.3	9.45	12.07 ± 0.07
45.1	5.26 ± 0.14	75.6	26.2 ± 0.5	3.64	1.95 ± 0.03 ^d	36.4	22.2 ± 0.3 ^e	18.9	25.2 ± 0.2
75.6	11.14 ± 0.14	135.0	53.2 ± 1.3	3.64	1.99 ± 0.03	36.4	21.1 ± 0.4 ^h	28.3	37.1 ± 0.4
135.0	23.5 ± 0.5	151.0	68.1 ± 1.8	3.64	2.01 ± 0.04 ^e	45.5	31.9 ± 0.7	45.1	59.7 ± 1.2
189.0	39.3 ± 1.0	226.0	122.0 ± 3.0	3.64	1.99 ± 0.04 ^f	54.5	37.3 ± 0.9	67.7	93.5 ± 2.5
271.0	67.7 ± 1.9			7.27	3.94 ± 0.03	72.7	49.9 ± 1.8		
				10.9	6.26 ± 0.08	109.0	94.2 ± 3.2		
				18.2	10.1 ± 0.2	109.0	92.4 ± 2.6 ⁱ		
						145.0	142.0 ± 6.0		

^a [Np(VI)] = (1.6–2.0) × 10⁻⁴ M, [H⁺] = 0.56–0.66 M, and μ = 1.00 M (LiClO₄), unless otherwise noted. ^b [Np(VI)] = 0.09 mM. ^c [Np(VI)] = 0.119 mM. ^d [Np(VI)] = 0.288 mM. ^e [H⁺] = 0.056 M. ^f [H⁺] = 0.158 M. ^g [I₂] = 0.11 mM. ^h [Np(V)] = 0.176 mM. ⁱ LiI used as the source of I⁻.

Table II. Calculated Values of the Np(VI)-I⁻ Rate Parameters of Eq 4 and 5^a

T, °C	Eq 4		Eq 5	
	k', M ⁻¹ s ⁻¹	10 ⁻² k'', M ⁻² s ⁻¹	k, M ⁻¹ s ⁻¹	a, M ⁻¹
1.8	90 ± 4	6.49 ± 0.51	101 ± 5	3.7 ± 0.4
13.1	229 ± 8	13.91 ± 0.93	245 ± 10.0	3.7 ± 0.4
25.0	523 ± 6	29.9 ± 2.5	530 ± 6	4.5 ± 0.4
34.8	1260 ± 16	21.2 ± 8.1	1260 ± 16	1.6 ± 0.6

^a Uncertainties are calculated on the basis of external consistency. All values of \bar{k}_{obsd} are weighted by (1/σ_m)².

ionic strengths of 0.30, 0.70, 1.50, and 2.00 M, the respective values for \bar{k}_{obsd} (s⁻¹), were 2.17 ± 0.02, 1.96 ± 0.03, 2.24 ± 0.06, and 2.63 ± 0.02.

By writing the rate law in the form of eq 5, the activation parameters for the complete data set were adjusted in terms of the Eyring formalism using a weighted, nonlinear least-squares computation.⁸ The values calculated are ΔH^{*} = 12.2 ± 0.3 kcal/mol, ΔS^{*} = -6 ± 1 eu, and a = 4.1 ± 0.4 M⁻¹ and the average deviation between observed and calculated values of k using these parameters is 6%.

Pu(VI)-I⁻ Kinetics. The integrated form of the first-order rate law, eq 1, also provided an adequate description of this system. The values of \bar{k}_{obsd} tabulated in Table III demonstrate that the rate parameter is independent of initial concentrations of Pu(VI), Pu(V), I₂, and hydrogen ion. The variation of the apparent rate constant with change in sodium iodide concentration was again slightly greater than first order at each temperature. In contrast, however, to the case where Np(VI) is the oxidant, the data provide evidence for a specific cation effect on the dynamics.

The \bar{k}_{obsd} , NaI data at 13.2, 25.0, and 37.2 °C were correlated using the functional form of eq 5. The values of the respective least-squares adjusted parameters k (M⁻¹ s⁻¹) and

a (M⁻¹) are as follows: 6.71 ± 0.09, 0.36 ± 0.20; 17.01 ± 0.13, 1.72 ± 0.21; 45.1 ± 1.7, 1.2 ± 0.5. The activation parameters were evaluated as described above, with the results ΔH^{*} = 13.8 ± 0.1 kcal/mol, ΔS^{*} = -8.0 ± 0.4 eu, and a = 1.3 ± 0.2 M⁻¹. For this data set, the average deviation between \bar{k}_{obsd} and the calculated values using the stated parameters was 3%.

It was originally planned to include a dynamic study of the reaction between the isostructural Am(VI) and I⁻ to extend the range of ΔG^o since the value of E^o is +1.53 V for the Am(V)-Am(VI) couple. This reaction proceeds at a rate that is not amenable for study using the available equipment. At 25 °C, μ = 1.00 M, and [H⁺] = 0.45 M and with initial concentrations of [Am(VI)] = 0.273 mM and [I⁻] = 0.316 mM, the reaction was completed within the time of mixing, ca. 2 ms. From this, a lower limit for the reaction, k > 3.0 × 10⁶ M⁻¹ s⁻¹, is calculated.

Discussion

The major, if not sole, path in these reactions is first order in each of the reactants. The apparent deviation from first-order behavior may well be the result of activity coefficient variations. The results obtained when LiI was substituted for NaI provide no compelling direct evidence for a specific Na⁺ or Li⁺ effect on the rate in the case of the Np(VI)-I⁻ system. The "medium" effects may well reflect the changes in pertinent activity coefficient ratios caused by replacement of the perchlorate ion with iodide ion.

An alternative rationalization, eq 4, was explored in some detail for Np(VI) as the oxidant. The values calculated for k'', at each of the temperatures where the reaction was studied, are presented in Table II. The variation of k'' with temperature is not described by the usual Arrhenius formulation. This result does not provide evidence for the identification of k'' as a rate parameter that describes a parallel reaction path second order in [I⁻].

Table III. Rate Parameters for the Reaction of Pu(VI) with I^{-a}

13.2 °C		25.0 °C		37.2 °C	
[I ⁻], mM	$\bar{k}_{\text{obsd}}, \text{s}^{-1}$	[I ⁻], mM	$\bar{k}_{\text{obsd}}, \text{s}^{-1}$	[I ⁻], mM	$\bar{k}_{\text{obsd}}, \text{s}^{-1}$
11.3	0.0736 ± 0.001	4.51	0.0770 ± 0.0004	11.3	0.484 ± 0.015
25.7	0.154 ± 0.001	4.51	0.0791 ± 0.0008 ^c	22.6	1.08 ± 0.03
33.8	0.228 ± 0.003	4.51	0.0782 ± 0.0007 ^d	33.8	1.76 ± 0.05
45.1	0.311 ± 0.007	11.3	0.193 ± 0.005	45.1	2.15 ± 0.03
67.7	0.453 ± 0.008	22.6	0.392 ± 0.006	67.7	3.23 ± 0.05
90.2	0.619 ± 0.008	33.7	0.576 ± 0.005 ^e	90.2	4.58 ± 0.20
90.2	0.631 ± 0.005 ^b	33.85	0.603 ± 0.005	90.2	4.73 ± 0.06 ^f
		45.1	0.812 ± 0.008	90.2	4.50 ± 0.04 ^g
		67.4	1.18 ± 0.04 ^e		
		67.7	1.33 ± 0.01		
		90.2	1.80 ± 0.02		

^a Initial concentrations are [Pu(VI)] = 0.16 mM, [H⁺] = 0.05 M, and μ = 1.00 M (LiClO₄), unless otherwise noted. ^b [I₂] = 0.46 mM. ^c [H⁺] = 0.050 M. ^d [H⁺] = 0.259 M. ^e LiI used as source of I⁻. ^f [Pu(VI)] = 0.47 mM. ^g [Pu(V)] = 0.16 mM.

A mechanism consistent with the molecularity of the reaction is



as the rate-determining step. The recombination and equilibrium reactions that generate the product I_3^- which would follow eq 6 are assumed to be rapid. The data presented do not provide direct evidence for the participation of a radical I^0 species in the reaction scheme. It should be noted, however, that the thermodynamic properties of this radical, estimated by Margerum,⁹ provide no criteria which eliminate the possibility of the proposed mechanism.

If we assume that the reactions between the AnO_2^{2+} and Γ^- ions proceed solely by outer-sphere transition states and that the other relevant criteria are satisfied, it is of interest to compare these reactions in terms of the Marcus cross relations.⁴ The results of such calculations¹⁰ [k_{obsd} ($\text{M}^{-1} \text{s}^{-1}$), k_{calcd} ($\text{M}^{-1} \text{s}^{-1}$)] are as follows, for the oxidants Np(VI), Pu(VI), and Am(VI) at 25 °C, respectively: 530, 2×10^3 ; 17, 8; $>3 \times 10^6$, 1×10^7 . The agreement between calculated and observed values of the rate constants is adequate and provides a reasonable description of the variation in ΔG^\ddagger with change in ΔG° for a series of closely related reactions.

It is of interest to note that the differences in the rates of reduction of Np(VI) and Pu(VI) by Γ^- are governed by differences in ΔH^\ddagger . This feature has not been previously observed for reactions of Np(VI) and Am(VI) with common reductants,^{11,12} similar systems where a priori considerations would

dictate that there be no significant variation in the respective values of ΔS^\ddagger . The extension of the Marcus formalism⁴ to calculations of ΔH^\ddagger and ΔS^\ddagger offers no apparent rationalization of these observations.

Registry No. NpO_2^{2+} , 18973-22-3; PuO_2^{2+} , 22853-00-5; Γ^- , 20461-54-5.

References and Notes

- (1) Work performed under the auspices of the U.S. Energy Research and Development Administration.
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- (7) This value was determined by oxidation of a weighed sample of ^{239}Pu and is in good agreement with the previously published value cited in ref 3.
- (8) The functional form is $\bar{k}_{\text{obsd}} = 2kT/h \exp(-\Delta H^\ddagger/RT) \exp(\Delta S^\ddagger/R) [\Gamma^-] \exp(a[\Gamma^-])$. We thank Dr. E. A. Deutsch, University of Cincinnati, for his computational assistance.
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- (10) The values for $K_{1,2}$ were calculated from potentials listed in ref 4 and 9. The self-exchange reaction between Γ^- and I^0 was estimated as $10^{10} \text{ M}^{-1} \text{ s}^{-1}$. The value for the Np(V)-Np(VI) exchange reaction, $105 \text{ M}^{-1} \text{ s}^{-1}$,¹¹ was used for all the An(V)-An(VI) reactions.
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Kinetics and Mechanisms of the Reductions of Thallium(III) and Chromium(III) by Uranium(III) in Perchlorate Media

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The kinetics and mechanisms of the reaction of U(III) with Tl(III) and Cr(III) have been examined in perchlorate media. The Tl(III) reaction was found to obey the rate law $-d[\text{U(III)}]/dt = [\text{U}^{3+}][\text{Tl}^{3+}]\{k_{-1}K/(H + K)\}$ in which k_{-1} has a value of $(3.6 \pm 0.2) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at 20 °C and an ionic strength of 2.0 M, whereas the Cr(III) reaction was found to exhibit a mechanism dominated by a reaction path having an inverse second-order acid concentration dependence. The rate constants are compared with those obtained for other similar systems; it is suggested, that the acid concentration independent and the inverse acid concentration dependent reaction paths of many electron-transfer reactions involving metal ions exhibit a limiting rate of 10^6 – $10^7 \text{ M}^{-1} \text{ s}^{-1}$. Plausible reasons for this limiting value are discussed.

Introduction

Uranium(III) is a sufficiently powerful reducing agent to reduce a wide variety of metal ions at measurable rates, thus making it an ideal reagent for comparative studies. Detailed examinations of the kinetics and mechanisms of reactions of U(III) with Fe(III), V(IV), V(III),¹ Co(III),² and several aquoamine complexes of Co(III)³ have been reported, and this paper extends these studies to the reduction of Tl(III) and to the determination of the activation parameters of the U(II-I)-Cr(III) reaction for which the rate law had been previously reported.⁴ Tl(III) and Cr(III) were chosen for study because both are extensively hydrolyzed in aqueous solution, and the participation of hydrolyzed species in the rate law was expected, thus providing further data necessary to permit comparisons of the rate constants and rate parameters of the

acid-independent and acid-dependent reaction paths for the reactions of the U(III) ion.

Experimental Section

Solutions of U(III)¹ and Cr(III)⁴ were prepared and analyzed as described previously. U(IV) solutions were obtained by passing oxygen through U(III) solutions and purging with argon gas. A stock solution of $\text{Tl}(\text{ClO}_4)_3$ was prepared by dissolving analytical reagent grade Tl_2O_3 (Merck) in 9 M HClO_4 and analyzed by titration with standard I_2 .⁵ All solutions were purged with high-purity argon gas for at least 30 min prior to use. Kinetic measurements were made with a stopped-flow spectrophotometer and computerized data acquisition systems.⁶

Results

(a) **U(III)-Tl(III) Reaction.** The reaction was followed at 350 nm, where U(III) was found to be the only absorbing species, with an extinction coefficient of $1550 \pm 60 \text{ M}^{-1}$. The