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Pulse Radiolysis Studies of Uranium(VI), Neptunium(VI), Neptunium(V), and Plutonium(VI) in Aqueous Perchlorate Media¹

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Reactions of several actinide (An) perchlorates with e_{aq}^- and OH radicals produced by pulse radiolysis of solutions of these compounds are reported. Kinetic data for the formation of a U(VI)-H₂O₂ complex are reported. Rate parameters for the reaction of the e_{aq}^- with various actinides have been determined and their significance discussed.

Introduction

The dynamics of the oxidation-reduction reactions of U(VI), Np(VI), and Pu(VI) with a variety of reagents² have been characterized. There has been no systematic study of the reactions of these ions with the reductant e_{aq}^- and the oxidizing radical OH under conditions where the structure of the actinyl ion is known with reasonable certainty. Pikaev et al.^{3,4} have studied reactions of e_{aq}^- with Np and Pu in various oxidation states in highly alkaline solutions where according to these investigators "Owing to insufficient information on the forms in which neptunium and plutonium exist in an alkaline medium, it is impossible to draw definite conclusions as to the reasons for their different reactivities with e_{aq}^- ".³ We are presently engaged in a systematic study of such reactions with the intent of extending the phenomenological description of the reactivity patterns of these ions and providing additional insight into the mechanisms of redox reactions that occur in systems with large thermodynamic driving forces.

Experimental Section

Stock solutions of perchloric acid, uranium(VI), neptunium(VI), neptunium(V), and plutonium(VI) perchlorates were prepared and standardized as previously described.⁵⁻⁷

The radioactivity associated with the samples necessitated the use of the gas-saturating and cell-filling device depicted in Figure 1. A is a standard 5/20 joint which mates with the irradiation cell, B is a glass frit, and C is the gas inlet. Helium or N₂O is bubbled through the solutions for deaerating or saturating with N₂O, respectively. The levels of residual oxygen in solutions treated with this system compared favorably to those generally attained using the conventional syringe techniques.⁸ The oxygen content of the solutions were determined on a Van Slyke-gas chroma-

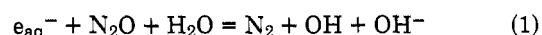
tograph combination⁹ and was found to be of the order of 0.1 μ M in all cases.

Spectra of the transient species produced by single electron pulses were obtained using a streak camera-TV scanning method described in previous publications.^{10,11} The rate data were obtained by conventional photomultiplier techniques.¹²

The kinetic data were scanned from a smoothed trace of the Polaroid film by an automatic line follower (Hewlett Packard Type F3B), converted to digital form in a 400 channel analyzer, and processed by a Xerox Sigma 5 computer. The functional expression was the usual integrated form of a first-order rate process. The statistical adjustment of the unweighted data in this form used a non-linear least-squares program with parameters k , I_0 , and I where k is the pseudo-first-order rate constant, I_0 is the initial light intensity, and I is the light intensity at time t . In all cases these three parameters provided an adequate description of the data. Standard deviations of the rate parameters quoted in the text were calculated on the basis of external consistency.

Results and Discussion

A. *Reactions in N₂O-Saturated Solutions.* The rapid occurrence of the reaction



makes feasible the development of the reactivity patterns for what is predominantly a one radical system, OH, in aqueous solutions. The redox potential E_B^0 of this radical has been estimated to be about 1.9 V¹³ and the second-order rate parameters for reactions with inorganic reductants are in the range of 10^6 – 10^{10} M⁻¹ s⁻¹.¹⁴

When N₂O-saturated solutions of U(VI), 10^{-3} M, pH 5,

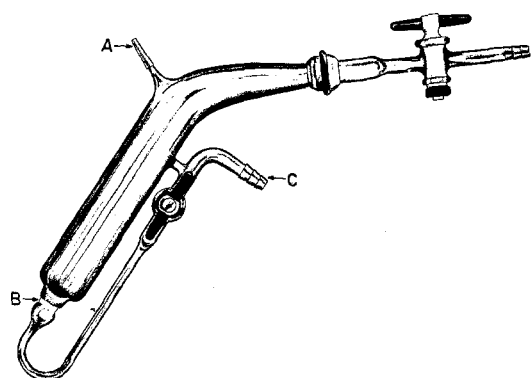


Figure 1. Cell filling device.

were irradiated with 3- μ s pulses of electrons there was no observable change in the spectrum of the solution over a 200- μ s time interval using the streak camera. After several seconds the streak camera recorded a new spectrum (Figure 2) that was stable over a period of hours. The rate at which this new spectrum develops and the time invariance effectively preclude the identification of this spectrum as characteristic of a species produced by the direct reaction of U(VI) and OH.

The identification of this spectrum as that of a U(VI)-H₂O₂ complex is based on the following evidence:

(A) A spectrum identical with the one recorded by the streak camera was obtained from a solution of 10⁻⁴ M U(VI), 10⁻³ M H₂O₂, at a pH 5.3, with broad maxima at 360 nm (ϵ 820 M⁻¹ cm⁻¹), 325 nm (ϵ 770 M⁻¹ cm⁻¹), and 240 nm (ϵ 1.9 \times 10³ M⁻¹ cm⁻¹).

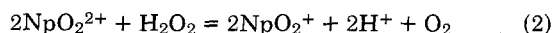
(B) A ratio of [U(VI)]/[H₂O₂] = 1.05 \pm 0.05 was determined from spectrophotometric titrations of U(VI) with H₂O₂ at pH of 5.3.

Gurevich et al.¹⁵ have previously described a one-to-one complex of UO₂²⁺ and H₂O₂ by titration of a solution of UO₂(NO₃)₂ with aqueous H₂O₂. The "difference spectrum" obtained in this investigation clearly delineates three peaks as noted in the text.

This U(VI)-H₂O₂ complex is formed at a rate that may be conveniently studied using the stopped flow technique. Table I summarizes our results using this method as well as that of the pulse radiolysis technique.

The spectrum and dynamic stability of Np(VII) in acidic media have been established.¹⁶ When N₂O-saturated solutions, 1.0 \times 10⁻³ M Np(VI), pH 5.0, were irradiated with 3- μ s pulses of electrons there was no spectrophotometric evidence for the formation of Np(VII). In fact, irradiation with 15 pulses (3 μ s wide and 18 krad per pulse) resulted in quantitative reduction to Np(V) as determined by absorbance measurements at 980 nm. This is very probably the result of the reduction of Np(VI) by H₂O₂, where the H₂O₂ is formed by the radiation.

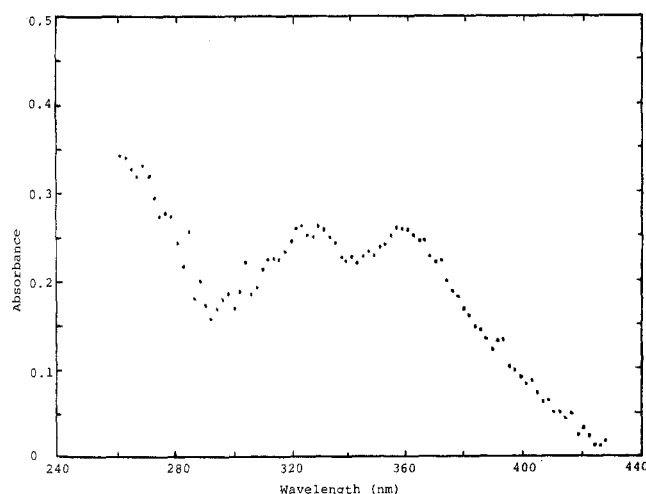
Evidence consistent with this interpretation is provided by the following comparison. For the reaction



the rate of appearance of NpO₂⁺ is

$$d[\text{NpO}_2^+]/dt = k[\text{NpO}_2^{2+}][\text{H}_2\text{O}_2] \quad (3)$$

this reaction was studied by following the appearance of the absorption at 980 nm due to Np(V) at 25 °C. In a solution containing 1.0 \times 10⁻³ M Np(VI), \sim 2 \times 10⁻⁵ M H₂O₂

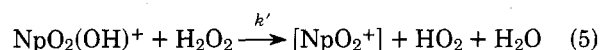
Figure 2. Spectrum of the U(VI)-H₂O₂ complex at pH 5.3.

(generated by pulse radiolysis) at a pH of 5.0 and an ionic strength of 0.005, the rate of formation of Np(V) followed a second-order rate law with a rate constant of (5.89 \pm 0.05) \times 10⁵ M⁻¹ s⁻¹.

In a previous kinetic study of reaction 2¹⁷ by conventional spectrophotometric techniques the empirical form of the rate law that was determined is

$$(d[\text{NpO}_2^+]/dt)_0 = \frac{k'[\text{NpO}_2^{2+}]_0[\text{H}_2\text{O}_2]_0[\text{H}^+]_0^{-1}}{1 + b[\text{NpO}_2^+]_0[\text{NpO}_2^{2+}]_0^{-1}} \quad (4)$$

A plausible mechanism has been developed by Newton² that is consistent with eq (4). From this mechanism the value calculated for the rate constant $k' \simeq$ 10⁶ M⁻¹ s⁻¹ for the reaction



is in good agreement with the value determined in this pulse radiolysis study.

In contrast to the situation in neutral N₂O-saturated solutions of Np(VI), pulsing solutions of 1 mM NpO₂(ClO₄)₂ in 3, 0.5, and 0.1 M NaOH resulted in producing a solution which exhibited an absorption spectrum corresponding to that reported for Np(VII).¹⁸ This is in agreement with the results of Pikaev, who reported the oxidation of Np(VI) to Np(VII) induced by Co γ radiation, in highly alkaline solution (1.0 M and greater).¹⁹ Since the structure or redox potential of Np(VI) in these highly alkaline solutions is not well established, one cannot draw any conclusions as to the mechanism of this process at present. Further work in this area should prove to be fruitful.

B. Reactions of e_{aq}^- with An(VI) Ions. As noted earlier, the integrated form of the first-order rate law was found adequate to correlate the absorbance and time data for each separate experiment. The precision attained in duplicate determinations is demonstrated by the following: 24 °C, ionic strength = 0.001, pH 5.6, Pu(VI) = 1.20 \times 10⁻⁵ M, 4 ns pulse, the values calculated for 10⁻⁶ k (s⁻¹) are 0.906 \pm 0.007 and 1.006 \pm 0.003.

It is apparent that the major uncertainties associated with these rate parameters are other than those based on internal consistency.

The pseudo-first-order rate constant is a linear function of the An(VI) concentration

TABLE I: Rate Constants for the U(VI)-H₂O₂ Complex at 25 °C

U(VI) concn, M	H ₂ O ₂ concn, M	pH	k, M ⁻¹ s ⁻¹
5 × 10 ⁻⁵ to 5 × 10 ⁻⁴	5 × 10 ⁻⁴ to 1.0 × 10 ⁻³	5.2	(5.86 ± 0.05) × 10 ³ ^b
2.5 × 10 ⁻⁴	2.5 × 10 ⁻³	5.2	(1.31 ± 0.16) × 10 ⁴ ^c
1.0 × 10 ⁻⁴	2 × 10 ⁻⁵ ^a	5.2	1.39 × 10 ⁴ ^d

^a Produced by pulse radiolysis. ^b Twenty-six independent observations using stopped flow. ^c Ten independent observations using stopped flow. ^d Pulse radiolysis.

TABLE II: Rate Constants for e_{aq}⁻ + An^a

	pH	[M](× 10 ⁻⁴)	k(10 ¹⁰ M ⁻¹ s ⁻¹)	E ⁰ , V ^b
Pu(VI)	5.6	0.12–1.00	6.44 ± 0.37	–0.916
Pu(VI)	6.1	0.09–1.08	5.76 ± 0.27	
Np(VI)	5.3	0.20–2.00	6.32 ± 0.05	–1.137
Np(VI)	5.8	0.202–3.03	5.43 ± 0.18	
Np(V)	5.3	0.21–2.10	1.97 ± 0.04	–0.739
Np(V)	6.1	0.208–1.08	2.13 ± 0.03	
U(VI)	5.3	0.50–10.0	1.73 ± 0.01	–0.063
U(VI)	6.8	0.10–1.00	1.25 ± 0.02	

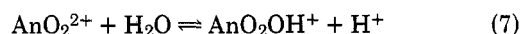
^a 24 °C, I = 1 × 10⁻³. ^b For the reactions, AnO₂²⁺ + H⁺ = AnO₂²⁺ + 0.5H₂.²

$$k = a + b[\text{An(VI)}] \quad (6)$$

The results of the least-squares adjustment of *k* vs. An(VI) concentration data in terms of eq 6 are presented in Table II, where *b* is identified as the second-order rate parameter for the reaction of e_{aq}⁻ with An(VI).

The rate data in Table II demonstrate that for the reduction of Np(V) there is no evidence of a hydrogen-ion dependent path. There is a small increase in the values of the apparent rate constants with increasing hydrogen ion concentration²⁰ for An(VI) ions although the difference in the case of Pu(VI) is not statistically significant at the 2σ level. In addition there is no apparent correlation between the rate parameter and the oxidation potentials of the reductants.

The An(VI) ions in aqueous noncomplexing media are colinear molecules (O–An²⁺–O) with six water molecules in the equatorial plane. The An(V) ions have a similar structure with only small differences in the O–An bond lengths. In the solutions investigated in this paper, it is probable that the equilibrium



is of some importance. The value of the equilibrium quotient for eq 7 is estimated²¹ to be in the range of 10⁻⁵ to 10⁻⁶. For Np(V) the value of the corresponding equilibrium quotient is probably of the same order of magnitude. There is, therefore, no drastic reorganization of the coordination spheres necessary in the transformation of An(VI)–An(V) ions.

The Np(IV) has eight molecules of water in the first coordination sphere. In the dilute acid region where these investigations were conducted it is highly probable that the ion is hydrolyzed to an appreciable extent.²² A priori, it would seem that the change in the primary coordination spheres upon going from Np(V) to Np(IV) would provide a significant reaction barrier contrary to the demonstrated results.

The lack of correlation between the oxidation potential of the An(V)–An(VI) ions and/or structural changes with the apparent rate constants can be rationalized on the basis

that all the reactions are diffusion controlled. A more detailed insight into the mechanism is given by the qualitative description that some reaction of e_{aq}⁻ may proceed by a tunneling mechanism,²³ i.e., the transmission coefficient of the electron through the barrier is completely determined by the overlap of the relevant wave functions for the quantum subsystem of the electron.

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