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Pulse-Radiolysis Studies of Americium Ions in Aqueous Perchlorate Media[1]

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The streak-camera technique was used to characterize the transient absorption spectra of Am(II) and Am(IV) in perchlorate media: λ_{max}(Am(II)) 312 nm, λ_{max}(Am(IV)) 320–340 nm. Second-order rate constants ($M^{-1}\ s^{-1}$) were measured for the following reactions: Am(III) + e_{aq}^-, $(1.55 \pm 0.04) \times 10^8$; Am(III) + OH, $(4.1 \pm 0.4) \times 10^8$; Am(IV) + Am(IV), $(5 \pm 1) \times 10^6$; Am(V) + e_{aq}^-, $(3.18 \pm 0.08) \times 10^{10}$, pH 6.0; Am(VI) + e_{aq}^-, $(3.9 \pm 0.9) \times 10^{10}$, pH 6.0.

Introduction

The chemistry of Am ions in aqueous perchloric acid media has been concerned with the 3+, 5+, and 6+ oxidation states where the species are the hydrated cations Am^{3+}, AmO_2^+, and AmO_2^{2+}. Evidence for the existence of the 4+ ions has been previously obtained only in strongly complexing media such as concentrated fluoride or phosphate solutions and Am^{2+} was identified in CaF_2 crystals.[2] The characterization of the oxidation–reduction patterns of Am(III), -(V), and -(VI) is hampered by the intense α-particle self-irradiation that occurs in aqueous solutions. This explains, in part, the fact that quantitative data are available for only a limited number of oxidation–reduction reactions of americium ions.[3]

The primary considerations that motivated the present investigation were to explore the dynamic redox reactivity patterns of Am(III), -(V), and -(VI) with the reductant e_{aq}^- and the oxidizing radical OH when the latter are generated by pulse-radiolysis techniques and to characterize the Am(II) and Am(IV) ions produced in perchlorate media.[4]

Experimental Section

The lithium hydroxide, perchloric acid, and *tert*-butyl alcohol stock solutions were prepared from analytical grade reagents and standardized by conventional techniques. The ^{243}Am was purified by a solvent extraction procedure[5] followed by precipitation of the americium(III) hydroxide which was washed, fumed to dryness with HNO_3–$HClO_4$ several times, and finally dissolved in 0.1 M $HClO_4$. Stock solutions of Am(III) were freshly prepared immediately prior to the pulse-radiolysis studies (after hydroxide precipitation and washing with triply distilled water until the supernatant was at a pH 7–8) and standardized spectrophotometrically at 503 nm (ϵ 450 ± 4). Am(V) and Am(VI) solutions were also prepared immediately prior to the pulse-radiolysis studies from the solid carbonate and carbonate solutions,[6] respectively, and standardized spectrophotometrically at 718 nm ($\epsilon_{Am(V)}$ 66 ± 1) L mol^{-1} cm^{-1} and 996 nm ($\epsilon_{Am(VI)}$ 107 ± 2) L mol^{-1} cm^{-1}.

The gas-saturating and cell-filling device has been previously described.[7] Spectra of the transient species produced by single electron pulses were obtained using a streak camera–TV scanning method described in a previous publication.[8] The irradiation procedure and dose measurements have been described.[9] The rate data were obtained by photomultiplier techniques where the output was stored in a Biomation Transient Recorder which in turn was interfaced with a Xerox Sigma 5 computer.

The functional forms used were the standard integrated expressions for first- or second-order processes. The statistical adjustment[10] of the unweighted data in these forms used nonlinear least-squares programs (typically 300 data points per determination) with the three adjustable parameters A_0, A_∞, and k. A_0 and A_∞ are the absorptivities at time zero and at completion of the reaction, respectively, and k is either the apparent first-order rate constant or the second-order rate parameter/(molar absorptivity × path length). In all cases reported 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.

Table I. Apparent First-Order Rate Constants for the Reactions of e_{aq}^- and OH with Am(III) in Aqueous Perchlorate Media[a]

Eq 2 (e_{aq}^-)[b]		Eq 4 (OH)[c]	
[Am(III)], mM	$10^{-5}k_1'$ s^{-1}	[Am(III)], mM	$10^{-5}k_2'$ s^{-1}
7.90×10^{-2}	1.32 ± 0.02	0.733	4.88 ± 0.07
7.90×10^{-2}	1.32 ± 0.01	0.733	4.17 ± 0.04
0.158	1.35 ± 0.02	1.42	9.52 ± 0.09
0.158	1.43 ± 0.02	2.86	13.4 ± 0.1
0.316	1.65 ± 0.02	2.86	13.3 ± 0.1
0.316	1.70 ± 0.02	5.69	24.8 ± 0.3
0.632	2.18 ± 0.02	8.22	31.5 ± 0.5
0.632	2.10 ± 0.02		
1.24	3.10 ± 0.02		
1.24	3.04 ± 0.02		

[a] $T = 23 \pm 2$ °C, $\mu = 0.11$ M ($LiClO_4$). Uncertainties are standard deviations based on external consistency. [b] λ 650 nm, pH 5.8, He-saturated solutions 0.1 M in *tert*-butyl alcohol. [c] λ 320 nm, pH 5.1, N_2O-saturated solutions. Initial [OH] ≈ 50 μM.

Results and Discussion

Spectra of Am(II) and Am(IV). The streak-camera method was used to observe the transient absorption spectrum that is identified as characteristic of the aquo ion Am(II). Am(II) was prepared by the reaction of Am(III) with e_{aq}^- and the spectrum is presented in Figure 1. The maximum at 312 nm is in a region that was not accessible to the investigators[11] who reported the spectrum of Am(II) in a CaF_2 crystal, a fact which precludes comparison between the solution and solid-state observations.

The transient absorption spectra identified as characteristic of Am(IV) were observed for the products of the reactions e_{aq}^- + Am(V) and OH + Am(III). The spectrum presented in Figure 2 for the latter reaction shows one broad band with a maximum between 320 and 340 nm.[12] The spectrum of the transient formed from the former reaction is similar to that displayed in Figure 2. The previous spectrophotometric studies of AmF_4 (solid) indicated a strong absorptivity below 350 nm[13] but the near-UV region was not accessible for detailed examination in that study.

Dynamic Studies. Reactions of Am(III). The data presented in Table I summarize the results obtained in the kinetic studies of the reactions of Am(III) with the hydrated electron and

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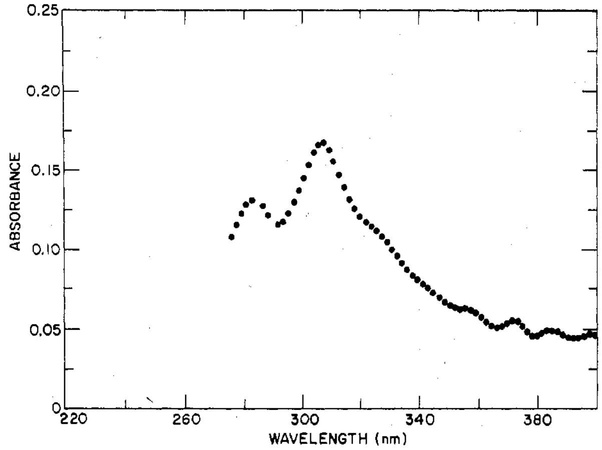

Figure 1. Spectrum of Am(II) produced by the reaction of e_{aq}^- with Am(III) (10^{-2} M, pH 5.3, 0.1 M *tert*-butyl alcohol, He saturated) obtained 50 μs after the electron pulse.

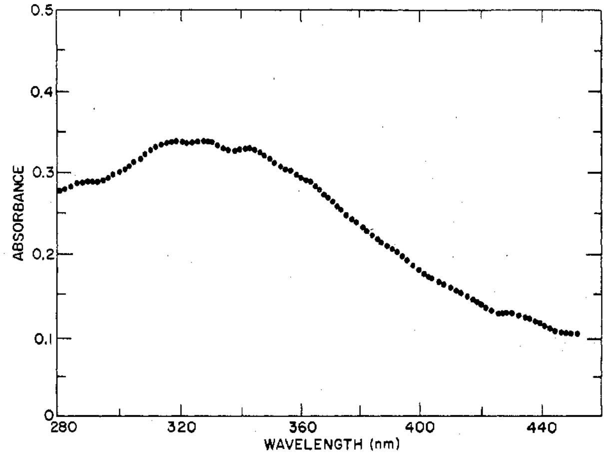

Figure 2. Spectrum of Am(IV) produced by the reaction of OH with Am(III) (10^{-3} M, pH 5.8, solution saturated with N_2O) obtained 100 μs after the electron pulse.

the OH radical. The pseudo-first-order rate constants were determined by monitoring the disappearance of the hydrated electron in the former system and the appearance of Am(IV) in the latter, i.e.

$$e_{aq}^- + \text{Am(III)} \xrightarrow{k_1} \text{Am(II)} \quad (1)$$

$$-\text{d} \ln [e_{aq}^-]/\text{d}t = k_1[\text{Am(III)}] \quad (2)$$

$$\text{OH} + \text{Am(III)} \xrightarrow{k_2} \text{Am(IV)} + \text{OH}^- \quad (3)$$

$$\text{d}[\text{Am(IV)}]/\text{d}t = k_2[\text{OH}][\text{Am(III)}] \quad (4)$$

The variation of k_1' (pseudo-first-order rate constant) with change in Am(III) concentration was correlated by the expression

$$k_1' = a + k_1[\text{Am(III)}] \quad (5)$$

where k_1 is the second-order rate constant. The least-squares value calculated for the parameters are $a = (1.15 \pm 0.02) \times 10^5\ \text{s}^{-1}$ and $k_1 = (1.55 \pm 0.04) \times 10^8\ \text{M}^{-1}\ \text{s}^{-1}$. There are several points to be noted relevant to this result.

The product Am(II) reacts rapidly with the substrate. In a series of studies where the disappearance of Am(II) was monitored at 312 nm (pH 5.2, He-saturated solution 0.1 M in *tert*-butyl alcohol) the rate was found to be complex as well as dependent upon both the intensity of the radiation and the initial Am(III) concentration. The reaction $e_{aq}^- + \text{Am(III)} \rightarrow \text{Am(II)}$ is slow enough that reactions such as $e_{aq}^- + e_{aq}^- \rightarrow H_2 + 2OH^-$, $e_{aq}^- + H \rightarrow H_2 + OH^-$, or $e_{aq}^- + OH \rightarrow OH^-$ can cause unnecessary complications. Under the experimental constraints that minimize such extraneous reactions, i.e., high concentrations of Am(III) and low-dose rates, the disappearance of Am(II) is adequately described in terms of a first-order process. For example, in solutions 26 mM in Am(III) irradiated with pulses of 20 and 10 ns the respective values calculated for the first-order rate parameters (s^{-1}) were $(9.7 \pm 0.3) \times 10^4$ and $(9.8 \pm 0.3) \times 10^4$. This value may well describe the oxidation of Am(II) by reaction with water.

It is of interest to compare the value of the second-order rate parameter, $k_1 = (1.55 \pm 0.04) \times 10^8\ \text{M}^{-1}\ \text{s}^{-1}$, obtained for the reaction between e_{aq}^- and Am(III) with that reported for Sm(III) as the oxidant, $k = (1.96 \pm 0.10) \times 10^{10}\ \text{M}^{-1}\ \text{s}^{-1}$. The properties of cations that have been considered to be of importance in reactions with the hydrated electron are charge, ionic radii (0.99 Å for Am(III), 0.96 Å for Sm(III)), and formal potential (1.5 V for Am(III)/Am(II), 1.56 V for Sm(III)/Sm(II)).[14] It is apparent that these factors do not account for the observed difference in the rate parameters.

A rationalization of the observations is based on the marked differences between the 4f orbitals of Sm(III) and the 5f of Am(III). One feature salient to the present discussion is that the latter have greater spatial extension, and as a consequence, overlap of 5f orbitals with ligands in the primary coordination sphere can provide a 5f covalent contribution to ionic bonding. This would then be reflected in a large rearrangement free energy of the formation of the activated complex with Am(III) compared to the case of Sm(III) with concomitant decrease in the rate of reduction.

The variation of k_2' (pseudo-first-order rate constant for the reaction of OH with Am(III)) with change in Am(III) concentration was also correlated by a linear expression $k_2' = a' + k_2[\text{Am(III)}]$. The least-squares parameters calculated from the data in Table I are $a' = (1.6 \pm 0.6) \times 10^5\ \text{s}^{-1}$ and k_2 (second-order rate constant) $= (4.1 \pm 0.4) \times 10^8\ \text{M}^{-1}\ \text{s}^{-1}$.

The following observations demonstrate the dynamic stability of Am(IV). At pH 5.2, in 0.11 M $LiClO_4$ and N_2O-saturated solution, and over the range of initial Am(III) concentrations, 1.03–8.22 mM, the average value obtained for $2k_3/\epsilon l$ is $(2.7 \pm 0.5) \times 10^3\ \text{s}^{-1}$ (12 independent determinations). All the experiments were carried out in a cell of 5-cm path length and a value of $750 \pm 75\ \text{M}^{-1}\ \text{cm}^{-1}$ has been estimated for the molar extinction coefficient of Am(IV) at 320 nm using the following procedure. The dose absorbed by the solution was measured as described[9] using *G*(OH) (number of OH radicals produced per 100 eV absorbed) of 2.7. Assuming that the concentration of Am(IV) was equal to the initial yield of OH radicals, the initial yield of Am(IV) was calculated. From the initial absorbance of the solution at 320 nm, the concentration of Am(IV), and the path length, the value of ϵ(Am(IV)) was calculated. From these data the average value calculated for the apparent second-order rate constant of the reaction

$$\text{Am(IV)} + \text{Am(IV)} \xrightarrow{2k_3} \text{Am(III)} + \text{Am(V)} \quad (6)$$

is $k_3 = (5 \pm 1) \times 10^6\ \text{M}^{-1}\ \text{s}^{-1}$.

The tetravalent actinide ions show decreasing dynamic stability toward disproportionation in going from U(IV) to Pu(IV), a trend extended by the present results. Quantitative comparison of the dynamics of the adjacent Pu(IV) disproportionation reaction[3] are not feasible because of differences in the empirical forms of the rate laws. In a qualitative sense the differences in the kinetic stabilities of Pu(IV) and Am(IV) toward disproportionation are reflected in the fact that the former is of importance in characterizing the ionic composition of Pu solutions [where *all* four valence (3+, 4+, 5+, 6+) states can coexist] while the latter is only of significance as transients

Table II. First-Order Rate Constants for the Reaction of e_{aq}^- with Am(VI) and Am(V)[a]

10^5[Am(VI)], M	$10^{-6}k$, s^{-1}	10^5[Am(V)], M	$10^{-6}k$, s^{-1}
pH 6.0		pH 6.0	
1.20	1.03 ± 0.23	1.24	0.495 ± 0.002
1.20	0.96 ± 0.18	1.24	0.507 ± 0.002
4.80	1.62 ± 0.15	2.48	0.893 ± 0.009
7.20	2.23 ± 0.14	4.96	1.72 ± 0.06
9.60	3.04 ± 0.15	9.92	3.10 ± 0.03
12.0	3.22 ± 0.21	9.92	3.16 ± 0.02
		19.8	6.28 ± 0.06
		19.8	6.65 ± 0.07
pH 5.3		pH 5.2	
1.04	0.60 ± 0.02	1.40	0.657 ± 0.005
1.04	0.60 ± 0.02	1.40	0.688 ± 0.005
2.08	0.95 ± 0.02	2.80	0.919 ± 0.012
4.16	1.61 ± 0.05	2.80	0.974 ± 0.006
6.24	2.26 ± 0.06	5.64	1.86 ± 0.07
8.33	2.86 ± 0.09	11.3	3.40 ± 0.03
		28.0	7.61 ± 0.13
		28.0	7.79 ± 0.12

[a] $T = 23 \pm 2$ °C, all solutions 0.1 M in *tert*-butyl alcohol, $\mu = 0.11$ M ($LiClO_4$).

in the oxidation of Am(III) or reduction of Am(V).[15]

Reactions of Am(VI) and Am(V). The rate of the reactions of e_{aq}^- with Am(VI) and Am(V) were obtained by monitoring the decrease in absorptivity of the hydrated electron at 650 nm in He-saturated solutions. In each experiment the integrated form of the first-order rate law provided an adequate description of the absorbance–time data.

In Table II the variation of the rate parameter with change in Am(VI) and Am(V) concentrations is tabulated. From these data, the values calculated for the apparent second-order rate constants (via a linear least-squares adjustment) are as follows: Am(VI), $(3.9 \pm 0.9) \times 10^{10}$ at pH 6.0 and $(3.11 \pm 0.07) \times 10^{10}$ at pH 5.3; Am(V), $(3.18 \pm 0.08) \times 10^{10}$ at pH 6.0 and $(2.8 \pm 0.1) \times 10^{10}$ at pH 5.2.

A comparison of these results with those previously reported for the reactions of An(VI) ions with e_{aq}^-[7] shows no readily discernible correlation of the apparent rate constants with formal reduction potentials of the An(VI)/An(V) couples which vary from 0.06 V for U to 1.6 V for Am. In addition, there is no change in the rate parameters that can be rationalized in terms of a variation in electron affinity that results from spin pairing of the 5f electrons. The free energy of rearrangement and changes in the O–An and H_2O–An bonds necessary to produce the appropriate coordination configurations of the dioxo(V) ions may vary across the series, but such changes are not reflected in the values of the apparent rate constants. The magnitude of these rates, when considered in conjunction with the above comments, suggests that the processes are controlled by reactant diffusion.

The result that the rates of the reactions between e_{aq}^- and Am(V) or Am(VI) are essentially the same is phenomenologically consistent with the previous results noted for Np(V) and Np(VI). Any interpretation of these results, however, should take account of the marked differences in the primary coordination spheres of the O–An–O reactant and the hydrated An(IV) product. The following discussion represents an attempt to develop a reasonable reaction scheme.

The rate of reaction between e_{aq}^- and Am(V) is near the diffusion-controlled limit. However, the criteria presented by Marcus[16] for an electron-transfer process to occur via a nonadiabatic mechanism are satisfied. A consequence of a reaction that proceeds by the latter mechanism is the production of an Am(IV) species in an excited electronic state[17] with an inappropriate coordination configuration. This species then rearranges to the electronic and molecular configuration appropriate to the more stable Am(IV) product. Supporting evidence for the interpretation advanced will require additional types of experiments such as pulse-radiolysis conductivity and resonance-Raman investigations. We are presently initiating the development of such experimental techniques.

Registry No. Am^{2+}, 16399-95-4; Am^{3+}, 22541-46-4; Am^{4+}, 22541-71-5; AmO_2^+, 22878-02-0; AmO_2^{2+}, 12323-66-9; OH, 3352-57-6.

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