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Articles

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Reactions of Uranium(V), Neptunium(V), and Plutonium(V) with the Carbonate Radical Ion[†]

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The rates for the reactions of the tris(carbonato)actinide(VI) ions with e_{aq}^- have been determined to be (1.18 ± 0.6) × 10^{10}, (2.34 ± 0.12) × 10^{10}, and (2.28 ± 0.11) × 10^{10} M^{-1} s^{-1}, respectively, for U, Np, and Pu. The values determined for the rates of the reactions of CO_3^- + An(V) (An = actinide) are 4.88 × 10^8, 1.52 × 10^7, and 2.73 × 10^7 M^{-1} s^{-1}, respectively, for U, Np, and Pu. The results of these latter reactions are interpreted with use of the Marcus cross relations with values for the An(IV)/An(V) couples determined by using cyclic voltammetry.

Introduction

Raman scattering observations have been reported consistent with the concept that the linear dioxo cations UO_2^{2+}, NpO_2^{2+}, and PuO_2^{2+} retain the O–An^{2+}–O (An = actinide) structure in basic carbonate media.[1] In such carbonate solutions the predominant actinide species is the tris(carbonato) species, $[AnO_2(CO_3)_3]^{4-}$, where the carbonate ions are bidentate. The linear O–An^{n+}–O configuration is retained when there is a one-electron reduction of these ions.[2]

The formal potentials[3a,b] for the reduction of the $[AnO_2(CO_3)_3]^{4-}$ to $[AnO_2(CO_3)_3]^{5-}$ ions in 1 M Na_2CO_3 solutions are respectively −0.538, +0.445, and +0.334 V vs. NHE for An = U, Np, and Pu. On the basis of kinetic considerations, Henglein[4a] estimated a value of $E° = 1.5$ V for the reaction

$$CO_3^{-}\cdot(aq) + e_{aq}^- \rightarrow CO_3^{2-}(aq) \qquad (1)$$

It is evident that the carbonate radical ion $CO_3^{-}\cdot(aq)$ has the potential to oxidize any of the $[AnO_2(CO_3)_3]^{5-}$ ions. We have recently reported[4b] that the OH radical produced by pulse radiolysis with a higher oxidation potential cannot oxidize An(VI) to An(VII). This eliminates the possibility that such an oxidation can occur via the $CO_3^{-}\cdot$ radical ion. In the present paper we present the results obtained in a pulse radiolysis study of carbonate solutions of these actinides in which we oxidize An(V) in carbonate solution produced in situ through the reduction of An(VI) by the hydrated electron. Among the considerations that prompted this study was the attempt to develop a phenomenological description of the redox patterns of actinide ions in aqueous carbonate media. The results are discussed in terms of the reduced Marcus[5] equations.

Experimental Section

The pulse radiolysis apparatus utilized the ANL Linac. A 14-MeV electron pulse from 4 to 40 ns duration was directed into a 2-cm irradiation cell. The apparatus, data acquisition, and analysis techniques have been previously described.[6,7]

Cyclic voltammograms were obtained with a potentiostat/galvanostat previously described[3a] with platinum-inlay electrodes and a platinum-wire counterelectrode. The reference electrode was saturated sodium chloride calomel (SSCE). The potentials for Np and Pu were measured with use of this configuration. The quasi-reversible nature of the charge-transfer process manifests itself in the increase of peak potential separation as the scan rate is increased. This ratio of unity for anodic to cathodic peak currents (i_{pa}) and the lack of dependence on the scan rate (ν) of the ratio i_{pa}/ν is evidence for the reversible nature of these potentials.

Table I. Kinetic and Thermodynamic Parameters for CO_3^- and $[An(CO_3)_3]^{5-}$ Complexes

reactant	$k(CO_3^- +$ reactant), M^{-1} s^{-1} [a]	$E°$, V (vs. NHE)	k^{ht}, cm/s
CO_3^-	0.9 × 10^7	1.5	
$[UO_2(CO_3)_3]^{5-}$	4.88 × 10^8	−0.538	8.9 × 10^{-5}
$[NpO_2(CO_3)_3]^{5-}$	1.52 × 10^7	0.445	2.7 × 10^{-3}
$[PuO_2(CO_3)_3]^{5-}$	2.73 × 10^7	0.334	6.7 × 10^{-4}

[a] Standard deviations of rate parameters ±5%.

Table II. Rate Parameters for the Reaction of the Hydrated Electron with $[AnO_2(CO_3)_3]^{4-}$

actinide	10^4[An(VI)], M	$[Na_2CO_3]$, M	$10^{-10}k(e_{aq}^- + [AnO_2(CO_3)_3]^{4-})$,[a] M^{-1} s^{-1}
U(VI)	2.0–8.0	0.1	1.18 ± 0.01[b]
Np(VI)	0.2–8.0	0.05	2.34 ± 0.12[c]
Pu(VI)	0.2–8.0	0.05	2.28 ± 0.11[c]

[a] Error limits are standard deviations based on external consistency. [b] Reference 16. [c] This work; other values reported in ref 17 are 1.9 × 10^{10} M^{-1} s^{-1} for Np(VI) and 2.3 × 10^{10} M^{-1} s^{-1} for Pu(VI) in 0.1 M Na_2CO_3 solutions.

It is conceivable that errors in the redox potential determined by this method could be introduced by double-layer effects on the platinum electrode. However, the behavior of these species in carbonate media

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shows no evidence for a pronounced ionic strength or specific ion[4c] effect such as would be expected if there were large double-layer effects that could possibly affect the values of the formal potentials measured. For the standard redox potential of uranium in carbonate media, we used the value reported in ref 3b, obtained by a chronopotentiometric method. The rate constants for heterogeneous electron transfer (k^{ht}) listed in Table I were calculated on the basis of the rate of change of the peak potential separation as a function of scan rate determined as described, with use of the method of Nicholson.[3c]

Na_2CO_3 solutions were prepared with use of AR Na_2CO_3 and triple-distilled water. Standardized stock solutions of $UO_2(ClO_4)_2$ were combined with the carbonate solution to produce the $UO_2(CO_3)_3^{4-}$ stock solutions. $[^{237}NpO_2(CO_3)_3]^{4-}$ and $[^{242}PuO_2(CO_3)_3]^{4-}$ stock solutions were prepared in a similar manner. The latter two perchlorate solutions were prepared and standardized by previously described procedures.[8] The solutions were helium saturated.

Results

Reactions of e_{aq}^- with $AnO_2(CO_3)_3^{4-}$. The disappearance of hydrated electrons with initial concentrations of 1–2 μM was followed at 600 nm. Relative to the concentrations of the actinyl ions (12–200 μM) the e_{aq} concentration was sufficiently low to produce good pseudo-first-order rates. The measured first-order rate parameter was a linear function of the An(VI) concentration. Values for the second-order rate parameter are calculated from this function and listed in Table II.

Reactions of CO_3^- with An(V) Ions. With a solution of An(VI) ions in 0.05 M Na_2CO_3 (saturated with He) the sequence of reactions given by eq 2–7 are assumed to occur upon irradiation.

$$H_2O \rightsquigarrow e_{aq}^-, OH, H, H_2O_2, H_2 \tag{2}$$

$$An(VI) + e_{aq}^- \rightarrow An(V) \tag{3}$$

$$An(VI) + H \rightarrow An(V) + H^+ \tag{4}$$

$$CO_3^{2-} + OH \rightarrow CO_3^- + OH^- \tag{5}$$

$$CO_3^- + An(V) \rightarrow CO_3^{2-} + An(VI) \tag{6}$$

$$CO_3^- + CO_3^- \rightarrow CO_2 + CO_4^{2-} \tag{7}$$

If the solution is saturated with N_2O, e_{aq}[9] will react principally by reaction 8, restricting any possible production of An(V) to reaction 4. Assuming that no An(V) is produced

$$\begin{gathered} e_{aq}^- + N_2O + H_2O \rightarrow OH + N_2 + OH^- \\ k_8 = 9.1 \times 10^9\ M^{-1}\ s^{-1} \end{gathered} \tag{8}$$

via reaction 4, the disappearance of $CO_3^-\cdot$ would occur exclusively by reaction 7. Using $\epsilon_{CO_3^-\cdot}^{600} = 1830\ M^{-1}\ cm^{-1}$, we have obtained a rate constant, $2k_7 = 1.8 \times 10^7\ M^{-1}\ s^{-1}$, which corresponds well with previous values,[10] indicating that reaction 4 can be neglected. This is consistent with previous observations.[4,11]

The results are presented in Table II. Included in this table are values measured for the formal reduction potentials of the An(VI)/An(V) couples in the carbonate media as well as the values for the heterogeneous exchange reactions derived from the electrochemical measurements and values calculated by following the method described in ref 3c.

Discussion

Henglein has pointed out[4a] that the carbonate radical ion can react either by transfer of O^- from $CO_3^-\cdot$ or the transfer of e to $CO_3^-\cdot$. Since the substrates that are oxidized by $CO_3^-\cdot$ in this study retain their linear O–An–O configuration and their coordination spheres are saturated with three bidentate CO_3^{2-} ligands, the preferred mechanism would most probably be that of electron transfer. Indeed, a plot of log $k(\mathrm{An(V)} + CO_3^-\cdot)$ vs. $E°$ is linear (Figure 1).

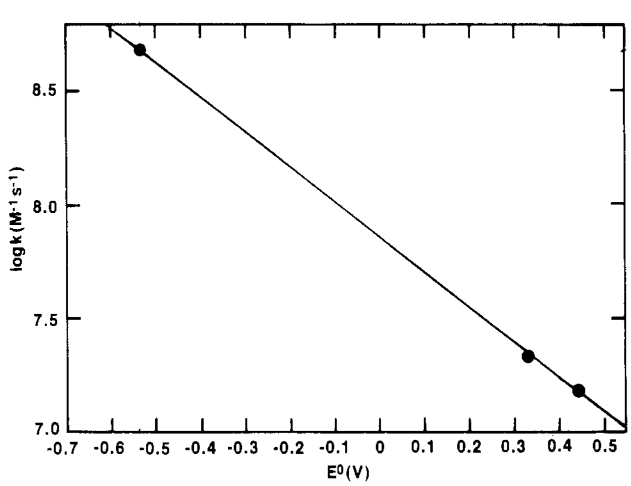

Figure 1. Rate constant of the reaction of An(V) with $CO_3^-\cdot$ vs. the redox potential of the actinide ions.

Table III. Calculated and Observed Values for k_{12}

An	log k_{12}(calcd)	log k_{12}(obsd)
U	9.75	8.69
Np	7.05	7.18
Pu	7.10	7.44

Such linearity prompted an attempt to analyze the results in terms of the Marcus cross relations[5] for outer-sphere electron-transfer reactions. In this formalism

$$k_{12} = (k_{11}k_{22}k_{12}f_{12})^{1/2} \tag{9}$$

where $\log f_{12} = (\log K_{12})^2/[4 \log (k_{11}k_{22}/Z_{\mathrm{chm}}^2)]$. k_{12} is the rate parameter for reaction 6, and K_{12} is the value of the equilibrium constant calculated from the potential values. k_{22} and k_{11} are the rate parameters for the respective self-exchange reactions

$$^*An(V) + An(VI) \rightleftarrows {}^*An(VI) + An(V) \tag{10}$$

$$^*CO_3^-\cdot + CO_3^{2-} \rightleftarrows {}^*CO_3^{2-} + CO_3^-\cdot \tag{11}$$

The value for the exchange reactions of the actinide ions can be calculated from the values of the heterogeneous exchange reactions via

$$k^{\mathrm{ht}}/Z_{\mathrm{el}} = (k^{\mathrm{hm}}/Z_{\mathrm{chm}})^{1/2} \tag{12}$$

where Z_{el}, the collision frequency for the heterogeneous electrode reaction, equals 10^4 cm s^{-1} and Z_{chm}, the collision frequency for the homogeneous chemical reaction, equals 10^{11} M^{-1} s^{-1}. The values for the heterogeneous exchange rates for reaction 10 listed in Table I were determined as described; that for uranium was calculated from the data reported in ref 3b. The value for exchange reaction 11 is not known.

However, we found that varying the values of k_{11} from 1 to 10^4 had very little effect on the value of k_{12} calculated from eq 9. The values of k_{12} in Table III were calculated with use of a value of $k_{11} = 100\ M^{-1}\ s^{-1}$.[12]

The fairly good agreement shown in this table between our experimental and calculated values as compared to cases in which the Marcus cross relation fails[13] may reflect the fact that we are studying a homologous series of actinides with one type of ligand, the carbonato group, and the agreement in-

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dicates that in this case the reaction goes by an outer-sphere mechanism. The largest deviation is in the case of uranium. This may be due to the uncertainty in the value of the redox potential or the value of k^{ht} used.

Reasons for the variation between observed and calculated rate parameters, in reactions characterized by such $\Delta G°$ values as exhibited by these compounds, have been discussed by Marcus and Sutin[14] and extensively documented by Weaver and Yee.[15] Additional insight into the mechanism of these reactions requires additional studies using actinides that will extend to $\Delta G°$ range.

Registry No. CO_3^-, 16518-46-0; $[UO_2(CO_3)_3]^{5-}$, 20274-15-1; $[UO_2(CO_3)_3]^{4-}$, 17872-00-3; $[NpO_2(CO_3)_3]^{5-}$, 64520-72-5; $[NpO_2(CO_3)_3]^{4-}$, 64519-49-9; $[PuO_2(CO_3)_3]^{5-}$, 89873-83-6; $[PuO_2(CO_3)_3]^{4-}$, 89850-08-8.

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Hypersensitivity in the 4f → 4f Absorption Spectra of Neodymium(III) Complexes in Aqueous Solution

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Absorption difference spectra are reported for six different Nd^{3+}/ligand systems vs. $NdCl_3$ in aqueous solution. These spectra were obtained as a function of Nd^{3+}/ligand solution pH. The ligands differ with respect to their donor (ligating) atoms, their substituent groups, their chelation geometries, and their total coordination numbers. However, each includes two carboxylate groups in its structure. The difference spectra (ΔA vs. λ) and oscillator strength ratios [f(complex):f($NdCl_3$(aq))] associated with the ${}^4I_{9/2} \rightarrow {}^4G_{5/2}$, ${}^2G_{7/2}$ absorption band (570–595 nm) exhibit *hypersensitive* behavior with respect to ligand type and solution pH. The variations observed in the ΔA spectra and in the oscillator strength ratios, with respect to both ligand type and solution pH, are rationalized in terms of ligand structure, ligand coordination properties, and ligand field geometry. Intensity calculations, based on a theoretical model for 4f → 4f electric dipole strengths, are carried out for a set of model structures assumed to be similar to those of several of the complexes studied experimentally. The results of these calculations are compared to the observed intensity data and are discussed in terms of spectra–structure correlations in the ${}^4I_{9/2} \rightarrow {}^4G_{5/2}$, ${}^2G_{7/2}$ "hypersensitive" transition region.

Introduction

Among the trivalent lanthanide ions, neodymium(III) has perhaps been used most frequently as an absorption probe of lanthanide–ligand interactions in solution media. The absorption band associated with the nearly degenerate ${}^4I_{9/2} \rightarrow {}^4G_{5/2}$ and ${}^2G_{7/2}$ transitions of Nd(III) exhibits strong "hypersensitive" behavior,[1-5] making it especially suitable for probing the coordination environment about the Nd(III) ion. The total (integrated) intensity, intensity distribution, and energy barycenter of this band are each strongly modulated by ligand coordination properties. Furthermore, this band occurs in a readily accessible region of the spectrum (~ 570–590 nm), and it is not overlapped by any other Nd(III) absorptions.

As a class, nearly all the hypersensitive multiplet–multiplet (4f → 4f) transitions of lanthanide ions share a common set of selection rules at the intermediate-coupling level. These rules are just those of radiative electric quadrupolar processes for 4f → 4f transitions.[1,2,6-9] However, it is nearly certain that essentially all of the observed intensity in these transitions is electric dipolar in nature. A number of proposals have been offered regarding the intensity mechanisms operative in these transitions,[1,2] and it is likely that each of the proposed mechanisms contributes to the observed intensities (and their *hypersensitivity* to the ligand environment). The most commonly invoked mechanism for hypersensitivity is that contained in the "inhomogeneous dielectric" theory of Jørgensen and Judd[6] and in the "ligand polarization" model proposed by Mason, Peacock, and Stewart.[1,7] According to this mechanism, the electric dipolar components of the radiation field induce a set of transient (electric) dipoles in the ligand environment that may couple to the 4f-electron distributions via electrostatic quadrupole (Ln)–dipole (ligand) interactions. These quadrupole-induced dipole interactions can lead to large amplifications of the 4f → 4f electric quadrupole transition probabilities. Thus, the observed spectral transition is electric quadrupolar with respect to the 4f → 4f processes involved but is electric dipolar with respect to the overall radiation–molecule interaction processes. This accounts for the hypersensitive transitions often being referred to as "pseudoquadrupolar" in nature. It also accounts for the correlation of hypersensitivity behavior with ligand (electric) dipolar polarizability.

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