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A Kinetic Study of Americium(III) and *trans*-1,2-Diaminocyclohexanetetraacetate

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The rates of formation and dissociation of $AmDCTA^-$ (DCTA = *trans*-1,2-diaminocyclohexanetetraacetate) have been measured respectively by stopped-flow and conventional spectrophotometric methods. A mechanism is proposed which involves coordination of Am(III) to three acetate groups of $H_n(DCTA)^{n-4}$ to form the relatively long-lived intermediate AmHDCTA* which subsequently loses the proton. The slow step of the formation reaction is postulated to be associated with the formation of an americium–donor nitrogen bond.

Introduction

The kinetics of lanthanide and actinide complexation by aminopolycarboxylates have been studied by several authors.[1-12] The majority of these studies involve exchange of metal cations which was found to occur through two mechanisms. The major path for the exchange at pH 6 involves hydrogen ion catalysis in which the metal complex is protonated in a series of proton additions leading ultimately to the decomposition of the complex and, hence, to metal exchange. A second term in the kinetic equation is acid independent. Some authors have interpreted this as related to a metal ion catalyzed decomposition of the complex in which the ligand serves as a bridge between the incoming and outgoing metal ions. However, alternate explanations are possible for the hydrogen ion independent path which do not involve formation of a binuclear intermediate.

Glentworth[2] found both acid-dependent and -independent terms in the Ce(III) isotopic exchange reaction with $CeDCTA^-$. D'Olieslager and Choppin[3] observed only an acid-dependent term in the equation for the exchange reactions between $LaEDTA^-$ and $^{152-154}$Eu(III), ^{144}Ce(III), and ^{241}Am(III). Subsequently, Choppin and Williams[4] showed that the dynamics of the metal-exchange reaction between $EuEDTA^-$ and Am^{3+} has an empirical rate law with acid-dependent and -independent terms. Both DeJonghe,[5] who studied ^{177}Tm(III) exchange in $TmEDTA^-$, and D'Olieslager and Oeyen,[6] who studied the $^{152-154}$Eu(III) exchange of $EuDCTA^-$, found kinetic descriptions with both terms. Studies that use radioactive isotopes of the aquo ions are complicated by the necessity of incorporating the criteria of isotopic equilibria in the treatment of the data. The procedure of Margerum et al.[12,13] used the exchanging metal ion in excess over the bound metal ion. This exchanging metal ion has a higher formation constant with the ligand than the chelated metal ion. In such cases the equilibrium concentration of the original chelated species is small enough to be neglected, greatly simplifying the data treatment.

The formation rates of metal chelates may be measured directly by stopped-flow techniques.[12-14] Nyssen and Margerum[12] used stopped-flow spectrometry to study the direct formation of the La–DCTA complex and conventional spectrometry to measure the decomposition of the DCTA complexes of Y and all (except Pm) of the lanthanide elements. They derived a mechanism for lanthanide complexation by DCTA in whch the complex LnHDCTA* is formed as an intermediate species in a rapid preequilibrium step. In their scheme this intermediate has the metal ion bound to three acetates of the ligand. They postulated slow deprotonation of LnHDCTA* as the rate-determining step in the formation of the stable complex $LnDCTA^-$.

We have investigated the formation and dissociation kinetics of $AmDCTA^-$ by both stopped-flow and conventional spectrophotometry to determine whether this mechanism for lanthanide complexation may be used to explain the kinetics of formation of trivalent actinide ion complexes with DCTA.

Experimental Section

The crystalline monohydrate acid form of DCTA (*trans*-1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetraacetic acid) was obtained from the Aldrich Chemical Co. It was recrystallized by dissolution in dilute base, followed by lowering the pH to about 5 with $HClO_4$.

The ^{243}Am was obtained from Argonne stocks and was used without any further purification.

The $LiClO_4$ used to adjust the ionic strength and the acetate buffer was made from reagent grade materials. Hydrogen ion concentrations, pcH, were calculated from pH measurements on a Beckman Model G digital pH meter using a combination electrode. The pcH calibration was made by measuring the pH of 0.1, 0.01, and 0.001 M acid solutions (μ = 0.1). The calibration was found to fit the equation

$$\mathrm{pcH} = \mathrm{pH} + 0.10$$

All aqueous solutions were prepared with triply distilled water.

The stopped-flow experiments were performed on a Durrum-Gibson (Model D 110) stopped-flow spectrometer. The flow system was thermostated to ±0.1 °C. The output of the spectrometer was stored in a Biomation 802 transient recorder which was interfaced for on-line operation with a Xerox Sigma V computer. Seven to twelve replicate determinations were carried out for each set of conditions. The absorbance was monitored at 245 nm ($\epsilon \sim 560$ cm^{-1} M^{-1}) where a strong absorption characteristic of $AmDCTA^-$ on the shoulder of an americium–acetate UV absorption was observed. The concentrations of all reagents and of the buffer were varied independently to determine their effect on the rate of reaction.

Though a detailed analysis of the UV absorption spectra of the $AmDCTA^-$ complex (Figure 1) was not made, it is believed that the 245-nm band on the shoulder of the larger band is due to metal-to-ligand charge transfer. A spectrum of Am(III) in acetate solution shows a broad band centered at ca. 200 nm. A similar spectrum of $AmDCTA^-$ in acetate medium exhibits a broadening of the amer-

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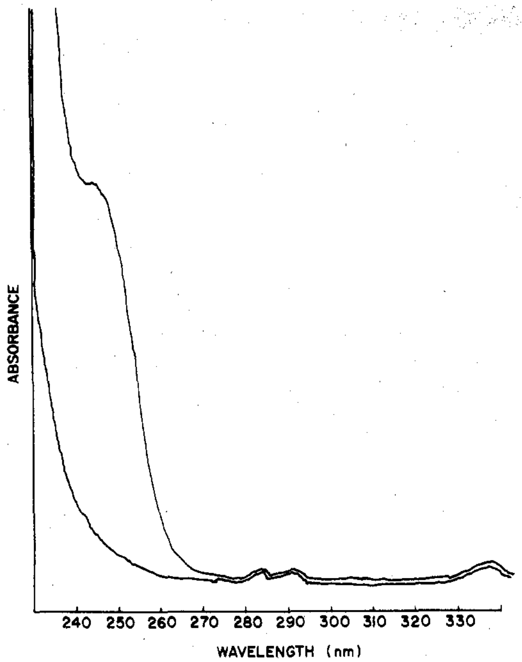

Figure 1. UV spectra: (1) Am(III) in 0.05 M acetate, pH 5.08; (2) $AmDCTA^-$ (5×10^{-4} M), pH 5.02.

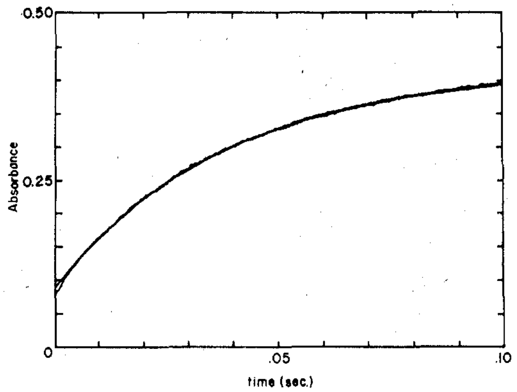

Figure 2. Sample oscilloscope trace from the stopped-flow spectrometer measuring the rate of the direct formation reaction $Am^{3+} + H_nDCTA^{(4-n)-} \rightarrow AmDCTA^- + nH^+$: $[Am^{3+}] = 0.0011$ M, [DCTA] = 0.0015 M, pH 4.48, $\mu = 0.1$ M, $T = 25.0$ °C.

icium–acetate absorption and a distinct shoulder at 245 nm corresponding to a different species. Since this band did not appear in a spectrum of DCTA in acetate, it was presumed to be due to charge transfer in the Am–N bonds of the $AmDCTA^-$ complex.

The dissociation kinetics of $AmDCTA^-$ were studied by combining the complex with excess Cu(II) to cause the reaction:

$$AmDCTA^- + Cu^{2+} \rightarrow CuDCTA^{2-} + Am^{3+}$$

These experiments were performed in a thermostated Cary 14 spectrometer monitoring the absorbance of $CuDCTA^{2-}$ ($\epsilon \sim 3000$ cm^{-1} M^{-1}) following the procedure of Margerum et al.[12,13] The concentration of Cu(II), acetate, and H^+ and the ionic strength were varied independently.

Results

Am(III)–DCTA Formation Kinetics by Stopped-Flow Spectrometry. The results of the experiments on the direct formation of $AmDCTA^-$ from Am(III) and H_nDCTA^{n-4} are presented in Table I. The first-order rate equation ($A = A_\infty + (A_0 - A_\infty)e^{kt}$) was found to adjust adequately the data of A and t for each individual experiment (Figure 2). This result is consistent with an intramolecular process with a rate given by

$$\text{rate} = k[AmH_nDCTA^*]$$

Table I. Direct Formation Reaction[a]

$$Am^{3+} + H_n(DCTA)^{n-4} \rightarrow Am(DCTA)^- + nH^+$$

($\mu = 0.10$ M ($LiClO_4$); 0.05 M Acetate)

run	[Am], M	[DCTA], M	pH	T, °C	k, s^{-1}	injections
1[b]	0.00123	0.0015	5.0	25.0	26.6 ± 0.1	9
2[b]	0.00123	0.0030	5.0	25.0	29.9 ± 0.2	9
3	0.00123	0.0015	5.0	25.0	25.2 ± 0.2	8
4	0.00123	0.0030	5.0	25.0	29.2 ± 0.4	8
5	0.00192	0.0015	5.0	25.0	27.8 ± 0.2	8
6	0.00121	0.0015	5.0	25.0	24.9 ± 0.1	9
7	0.00060	0.0015	5.0	25.0	26.3 ± 1.6	12
8	0.00121	0.0060	5.0	25.0	30.2 ± 0.4	11
9	0.00121	0.0015	4.0	25.0	15.9 ± 0.5	10
10	0.00110	0.0015	4.5	25.0	17.9 ± 0.1	10
11	0.00110	0.0015	5.4	25.0	29.6 ± 0.3	9
12	0.00110	0.0011[d] 0.0039[e]	5.0	25.0	27.9 ± 0.3	7
13	0.00110	0.0015	4.0	4.2	1.74 ± 0.01	10
14	0.00110	0.0015	4.5	4.2	2.62 ± 0.01	10
15	0.00110	0.0015	5.0	4.2	3.85 ± 0.02	10
16	0.00110	0.0015	5.4	4.2	4.49 ± 0.11	10
17[c]	0.00110	0.0015	4.0	34.8	31.5 ± 4.6	10
18	0.00110	0.0015	4.0	34.8	31.5 ± 1.3	9
19	0.00110	0.0015	4.5	34.8	42.5 ± 0.7	9
20	0.00110	0.0015	5.0	34.8	55.2 ± 2.9	10
21	0.00110	0.0015	5.4	34.8	67.4 ± 2.0	9

[a] Uncertainties in k correspond to one standard deviation. [b] $\mu = 0.05$ M ($LiClO_4$). [c] 0.01 M acetate. [d] [AmDCTA]. [e] [DCTA].

The rate can be related to the formation of the relatively long-lived intermediate AmH_nDCTA^* only if the latter is formed very rapidly and completely such that $[AmH_nDCTA] \sim \sum[H_iDCTA]_0$. Following the suggestion that, under similar conditions in the La–DCTA system, $LaHDCTA^*$ is the long-lived intermediate,[12] we propose $AmHDCTA^*$ as the intermediate species in our system.

A small pH dependence, $[H^+]^{-0.2}$, was observed at each temperature. This dependence may be resolved by considering the rate of reaction of Am(III) with the various protonated forms of H_nDCTA^{n-4} (only $HDCTA^{3-}$, H_2DCTA^{2-}, and H_3DCTA^- in the pH range studied since the concentrations of H_4DCTA and $DCTA^{4-}$ are negligible). The rate of reaction will be defined by the rate of the reaction of Am(III) with each of these protonated species and the rate constant

$$k_0 = \frac{k_3^{AmD}[H_3D] + k_2^{AmD}[H_2D] + k_1^{AmD}[HD]}{[H_3D] + [H_2D] + [HD]} \tag{1}$$

where D = DCTA. Substituting from the protonation relations for the various forms of the ligand and doing some mathematics give

$$k_0(1 + K_{H_3D}{}^H[H^+] + 1/[H^+]K_{H_2D}{}^H) = (k_2^{AmD} + k_3^{AmD}K_{H_3D}{}^H[H^+]) + k_1^{AmD}/[H^+]K_{H_2D}{}^H \tag{2}$$

where

$$K_{H_3D}{}^H = \frac{[H_3D]}{[H][H_2D]} = 10^{3.52}$$

$$K_{H_2D}{}^H = \frac{[H_2D]}{[H][HD]} = 10^{6.12} \tag{3}$$

If we assume

$$k_2^{AmD} > k_3^{AmD}K_{H_3D}{}^H[H^+] \tag{4}$$

eq 2 can be simplified to

$$k_0(1 + K_{H_3D}{}^H[H^+] + 1/[H^+]K_{H_2D}{}^H) = k_2^{AmD} + k_1^{AmD}/[H^+]K_{H_2D}{}^H \tag{5}$$

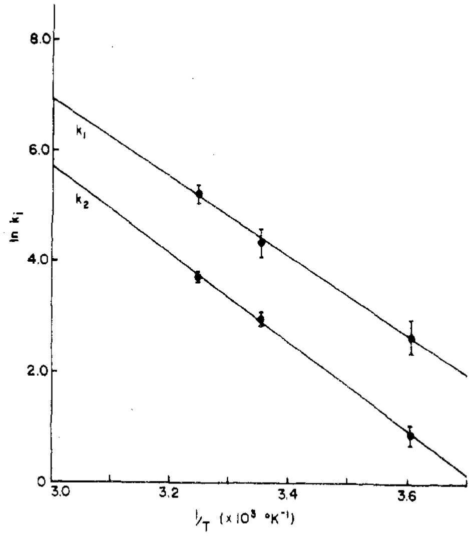

Figure 3. Arrhenius plots for k_1, k_2 from the stopped-flow experiments.

Table II. Results of Resolution of Dependence of Formation Rate on $[H^+]$[a]

k_1, s^{-1}	k_2, s^{-1} M^{-1}	T, °C	$LaDCTA^-$ formation[12]
14.0 ± 5.4	2.45 ± 0.51	4.2 ± 0.1	($T = 25$ °C)
76.4 ± 21.3	19.2 ± 1.9	25.0 ± 0.1	$k_1 = 22.6 \pm 6.5$ s^{-1}
185.5 ± 34.5	41.0 ± 3.3	34.8 ± 0.1	$k_2 = 6.8 \pm 1.4$ s^{-1} M^{-1}

[a] Error limits correspond to ±2σ.

Table III. Activation Parameters for AmDCTA Formation[a]

rate const	E_a, kcal mol^{-1}	ΔS^*, cal deg^{-1} mol^{-1}
k_1	14.1 ± 1.4	−4.5 ± 1.0
k_2	15.7 ± 1.1	−2.1 ± 0.8

[a] Error limits correspond to ±2σ.

A plot of $k_0(1 + K_{H_3D}{}^H[H^+] + 1/[H^+]K_{H_2D}{}^H)$ vs. $1/[H^+] \cdot K_{H_2D}{}^H$ yields a straight line whose slope is $k_1{}^{AmD}$ and whose intercept is $k_2{}^{AmD}$ (i.e., the first-order rate constant for the reaction of Am(III) with $HDCTA^{3-}$ and H_2DCTA^{2-}, respectively). The results of these plots at 4.2, 25.0, and 34.8 °C are contained in Table II. Arrhenius plots (Figure 3) of these data and calculation of the activation entropy give the activation parameters for the reactions between Am(III), $HDCTA^{3-}$, and H_2DCTA^{2-} (Table III).

This treatment was applied successfully also to Nyssen and Margerum's La–DCTA data (Table II) to resolve the slight inverse (also 0.2) dependence on H^+ found in that study (though it was not possible to calculate activation parameters from their data).

To determine whether our results would be directly comparable to Nyssen and Margerum's results, we ran one experiment in which La(III) was mixed with DCTA in the stopped-flow spectrometer. With conditions under which those authors observed $k_0 = 8.0 \pm 0.9$ s^{-1} at $\mu = 0.1$ M, we determined the reaction rate constant for $La^{3+} + H_nDCTA^{n-4} \rightarrow LaDCTA^- + nH^+$ of $k_0 = 9.0 \pm 0.4$ s^{-1} at $\mu = 0.05$ M which is quite satisfactory agreement.

Am(III)–DCTA Dissociation Kinetics by Conventional Spectrophotometry. For the Cu(II) displacement of Am(III) from $AmDCTA^-$, the equilibrium constant at 25 °C is

$$K_{eq} = \frac{[CuD^{2-}][Am^{3+}]}{[Cu^{2+}][AmD^-]} = \frac{\beta_{CuD}}{\beta_{AmD}} = \frac{10^{21.87}}{10^{18.79}} = 10^{3.08}$$

(β_{CuD},[15] β_{AmD}[16]) which indicates that the equilibrium lies >99.9% to the right. This result implies that the data may be treated as a simple dissociation and that the extent of back-reaction is negligible. The linearity of correlation of log $(A_\infty - A_t)$ with time supports this conclusion (cf. Figure 4).

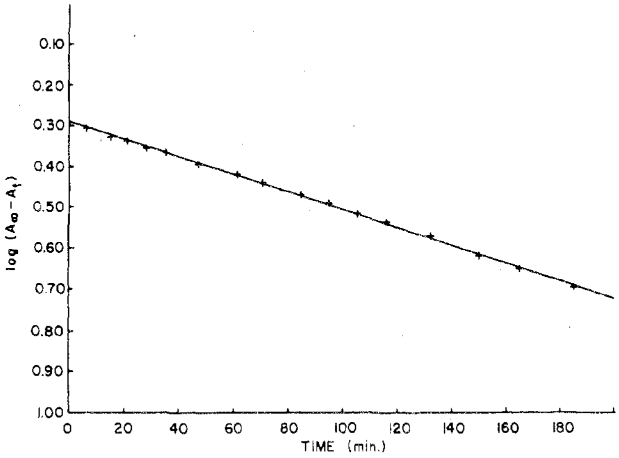

Figure 4. Sample plot of log $(A_\infty - A_t)$ vs. t for the dissociation reaction $AmDCTA^- + Cu^{2+} \rightarrow Am^{3+} + CuDCTA^{2-}$: $[AmDCTA^-] = 9.6 \times 10^{-5}$ M, $[Cu^{2+}] = 5 \times 10^{-4}$, [acetate] = 0.05 M, pH 5.0, $T = 25.0$ °C.

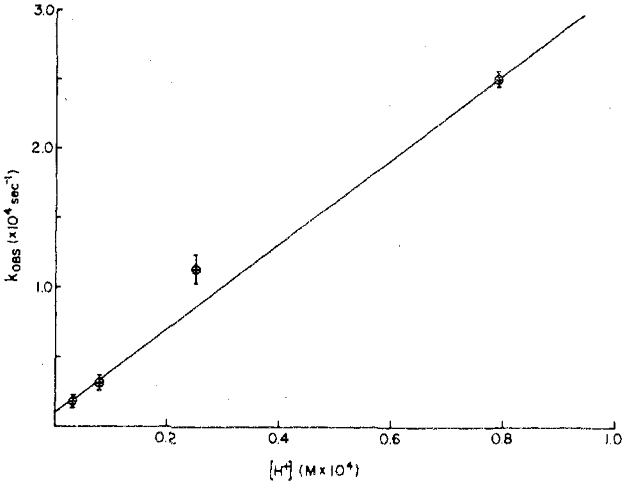

Figure 5. Resolution of the experimental dissociation rate into acid-dependent and acid-independent dissociation rates: $k_2{}^d = 3.04 \pm 0.03$ s^{-1} M^{-1}, $k_1{}^d = (8 \pm 2) \times 10^{-6}$ s^{-1}.

Table IV. $AmDCTA^-$ Dissociation Rate[a] ($[AmDCTA^-] = 1 \times 10^{-4}$ M, $T = 25.0$ °C)

$10^5 k_{obsd}$, s^{-1}	pH	μ	[acetate], M	$10^3 \times [Cu^{2+}]$, M
3.71 ± 0.04	5.0	0.1	0.05	0.5
3.19 ± 0.07	5.0	0.1	0.05	1.0
4.14 ± 0.19	5.0	0.1	0.01	1.0
12.2 ± 1.0	4.5	0.1	0.05	1.0
1.88 ± 0.67	5.4	0.1	0.05	1.0
25.0 ± 2.3	4.0	0.1	0.05	1.0
4.39 ± 0.28	5.0	0.5	0.05	1.0

$k_{AmD}{}^H = 3.04 \pm 0.03$ M^{-1} s^{-1}

$k_{AmD}{}^I = (8 \pm 2) \times 10^{-6}$ s^{-1}

[a] Error limits correspond to ±2σ.

The rate of dissociation was independent of each of the variables except $[H^+]$; a direct fractional power dependence of 0.8 on $[H^+]$ was observed indicating that the dissociation occurs by parallel paths involving acid-dependent and acid-independent terms. A similar dependence of 0.8 on $[H^+]$ was obtained in the study of Oeyen and D'Olieslager.[6] A plot of k_{obsd} vs. $[H^+]$ yields $k_{AmD}{}^H$ (the acid-dependent rate constant) and k_{AmD} (the acid-independent rate constant) as the slope and intercept, respectively, of a straight line (Figure 5). The rate constants thus determined are listed in Table IV.

Discussion

From our data we can assume that AmDCTA$^-$ forms via two paths, the first involving reaction between Am(III) and HDCTA^{3-} and the second reaction between Am(III) and H$_2$DCTA^{2-}. Let us consider these in turn. From

$$\frac{[\mathrm{AmD}][\mathrm{H}]}{[\mathrm{Am}][\mathrm{HD}]} = K_{\mathrm{e}(1)} = \frac{k_1^{\mathrm{f}}}{k_1^{\mathrm{d}}} \tag{6}$$

$$k_1^{\mathrm{f}} = k_1^{\mathrm{d}} K_{\mathrm{e}(1)} = k_1^{\mathrm{d}} \beta_{\mathrm{AmD}} \beta_{\mathrm{HD}}^{-1} \tag{7}$$

where

$$\beta_{\mathrm{AmD}} = [\mathrm{AmD}]/([\mathrm{Am}][\mathrm{D}]) = 10^{18.79}$$

$$\beta_{\mathrm{HD}} = [\mathrm{HD}]/([\mathrm{H}][\mathrm{D}]) = 10^{11.70}$$

and k_1^{d} is the experimentally measured acid-independent dissociation rate constant $k_{\mathrm{AmD}}^{\mathrm{I}}$ in Table IV (8×10^{-6} s^{-1}). The calculated formation rate constant k_1^{f} is 98 s^{-1} which agrees well with the value of 76.4 s^{-1} for k_1 determined at 25 °C in the stopped-flow results (Table II).

Treating the second reaction similarly we have

$$\frac{[\mathrm{AmD}][\mathrm{H}]^2}{[\mathrm{Am}][\mathrm{H_2D}]} = K_{\mathrm{e}(2)} = \frac{k_2^{\mathrm{f}}}{k_2^{\mathrm{d}}} \tag{8}$$

$$k_2^{\mathrm{f}} = k_2^{\mathrm{d}} K_{\mathrm{e}(2)} = k_2^{\mathrm{d}} \beta_{\mathrm{AmD}} \beta_{\mathrm{H_2D}}^{-1} \tag{9}$$

where

$$\beta_{\mathrm{H_2D}} = \frac{[\mathrm{H_2D}]}{[\mathrm{H}]^2[\mathrm{D}]} = 10^{17.82}$$

and

$$k_2^{\mathrm{d}} = 3.0\ \mathrm{s^{-1}\ M^{-1}}\ (\text{Table IV})$$

These values give $k_2^{\mathrm{f}} = 28.0$ s^{-1} in good agreement with k_2 (19.3 s^{-1}) measured by formation experiments. The values of β_{HD} and $\beta_{\mathrm{H_2D}}$ were taken from ref 17.

Nyssen and Margerum were unable to determine an acid-independent rate constant for the dissociation of LaDCTA$^-$ though they did determine an acid-dependent constant. Applying the relation derived for the acid-dependent path to their data gives $k_2^{\mathrm{LaD}} = 6.1$ s^{-1} which is in good agreement with the rate constant we have calculated from their data for the reaction between La^{3+} and H$_2$DCTA ($k_2^{\mathrm{LaD}} = 6.8$ s^{-1}).

From the stopped-flow results we know that the slow step in the formation of AmDCTA$^-$ is an intramolecular process, presumably occurring in the intermediate AmHDCTA*. The proton in AmHDCTA* may be associated with nitrogen as in the free ligand or with a carboxylate group as in the stable protonated complex,[18] or with both via hydrogen bonding. The similarity of the values of E_{a} and $\Delta S^{\ddagger}$ for the path associated with k_1^{AmD} and k_2^{AmD} may indicate that the reaction mechanisms are quite similar in both cases. However, these activation parameters include contributions from the formation of HL in one case and H$_2$L in the other. The magnitude of E_{a} (14–16 kcal/mol) is consistent with the formation of a bond in the rate-determining step. This activation energy also agrees well with the activation energies for LnDCTA$^-$ complexes as determined by Nyssen and Margerum[12] and by D'Olieslager and Oeyen.[6] The low activation entropy ($\Delta S^{\ddagger} = -2$ to -5 cal deg^{-1} mol^{-1}) may indicate that little rearrangement of the intermediate species occurs in forming the stable product AmDCTA$^-$; i.e., the reactive species is properly oriented in a step prior to the slow step of the reaction.

Brücher and Szarvas[8] found that the dissociation of lanthanide–EDTA complexes occurred through both a mono- and a diprotonated intermediate. However, they observed only a monoprotonated path for the dissociation of lanthanide–DCTA complexes and suggested that if a diprotonated LnH$_2$DCTA complex is formed, it dissociates rapidly and does not affect the rate of exchange reactions.

We can use the data in this work to estimate k^{f} and k^{d} for the reaction

$$\mathrm{Am^{3+}} + \mathrm{D^{4-}} \underset{k_0^{\mathrm{d}}}{\overset{k_0^{\mathrm{f}}}{\rightleftharpoons}} \mathrm{AmD^-}$$

For ionic reactions in solution, electrostatic theory[19] predicts $\log k^{\mathrm{f}} \propto Z_1Z_2$. Using $\log k_1^{\mathrm{f}}$ and $\log k_2^{\mathrm{f}}$ ($Z_1Z_2 = -9$ and -6, respectively), we estimate $\log k_0^{\mathrm{f}} \simeq 2.5 \pm 0.1$ ($Z_1Z_2 = -12$). For $\beta_{\mathrm{ML}} = 18.8$, this leads to a value of $\log k_0^{\mathrm{d}} \simeq -16.3 \pm 0.1$. This very small value of k_0^{d} indicates the very slight tendency of AmDCTA$^-$ to dissociate in a monomolecular process as compared to the bimolecular, [H$^+$]-catalyzed decomposition paths.

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Registry No. DCTA, 13291-61-7; Am^{3+}, 22541-46-4; Cu^{2+}, 15158-11-9; AmDCTA$^-$, 19594-47-9; La^{3+}, 16096-89-2.

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