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Dissociation Field Effect Kinetic Study of Aqueous Samarium(III) Complexation by Murexide

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The rates of formation of the aqueous samarium(III) murexide complex have been measured at 12 and 25° in the absence of inert electrolyte using the dissociation field effect (*E* jump) relaxation method. Specific rate constants for complex ion formation ($5.5 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ at 12°; $8.2 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ at 25°; $\mu \simeq 10^{-3}\ M$) are consistent with those obtained previously by the temperature jump technique under different ionic strength conditions, and the activation energy for complexation is comparable to that obtained for solvent exchange on an analogous cation, gadolinium, and for complexation in other closely related systems.

Introduction

There are occasional apparent discrepancies between specific rates measured by acoustic methods and by the temperature or pressure jump techniques.[2] Where such discrepancies involve metal ion complexation reactions they could be more readily resolved if instrumental limitations and solute solubilities were not so restrictive that they prevented a study for a single metal ion–ligand system over an extended range in concentration. However, for those families of metal ions for which complexation usually occurs by a dissociative (SN1) mechanism it is frequently possible instead to compare kinetic results obtained from acoustic and other methods by working with a single metal ion and several similar ligands.[3,4]

The loss of solvent from the first coordination sphere of aqueous lanthanide ions is thought to be rate determining in many complexation reactions.[3,4] This is particularly true for metal ion–ligand systems studied acoustically.[3-7] There has been some reluctance to correct overall rate constants for differences in ionic strength and temperature using theoretical equations in order to make comparisons with stepwise constants. In this work the specific rates for complexation of samarium(III) murexide have been measured as a function of temperature, at low ionic strength. The values are in good quantitative agreement with data obtained at other ionic strengths and temperatures.[8,9] It is also of incidental interest to remark that the present dissociation field effect (*E* jump) relaxation method kinetic study of a complex ion system is one of very few reported thus far in the literature.[10,11]

Experimental Section

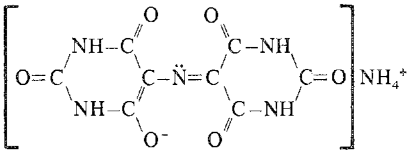
Samarium murexide solutions were prepared in freshly boiled, distilled, deionized water by mixing aliquots of stock aqueous samarium perchlorate (Research Organic/Inorganic Chemical Corp.) and murexide stock solutions prepared from 99.0% ammonium purpurate (Eastman Kodak Co.). The stock samarium perchlorate was standardized by cation exchange on Rexyn 101 (H) resin (Fisher Scientific Co.) and titration of the eluent perchloric acid with standardized potassium hydroxide. Murexide was used without further purification and solutions were prepared by weight. Fresh stock solutions prepared prior to each series of experiments were stored in the dark at ~5° and were discarded at the conclusion of the day. Sample solution pH ranged from 3.5 to 4.5, and since the kinetics of complexation were found to be independent of $[H^+]$, we have not tabulated this parameter.

The dissociation field effect (*E* jump) experiments were done spectrophotometrically in the visible region with an apparatus of local manufacture. An EMI 9783 B photomultiplier tube was used with a 50-ohm load resistance and the output was fed directly into a Hewlett-Packard 183 A oscilloscope with 1840 A and 1801 F plug-ins. The high voltage on the photomultiplier was adjusted for a 3-V light to dark signal. The amplitude of the relaxations observed ranged from 50 to 200 mV while the peak to peak high-frequency noise was typically 20 mV. The instrumental relaxation time was measured to be 24 nsec. The exceptionally high signal to noise ratio achieved in these experiments on a submicrosecond time scale is primarily attributable to a pulsing of the Osram high-pressure xenon arc lamp light source by well-known techniques. The precision of measured relaxation times was approximately ±15%. An electric field strength of 130 kV/cm in the sample solution was achieved with 47 kV square-wave pulses of 4-μsec duration. All relaxation times were measured after termination of the high voltage pulse, so all rate constants reported below are valid for zero electric field.

Relaxations were observed at 520 nm when metal ion was in excess and at 425 nm when murexide ion was in excess. Temperatures were maintained in the *E* jump sample cell to within ±0.1° by circulating water from a constant-temperature bath through the upper (ground) stainless steel electrode.

Results

Murexide is supplied as the ammonium salt



The first ionization is strong ($pK_1 \simeq 0$) and the second ionization is considerably weaker[12] ($pK_2 = 9.2$). This latter and higher ionization steps are unimportant in acid pH and the murexide is present entirely in the form of the monoanion, H_4A^-. Complexation with Sm^{3+} is consequently independent of pH, provided the solution is kept below pH 5 to suppress samarium ion hydrolysis, and the equilibrium can be expressed simply as

$$Sm^{3+} + H_4A^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} SmH_4A^{2+} \qquad (1)$$

Evidence for other complexes at higher pH was found in a potentiometric titration with a standard base. By analogy

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with calcium murexide[12] these equilibria probably involve Sm^{3+} with H_3A^{2-} and H_2A^{3-} but none were present to significant extent at the pH conditions used in this study.

The rate equation for reaction 1 is therefore given by[8]

$$\tau^{-1} = k_f\{\overline{[Sm^{3+}]} + \overline{[H_4A^-]}\} + k_b \qquad (2)$$

where τ is the relaxation time, k_f and k_b are the overall forward and backward rate constants, respectively, and the bars refer to equilibrium concentrations. Equation 2 can be expressed in another way by introducing the complex formation constant K_F as

$$\tau^{-1} = k_f\{\overline{[Sm^{3+}]} + \overline{[H_4A^-]} + K_F^{-1}\} \qquad (3)$$

Both eq 2 and 3 were used for the kinetic analysis and gave good agreement in the value obtained for k_f.

The ion equilibrium concentrations were calculated in a standard iterative procedure using the equation for the thermodynamic formation constant

$$K_F = \overline{[SmH_4A^{2+}]}/\overline{[Sm^{3+}]}\,\overline{[H_4A^-]}\gamma_1^{\,6} \qquad (4)$$

where γ_1 is the activity coefficient for a univalent ion, the mass balance equations for total acid and total metal

$$a = \overline{[H_4A^-]} + \overline{[SmH_4A^{2+}]} \qquad (5)$$

$$m = \overline{[Sm^{3+}]} + \overline{[SmH_4A^{2+}]} \qquad (6)$$

and a modified form of the Davies equation[13]

$$-\log \gamma_1 = A\{(\mu^{1/2}/(1 + Ba_0\mu^{1/2})) - 0.3\mu\} \qquad (7)$$

In eq 7, A and B are the Debye-Huckel parameters which are temperature dependent, μ is the ionic strength of the solution given by

$$\mu = 6m - 2a + 3\overline{[H_4A^-]} \qquad (8)$$

and a_0 is the distance of closest approach of the ions. To be consistent with previous studies[7] a_0 was taken to be 8.86 Å equal to the sum of the effective ionic radii plus two water molecule diameters. Iteration was terminated when successive γ_1 values agreed to within 0.001.

Since only very approximate values of K_F were known from our rudimentary spectrophotometric measurements, a second iterative procedure, which used the preceding iteration as a subroutine, was introduced to obtain K_F values from kinetics. The second iteration was initiated using an arbitrary value of K_F and terminated when successive $K_F = k_f/k_b$ values from eq 2, or K_F values from eq 3, differed by less than 100 (*i.e.*, less than 1% of K_F). Formation constants calculated in this manner, $K_F = 1.2 \times 10^4$ at 12° and $K_F = 2.4 \times 10^4$ at 25°, are consistent with a previous value for samarium murexide of 1.6×10^4 measured at 12° and 0.1 M ionic strength[8] and agree to within a factor of 2 of the approximate values obtained spectrophotometrically in this laboratory.

Pertinent concentration data and the observed relaxation times are collected in Table I. In Figure 1 the graphical solutions to eq 2 are shown. The solid lines are the linear least-squares fit to the experimental points giving a minimum average standard deviation in τ^{-1} of 1.33×10^4 and 1.76×10^4 sec^{-1} at 12 and 25°, respectively. The resultant rate constants are given in Table II together with previous values taken from the literature for other samarium complexation reactions. Overall forward rate constants were found to vary from only 7.9 to 8.5×10^8 M^{-1} sec^{-1} as the value of K_F in use varied over one order of magnitude. Variations in K_F from cycle to cycle were a consequence of the comparatively large variations in k_b, the intercept. Considerably less confidence can be placed in the values obtained for k_b which, within experimental error, may be considered to be invariant with temperature. The calculated activation enthalpy change for the forward reaction, $\Delta H_f^{\ddagger}$, is approximately 5 kcal mol^{-1}.

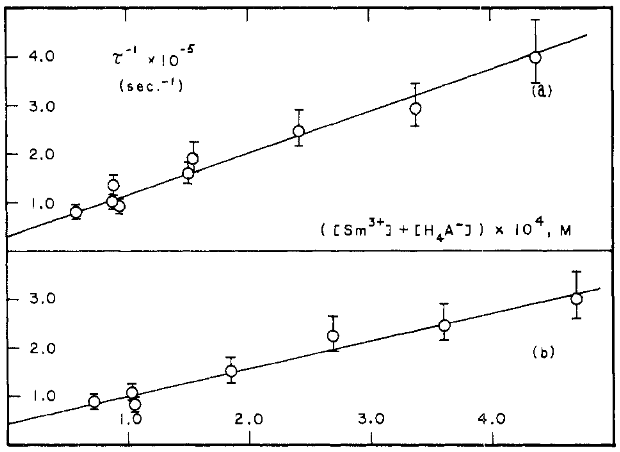

Figure 1. Graphical solution to the rate equation (eq 2) at (a) 25° and (b) 12°.

Table I. Concentration Data and Relaxation Times

10^4m, F	10^4a, F	$10^4(\overline{[Sm^{3+}]} + \overline{[H_4A^-]})$, F	$10^{-5}\tau^{-1}$, sec^{-1}
	25°		
5.197	1.027	4.373	4.01
4.156	1.027	3.380	2.95
3.118	1.027	2.424	2.47
2.079	1.027	1.442	1.91
1.039	1.027	0.942	0.93
0.5197	1.027	0.876	1.01
1.039	0.5135	0.893	1.35
0.5197	0.5135	0.584	0.81
1.039	2.054	1.412	1.59
	12°		
5.197	1.0096	4.435	3.00
4.156	1.0096	3.450	2.45
3.118	1.0096	2.505	2.24
2.079	1.0096	1.644	1.52
1.039	0.5048	0.947	0.83
0.5197	0.5048	0.626	0.88
0.5197	1.0096	0.918	1.06

Table II. Rate Constants for Samarium Complexation Reactions

Ligand	Medium μ	Method	T, °C	$10^{-8}k_f$, M^{-1} sec^{-1}	k_b, sec^{-1}
Murexide[a]	→0	*E*	25	8.2	3.4×10^4
Murexide[a]	→0	*E*	12	5.5	4.6×10^4
Murexide[b]	0.1 M	*T*	12	0.96	6.0×10^3
Anthranilate[c]	0.2 M	*T*	12.5	0.63	2.6×10^4
Oxalate[d]	→0	*P*	25	0.82	6.3

[a] Results from present work. [b] Reference 8. [c] Reference 9. [d] A. J. Graffeo and J. L. Bear, *J. Inorg. Nucl. Chem.*, 30, 1577 (1968).

Discussion

The value of 5.5×10^8 M^{-1} sec^{-1} for k_f at 12° and low ionic strength ($\mu \cong 10^{-3}$) is quantitatively consistent with the value of 0.96×10^8 M^{-1} sec^{-1} measured for the same system at the same temperature but at 0.1 M ionic strength.[8] An increase in the specific rate constant is expected from the Bronsted-La Mer theory for a reaction involving ions of op-

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posite charge as the ionic strength is decreased.[14] Using this theory and our value for k_f at low ionic strength, the value calculated at 0.1 M ionic strength is $0.8 \times 10^8\ M^{-1}\ \text{sec}^{-1}$. Consistency in this respect is also observed for the samarium anthranilate system measured in 0.2 M ionic strength.[9] Only the oxalate complexation of samarium[15] fails to correspond with the above ionic strength dependence which places further doubt on the resultant rate constants for the entire series of rare earth oxalates. By contrast the rate constants for the rate-determining step in a multistep mechanism show little dependence on the ionic strength[16] as expected since this step does not involve the collision of ions of opposite sign but only the desolvation of the cation in the complex. If one correlates the overall forward rate constant k_f with the rate-determining stepwise rate constant k_{ij}, according to $k_f = K_0 k_{ij}$, where K_0 is the outer ion-pair formation constant, then the decrease in k_f with increasing ionic strength is reflected entirely in a concomitant decrease in K_0.

The activation enthalpy change for the forward process $\Delta H_f^{\ddagger} \simeq 5$ kcal mol^{-1} is in good agreement with that observed for other closely related systems, *e.g.*, 2-4 kcal mol^{-1} for water exchange[17] on Gd^{3+} measured by ^{17}O nmr, 2-4 kcal mol^{-1} for samarium sulfate measured acoustically,[18] and 4.4 kcal mol^{-1} for dysprosium anthranilate measured by temperature jump.[19] Therefore, the value of $k_f = 8.2 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ at 25° and low ionic strength appears to conform well with the general scheme of the results for rare earth complexation reactions. With this figure for k_f measured at the experimental conditions of the acoustic experiments it should be possible to make a more realistic correlation between rate data from different relaxation techniques.[16]

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Reaction of Molecular Oxygen and Titanium Trichloride in Anhydrous Pyridine

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Molecular oxygen and titanium trichloride react in anhydrous pyridine to give the oxo-bridged titanium(IV) complex $Cl_3TiOTiCl_3 \cdot 4C_5H_5N$ in quantitative yield. The rate law $-d[O_2]/dt = k_{\text{exptl}} P_{O_2} [TiCl_3]$ was observed. Values for the specific rate constant of the homogeneous reaction ($k_1^{25°}$), $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ are 7.1×10^{-2} l mol^{-1} sec^{-1}, 10 kcal mol^{-1}, and -31 eu, respectively. A direct electron-transfer mechanism is proposed. Spectral evidence is presented for the existence of a dimeric titanium(III) species in solution. An initial rapid uptake of oxygen by titanium trichloride solutions is accounted for in terms of a $Ti_2Cl_9^{3-}$ dimer, whose concentration diminishes as the reaction progresses.

Introduction

Because of the assiduous care taken to exclude molecular oxygen in studies of nonaqueous solutions of titanium compounds in low oxidation states, little is known of the products and mechanisms of reactions involving titanium(III) and molecular oxygen in nonaqueous solvents. In the absence of solvent, titanium trichloride and molecular oxygen combine at elevated temperatures to give a 1:1 mole ratio mixture of titanium(III) oxychloride and titanium tetrachloride.[1] In moist air or basic to slightly acid aqueous solution, titanium trichloride is rapidly and irreversibly oxidized to hydrated titanium dioxide.[2] Bis(cyclopentadienyl)titanium(III) chloride,[3] bromide,[4] cyanide, cyanate, and thiocyanate[5] yield oxo-bridged dimers of the type $(Cp)_2(X)Ti\text{-}O\text{-}Ti(X)(Cp)_2$ when exposed to molecular oxygen in anhydrous solvents. Despite the detrimental effect of the irreversible oxidation by molecular oxygen upon the chemical, catalytic, and physical properties of compounds of titanium in low oxidation states, analyses of the products and mechanisms of these oxidations are useful in the formulation of chemical synthesis, the definition of solute species, and the empirical differentiation of the chemistry of titanium(III), a d^1 system, from the more thoroughly investigated chemistry of the low-spin d^7 Co(II) systems which also contain a single unpaired electron.

Results and Discussion

The chemistry of titanium(III) in this system is markedly different from that of low-spin cobalt(II) systems. When oxygen is passed through an aqueous solution of cobalt(II) chloride or nitrate and potassium cyanide, a μ-peroxo complex anion $[(NC)_5CoO_2Co(CN)_5{}^{6-}]$ is rapidly formed.[6] Reduction of oxygen by cobalt(II) stops at the peroxide state in the presence of ammonia with the formation of $[(NH_3)_5CoO_2Co(NH_3)_5]^{4+}$ salts.[7] With titanium trichloride as the

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