Within the tetrachloro series of compounds as well as for the trichloromolybdenum(III)–amine complexes, the potential data for the anodic process also show little dependence on the π-acceptor character of the coordination sphere in contrast to the situation for the cathodic processes. This point emphasizes the important role that the π-acceptor character of ligand plays in the stabilization of lower oxidation states.

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A Kinetic Investigation of Lanthanide(III) Complexation. II. Deuterium Isotope Effects and Activation Parameters for the Lanthanide(III)–Anthranilate Reaction

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Deuterium isotope effects and activation parameters have been measured for the rate constants k_{23} and k_{32} in the reaction

$$Ln^{3+} + An^- \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} LnAn^{2+}$$

where Ln^{3+} and An^- represent the 3+ lanthanide and the anthranilate (*o*-aminobenzoate) ions. The kinetics of several other selected lanthanide–ligand systems have been partially examined. Possible interpretations of the results in terms of the solvation of the 3+ lanthanide are discussed. The kinetic experiments were carried out using temperature-jump relaxation techniques.

Introduction

As part of a continuing study of complexation reactions of the lanthanides,[1] a more extensive kinetic investigation of the reaction between the anthranilate (*o*-aminobenzoate) ion and selected 3+ lanthanides has been carried out. The rate constants k_{23} and k_{32} for the reaction

$$Ln^{3+} + An^- \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} LnAn^{2+}$$

where Ln^{3+} is the 3+ lanthanide and An^- is the anthranilate ion, have been examined in D_2O and as a function of temperature in H_2O. Possible interpretations of the results in terms of the structure of the solvent about the lanthanide ions are discussed.

Experimental Section

The general experimental procedures and instrumentation are discussed in a previous paper.[1] All stock lanthanide perchlorate solutions were prepared by adding oxides of greater than 99.9% purity (American Potash and Chemical Corp., Lindsay Chemical Division) to known quantities of dilute perchloric acid. The purity of the oxides was checked by the technique of Stewart and Kato.[2] All of the oxides readily dissolved except that of terbium which required the addition of a small amount of H_2O_2.

The anthranilic acid (Eastman, practical) was recrystallized twice from ethanol containing decolorizing charcoal. After air drying, an uncorrected melting point of 145.0–146.8° was obtained, which was in agreement with the published value of 146.1°.[3] The melting point of methyl red (Matheson Coleman and Bell and Allied Chemical Co.) was 177–179°, uncorrected, which is in agreement with the published value of 178–179°.[4] Reagent grade sodium carbonate, sodium acetate, sodium hydroxide, and perchloric acid were used. All solutions were made up with distilled water which was further purified by passage through an ion-exchange apparatus, Model 306-4, Caw Engineering, Palo Alto, Calif. The density of deuterium oxide (Columbia Organic Chemical Co., Inc., and Bio-Rad Laboratories) was 1.1050 g/ml at 22.1° which agrees well with the value of 1.1049 g/ml reported in the literature.[5]

Stock solutions of lanthanide ions in D_2O were prepared by weighing out the oxide in sufficient 70–72% $HClO_4$ to dissolve the solid. After dissolution, sufficient D_2O was added to bring the solutions to the desired concentration. The amounts of 11.8 *M* $HClO_4$ added varied from 0.09 to 0.40 ml with a final dilution of the stock solutions to 25.0 ml. This gives a maximum of 0.35 HDO mol % (*e.g.*, erbium solution). Thus, the stock solutions contain a minimum of 99.4% D_2O.

Stock solutions of anthranilic acid and methyl red in D_2O were prepared by adding known amounts of the respective solids to D_2O. The stock anthranilic acid solution was 2.17×10^{-3} *M*, corresponding to the addition of the same concentration of H^+ to the D_2O (55.17 *M*). The amount of HDO in the solution was 0.004%. The $NaClO_4$–D_2O stock solutions were prepared by neutralizing Na_2CO_3 with $HClO_4$ and gently heating to dryness, care being taken to minimize the decomposition. Since the $NaClO_4$ is deliquescent, it was cooled in a closed desiccator, quickly weighed, and dissolved in D_2O. NaOD, which was

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[3] "Beilstein's Handbuch der Organischen Chemie," 2nd ed, Band XIV, Springer-Verlag, Berlin, 1951, p 205.

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prepared by treating Na metal with D_2O, was used to regulate the pD of the solutions. For the D_2O solutions, the measurements of "concentration pD" were made relative to the acetate buffer in H_2O solution. The pD scale is related to the pH scale by pD = pH meter reading + 0.40 when measurements are made relative to H_2O buffers.[6]

Results

The experimental data are consistent with the mechanism

$$\mathrm{HAn} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \mathrm{H^+ + An^-} \qquad (1)$$

$$\mathrm{HIn} \rightleftharpoons \mathrm{H^+ + In^-} \qquad (2)$$

$$\mathrm{Ln^{3+} + An^-} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \mathrm{LnAn^{2+}} \qquad (3)$$

in which reactions 1 and 2 equilibrate rapidly compared to reaction 3. The symbols Ln^{3+}, HAn, and HIn represent the lanthanide, anthranilic acid, and methyl red, respectively. Under these conditions one of the relaxation times for the system, which is determined from temperature-jump relaxation experiments, is

$$\frac{1}{\tau} = k_{23}\left\{\frac{[\mathrm{Ln^{3+}}]}{1+\alpha} + [\mathrm{An^-}]\right\} + k_{32} \qquad (4)$$

where

$$\alpha = \frac{[\mathrm{H^+}]}{K_a + [\mathrm{An^-}]\left\{\dfrac{K_{\mathrm{In}} + [\mathrm{H^+}]}{K_{\mathrm{In}} + [\mathrm{H^+}] + [\mathrm{In^-}]}\right\}} \qquad (5)$$

The symbols K_a and K_{In} represent the dissociation equilibrim concentration quotients for reactions 1 and 2. The pK_a has a value of 4.75 ± 0.07 at $\mu = 0.2$ ($NaClO_4$),[1] and pK_{In} is reported to be 5.00 at $\mu = 0$–0.50 and 20°, with a small temperature dependence.[7] As has been shown previously, the observed relaxation cannot be attributed either to reactions 1 and/or 2 or to the interaction of the lanthanide with the anionic form of the indicator.[1]

The rate constants k_{23} and k_{32} were obtained from plots of the reciprocal of the observed relaxation time, $1/\tau$, *vs.*

$$\frac{[\mathrm{Ln^{3+}}]}{1+\alpha} + [\mathrm{An^-}]$$

Least-squares lines were drawn through the experimental points from which the ratios of k_{23}/k_{32} were calculated and used as an estimate of the equilibrium concentration quotients for reaction 3, K_f. This estimated value was used to recalculate the least-squares line using new values of

$$\frac{[\mathrm{Ln^{3+}}]}{1+\alpha} + [\mathrm{An^-}]$$

Using the method of successive approximations, the final values of k_{23}, k_{32}, and K_f were obtained. In cases where K_f has been independently determined[1]

$$\frac{[\mathrm{Ln^{3+}}]}{1+\alpha} + [\mathrm{An^-}]$$

was calculated directly and only the least-squares line was drawn. For these cases the ratio k_{23}/k_{32} from the kinetic plot was within experimental error of K_f. A plot of typical data for dysprosium is shown in Figure 1 of ref 1. Other than that predicted by eq 4 and 5 no systematic variation in $1/\tau$ is observed as a function of pH in the region of pH 4–7. Thus it can be concluded that hydrolysis of the lanthanides has no observable effect upon the rate constants for the lanthanide–anthranilic acid systems studied.

Table I summarizes the kinetic data at three temperatures for the lutetium–anthranilate reaction in H_2O at $\mu = 0.2$ ($NaClO_4$). These data are plotted in Figure 1.

TABLE I

KINETIC DATA FOR LUTETIUM–ANTHRANILATE REACTION[a,d]

$10^4[\mathrm{Lu}]_t$,[b] M	$10^4[\mathrm{anth}]_t$,[b] M	pH	10^4X,[c] M	$10^{-3}/\tau$, sec^{-1}
		20.5°		
6.60	0.22	5.7	6.4	152
6.60	0.44	5.7	6.4	156
4.95	0.22	5.5	4.8	127
4.95	0.22	6.1	4.8	133
3.30	0.22	5.7	3.2	108
1.65	0.22	5.7	1.8	85
1.65	0.22	5.9	1.8	79
		12.5°		
12.3	0.22	5.7	12.0	158
12.3	0.44	5.9	12.0	160
8.25	0.22	5.3	8.0	125
8.25	0.22	5.8	8.0	121
6.50	0.22	5.2	6.3	107
4.94	0.22	5.1	4.8	87
4.94	0.22	5.2	4.8	92
3.30	0.22	5.6	3.2	81
3.30	0.22	5.1	3.2	88
1.65	0.22	5.5	1.6	65
0.83	0.22	5.9	1.0	51
		6.5°		
18.1	0.22	5.7	17.6	158
18.1	0.22	5.9	17.6	147
14.9	0.22	5.5	14.5	132
14.9	0.44	5.8	14.8	125
11.5	0.44	5.6	11.5	118
11.5	0.44	5.9	11.5	108
8.25	0.22	5.6	8.3	103
5.79	0.22	5.7	5.8	87
3.30	0.44	5.8	3.6	76
3.30	0.22	5.9	3.4	72
1.65	0.44	5.8	2.0	62

[a] $\mu = 0.2$ ($NaClO_4$); $\lambda = 515$ mμ; solvent H_2O; $[\mathrm{HIn}]_t = 10^{-5}$ M. [b] Total initial concentration of lutetium and anthranilic acid in all forms. [c] $\{([\mathrm{Lu^{3+}}]/(1+\alpha)) + [\mathrm{An^-}]\}$, where α is defined in the text (eq 5). [d] Complete tables of data have been deposited as Document No. NAPS-00208 with the ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001. A copy may be secured by citing the document number and by remitting $3.00 for photocopies or $1.00 for microfiche. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

Table II summarizes the kinetic and equilibrium data for the lanthanides studied. The trends in k_{23} in H_2O, $k_{23}(H_2O)$, and D_2O, $k_{23}(D_2O)$, at 12.5°, as well as $\Delta H^{\ddagger}_{23}$ and $\Delta S^{\ddagger}_{23}$ in H_2O, are presented in Figure 2 for future reference. As is usually observed for lanthanide complexation reactions, the enthalpy change ($\Delta H^{\ddagger}_{23} - \Delta H^{\ddagger}_{32}$) is small and the entropy change

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[7] L. Meites, Ed., "Handbook of Analytical Chemistry," 1st ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1963, pp 3-36.

TABLE II

SUMMARY OF KINETIC AND EQUILIBRIUM DATA FOR THE LANTHANIDE-ANTHRANILATE SYSTEMS[a]

Ln	$10^{-7}k_{23}$,[a,b] M^{-1} sec^{-1}	$\Delta H^{\ddagger}_{23}$, kcal/mol	$\Delta S^{\ddagger}_{23}$, eu	$10^{-4}k_{32}$,[a] sec^{-1}	$\Delta H^{\ddagger}_{32}$, kcal/mol	$\Delta S^{\ddagger}_{32}$, eu	$10^{-3}K_f$,[b,c] M^{-1}	$10^{-7}k_{23}(D_2O)$,[a,b] M^{-1} sec^{-1}
La	5.5	5.3[d]	−5	5.2	4.8[d]	−20	1.0 ± 0.6	5.5[e]
Pr	4.6	5.1 ± 2.2	−6 ± 8	3.9	3.4 ± 1.3	−25 ± 4	1.2 ± 0.1	1.6
Sm	6.3	2.9 ± 2.8	−13 ± 10	2.6	3.5 ± 1.0	−31 ± 3	2.4 ± 0.2	1.0
Eu	10.5	3.3[f]	−12	3.3	. . .	. . . .	3.2 ± 0.2	1.7
Gd	5.9	9.1 ± 1.8	+9 ± 6	4.7	6.5 ± 1.6	−14 ± 5	1.3 ± 0.1	1.1
Tb	3.5	. . .	. . .	3.2			1.1 ± 0.1	3.5[e]
Dy	1.4	4.4 ± 2.0	−10 ± 8	1.2	4.3 ± 1.0	−24 ± 4	1.2 ± 0.2	1.4[e]
Er	5.8	3.4 ± 2.2	−11 ± 8	4.9	1.1 ± 1.3	−33 ± 4	1.2 ± 0.2	1.1
Yb	6.9	5.4 ± 3.5	−4 ± 12	4.2	5.5 ± 1.2	−18 ± 4	1.6 ± 0.2	1.1
Lu	9.5	9.5 ± 2.0	+10 ± 6	4.1	2.0 ± 1.5	−24 ± 5	2.3 ± 0.2	2.1

[a] $\mu = 0.2$ ($NaClO_4$); temperature 12.5°. [b] The 95% confidence limit is 20%. [c] Error recorded is standard deviation. [d] Error in $\Delta H^{\ddagger}$ for La is 34% due to scatter of data. [e] D_2O points are within experimental error of H_2O points. [f] Result of measurements at two temperatures.

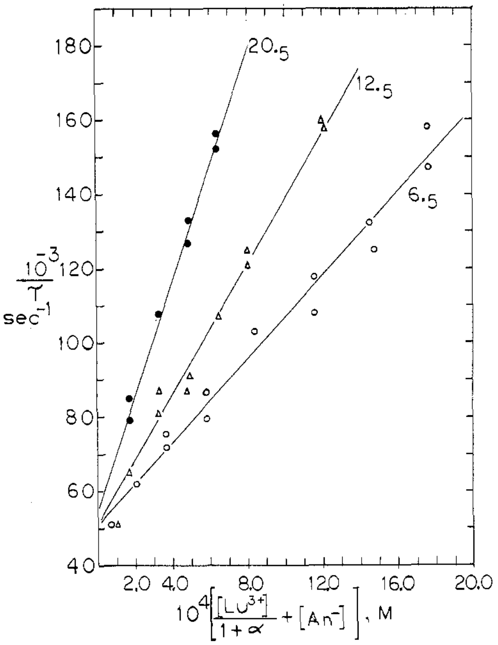

Figure 1.—Plot of $1/r$ vs. $\{([Lu^{3+}]/(1+\alpha)) + [An^-]\}$ at 20.5° (●), 12.5° (△), and 6.5° (○); $\mu = 0.2$ ($NaClO_4$).

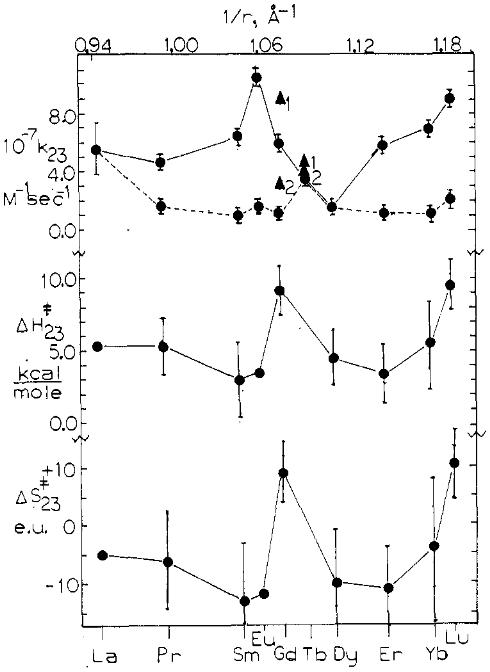

Figure 2.—Kinetic parameters, $k_{23}(H_2O)$, $k_{23}(D_2O)$, $\Delta H^{\ddagger}_{23}$, and $\Delta S^{\ddagger}_{23}$ for the lanthanide–anthranilate ion reaction; $\mu = 0.2$ ($NaClO_4$). Rate constants $k_{23}(H_2O)$ (solid line) and $k_{23}(D_2O)$ (dashed line) at 12.5°. The solid triangles represent k_{23} for the respective lanthanide–murexide reactions in (1) H_2O and (2) D_2O. $1/r$ is the reciprocal of the lanthanide ionic radius.

($\Delta S^{\ddagger}_{23} - \Delta S^{\ddagger}_{32}$) is positive.[8] However, it should be noted that the positive over-all entropy change for the the complexation reaction occurs because of a very negative value of $\Delta S^{\ddagger}_{32}$. For most lanthanides k_{32} in D_2O does not vary appreciably from k_{32} in H_2O. Thus specific values for k_{32} in D_2O are not recorded in Table II.

The ratio of k_{23} in H_2O to k_{23} in D_2O, $k_{23}(H_2O)/k_{23}(D_2O)$, can assume large values for certain lanthanides (*e.g.*, samarium, 6 ± 2; europium, 6 ± 2; gadolinium, 5 ± 2; ytterbium, 6 ± 3) and values of approximately 1 for others (lanthanum, terbium, and dysprosium). It is interesting that between gadolinium and terbium, which are next to each other in the series, $k_{23}(H_2O)/k_{23}(D_2O)$ drops from 5 ± 2 to approximately 1. The question of whether the ratio $k_{23}(H_2O)/k_{23}(D_2O)$ for a specific lanthanide is temperature dependent ($k_{23}(H_2O)$ and $k_{23}(D_2O)$ have different enthalpies of activation) is of importance. Experiments with lutetium show the following variation of $k_{23}(H_2O)/k_{23}(D_2O)$ with temperature: 3.8 ± 2 (7.5°), 4.5 ± 2 (12.5°), and 6.5 ± 2 (21.0°). Values of $k_{23}(H_2O)/k_{23}(D_2O)$ for gadolinium at 7.5 and 12.5° are 6.7 ± 2 and 5.3 ± 2, respectively. Therefore, it cannot be assumed that $k_{23}(H_2O)/k_{23}(D_2O)$ for a specific lanthanide is temperature independent.

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Discussion

It is tempting to associate the observed variations in the kinetic parameters measured for the lanthanide–anthranilate reactions with changes in the structural and kinetic properties of the solvated lanthanide ions. However, it must be remembered that these variations in kinetic parameters reflect changes occurring in the reactants Ln^{3+} and An^- and in the activated complex. The reactant ligand, anthranilate ion, is common to all of the reactions studied. It is possible that variations in $k_{23}(H_2O)/k_{23}(D_2O)$ could in part be attributed to internal hydrogen bonding in the anthranilate ion. Eigen and Eyring[9] have measured k_{12} and k_{21} (eq 1) to be 6.4×10^5 sec^{-1} and 5.8×10^{10} M^{-1} sec^{-1}, respectively. Values of k_{21} for other anions are: acetate, 5.1×10^{10} M^{-1} sec^{-1}; *m*-aminobenzoate, 4.6×10^{10} M^{-1} sec^{-1}; *p*-aminobenzoate, 3.7×10^{10} M^{-1} sec^{-1}. Therefore variations in $k_{23}(H_2O)/k_{23}(D_2O)$ cannot be rationalized on the basis of internal hydrogen bonding of the ligand. Variations in kinetic parameters across a series must then be related to changes in (i) the structural and/or kinetic properties of the solvated lanthanides and (ii) the activated complex for the complexation reaction, in which (i) and (ii) can be related. For example, a change in coordination number of the solvated lanthanide ion in the series could alter the mechanism of the complexation reaction.

The structural and kinetic properties of the solvated 3+ lanthanide ion have been of continuing interest. For many years it has been suggested that there is a coordination number change in the lanthanide series.[8] On the basis of changes in the apparent molal volume at infinite dilution,[10] conductivities at infinite dilution,[11–15] apparent molal heat capacities,[16] heats of dilution,[17] and *B* coefficients from viscosity data[18] on lanthanide salts in aqueous solution, it has been suggested that the change in coordination number occurs between neodymium and terbium. Arguments based on variations in the stability constants for lanthanide complexes suggest a coordination number change at gadolinium.[8,19–22] A recent X-ray study of EDTA complexes of the lanthanides shows coordination numbers of 9 and 8 for the europium and gadolinium complexes.[23] Powell and Rowlands have reported that complexation of lanthanides results in a change in coordination number at gadolinium or europium.[24] Structures for the solvated lanthanide have been suggested from spectral measurements of aqueous solutions containing europium salts.[25] From X-ray studies of concentrated erbium chloride solutions Brady suggested a highly ordered region of solvent about the lanthanide ion.[26] Thus there is evidence which is consistent with both a change in the coordination number of the solvated lanthanide in the series and a highly ordered solvent structure about the lanthanide ion.

The problem of the rate constant for the exchange of solvent at the solvated lanthanide center is of intrinsic interest itself. However, the relation of solvent exchange to the complexation reaction is of mechanistic interest. Marianelli[27] has investigated the rate of water exchange in aqueous gadolinium solution using oxygen-17 nmr broadening. The rate constant for solvent exchange at 298°K is $(9 \pm 2) \times 10^8$ sec^{-1} when a coordination number of 9 is assumed. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 3.2 ± 0.3 kcal/mol and -7 ± 4 eu, respectively. Reuben and Fiat have reported a rate constant for the solvent exchange of dysprosium in water as 6.3×10^7 sec^{-1}.[28]

Although the kinetics of a number of lanthanide complexation reactions have been studied, the detailed mechanism by which complexation occurs has not been established. Ultrasonic absorption measurements have been carried out on aqueous lanthanide sulfate solutions.[29,30] A single absorption occurs for each lanthanide–sulfate equilibrium studied. These observations seem to support a multistep mechanism, which involves diffusion-controlled ion-pair formation followed by the rate-determining displacement of water molecules by the ligand. The mechanism for chelation reactions, where two functional groups bind to the metal ion center, can be more complicated.[31] If the mechanism for substitution involves diffusion-controlled ion-pair formation followed by the rate-determining insertion of the functional groups of the bidentate ligand into the first coordination sphere of the metal ion, the insertion of the first or second functional group may be rate determining. In the former case k_{23} is equal to the product of the ion-pairing concentration quotient and the first-order rate constant for insertion of the first functional group into the coordination sphere. In the latter case k_{23} is equal to the product of the concentration quotients for both the ion pairing and insertion of the first functional group into the coordination sphere and the rate constant for

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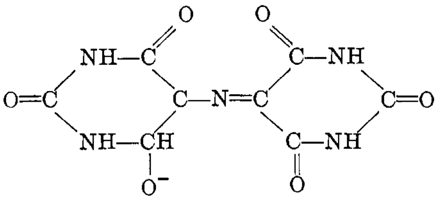
insertion of the second functional group into the coordination sphere of the lanthanide ion.

Geier has measured the bimolecular rate constants for complex formation between murexide



and the lanthanides in aqueous 0.1 M KNO_3 at 12° using the temperature-jump relaxation method.[32]

Figure 3 presents a comparison of the rate constants corresponding to k_{23} for the lanthanide–murexide system (open circles) with the rate constants obtained from the lanthanide–anthranilate study. There is of course no *a priori* reason why the trends should coincide. However, if there is to be any interpretation of the trends in $k_{23}(H_2O)$ in terms of the structural or kinetic properties of the solvated lanthanide ion, it is necessary that general trends be independent of the ligand. The two studies were carried out in different "inert" electrolytes and with different ligands. This work was carried out in $NaClO_4$ ($\mu = 0.2$) and Geier's work was in KNO_3 ($\mu = 0.1$). The samarium–anthranilic acid study at 12.5° was repeated using KNO_3. Both k_{23} and k_{32} are somewhat larger in KNO_3 than in $NaClO_4$: k_{23}, 6.3×10^7 M^{-1} sec^{-1} ($NaClO_4$) and 8×10^7 M^{-1} sec^{-1} (KNO_3); k_{32}, 2.6×10^4 sec^{-1} ($NaClO_4$) and 8×10^4 sec^{-1} (KNO_3). It has been found that nitrate coordinates with 3+ lanthanides,[8] but association also occurs between cerium and perchlorate.[8,33] For comparative purposes, values of $k_{23}(H_2O)$ and $k_{23}(D_2O)$ from this work for the gadolinium- and terbium-murexide systems at 12.5° and 0.2 M $NaClO_4$ are plotted as solid triangles in Figure 1.

Preliminary experiments on the gadolinium-, dysprosium-, and lutetium-acetate systems have been carried out. At 12.5° and $\mu = 0.2$ ($NaClO_4$) for the following lanthanides $k_{23}(H_2O)$, $k_{23}(D_2O)$, and $k_{23}(H_2O)/k_{23}(D_2O)$ are: gadolinium, 7.4×10^7 M^{-1} sec^{-1}, 0.7×10^7 M^{-1} sec^{-1}, 10; dysprosium, 9.2×10^7, 1.4×10^7, 7; and lutetium 13.4×10^7, 3.4×10^7, 4. Thus trends in $k_{23}(H_2O)$ and $k_{23}(H_2O)/k_{23}(D_2O)$ do not appear to be the same in the lanthanide–anthranilate and lanthanide–acetate systems. However, the differences may result from the fact that the first and second association constants for acetate–lanthanide complexes are nearly the same, and formation of the bisacetatolanthanide complex is being observed.

A comparison of the data from the lanthanide–murexide and –anthranilate reactions shows some common trends (Figure 3). The break between europium and dysprosium occurs in both reactions, while the regions from lanthanum to europium and from dysprosium to lutetium are not directly comparable. It has been suggested by Geier[32] that the rate of complex formation in the lanthanum to europium region is controlled by rapid solvent exchange which is independent of cation size, in the europium to erbium region by the solvent exchange which is dependent on the cation size, and in the erbium to lutetium region by the solvent exchange of a "cage" solvated lanthanide ion. Our results on the lanthanide–anthranilate reaction do not negate these proposals. However, preliminary results from the lanthanide–acetate system suggest that the detailed mechanism of the chelation process may play a role in determining the values of the bimolecular rate constants. The question of why the mechanism of the chelation reaction may change at certain points in the lanthanide series may be related to a changing coordination number or structure of the solvated lanthanide ion. However, an unequivocal statement cannot be made on this point.

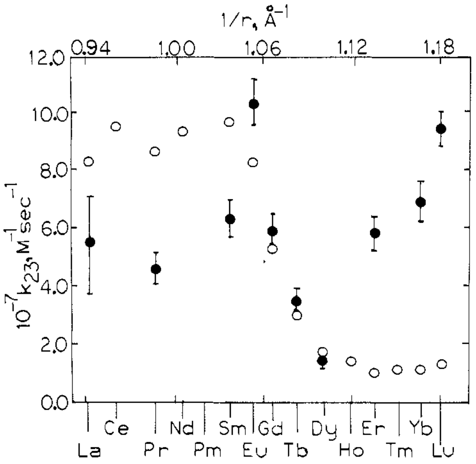


Figure 3.—Comparison of $k_{23}(H_2O)$ for this study (●, 12.5°, $\mu = 0.2$ ($NaClO_4$)) with those from ref 32 for the lanthanide–murexide reaction (○, 12°, $\mu = 0.1$ (KNO_3)). $1/r$ is the reciprocal of the lanthanide ionic radius.

Recently the kinetics of complex formation between lanthanides (La, Nd, Gd, Tb, Er, and Tm) and oxalate have been studied using the pressure-jump technique.[34] The trend and absolute values of the bimolecular rate constant for the process at 25° is essentially that observed for Geier at 12°. The activation parameters have also been determined and show a gradual increase from La (5.5 kcal/mol) to Tm (7.0 kcal/mol) with no break at gadolinium. Experiments on lutetium were not carried out. There appears to be no correspondence between the trends in $\Delta H^{\ddagger}$ observed for the lanthanide–oxalate and –anthranilate reactions.

It is interesting to note that the larger values of $\Delta H^{\ddagger}$ for the lanthanide–anthranilate reaction occur for the f^7(Gd) and f^{14}(Lu). This may reflect some special solvent structure for these species as compared to the other lanthanides studied. The varying values of $\Delta H^{\ddagger}_{23}$ and $\Delta S^{\ddagger}_{23}$ may reflect a changing coordination

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number. For example, if the mechanism for complex formation of gadolinium and lutetium complexes involved a change in coordination number from $\text{Ln}^{3+}_{\text{high}}$ to $\text{Ln}^{3+}_{\text{low}}$

$$\text{Ln}^{3+}_{\text{high}} \overset{K}{\rightleftharpoons} \text{Ln}^{3+}_{\text{low}} + n\text{H}_2\text{O} \tag{6}$$

$$\text{Ln}^{3+}_{\text{low}} + \text{An}^- \xrightarrow{k} \text{LnAn}^{2+} \tag{7}$$

the over-all rate constant $k_{23} = kK$ assuming eq 6 equilibrates rapidly compared to reaction 7. Thus $\Delta H^{\ddagger}_{23} = \Delta H^{\ddagger}_{7} + \Delta H_6$ and $\Delta S^{\ddagger}_{23} = \Delta S^{\ddagger}_{7} + \Delta S_6$, and ΔH_6 and ΔS_6 would both be positive. The conversion of cobalt(II) octahedral to tetrahedral complexes has positive values for the enthalpy and entropy changes.[35] These positive values added to the normal $\Delta H^{\ddagger}_{7}$ and $\Delta S^{\ddagger}_{7}$ would account for the more positive values of $\Delta H^{\ddagger}_{23}$ and $\Delta S^{\ddagger}_{23}$ for gadolinium and lutetium.

The observed trends in $k_{23}(\text{H}_2\text{O})$, $k_{23}(\text{D}_2\text{O})$, and consequently $k_{23}(\text{H}_2\text{O})/k_{23}(\text{D}_2\text{O})$ may arise in part from variations in the degree of hydrogen or deuterium bonding in the solvated lanthanide ions across the series. For example, the partial breakdown or loosening up of a hydrogen-bonded "cage" structure in H_2O relative to the analogous structure in D_2O could account for the variation in $k_{23}(\text{H}_2\text{O})/k_{23}(\text{D}_2\text{O})$. Values of $k_{23}(\text{H}_2\text{O})/k_{23}(\text{D}_2\text{O})$ of approximately 1 at terbium and dysprosium, occurring immediately after gadolinium where a coordination number change in H_2O is suggested, may result from a breakdown in both the hydrogen- and deuterium-bonding structures of the solvated lanthanide ion at this point.

Although the conclusions about the structure of the solvated lanthanide ion are drawn from variations in $k_{23}(\text{H}_2\text{O})$, $\Delta H^{\ddagger}_{23}$, $\Delta H^{\ddagger}_{23}$, and $k_{23}(\text{H}_2\text{O})/k_{23}(\text{D}_2\text{O})$ and are therefore speculative, it is felt that a number of interesting experiments are suggested from the results. The measurement of the kinetic parameters for a simple complexation reaction, such as lanthanide–acetate, would be extremely useful in determining the effect of chelation on the kinetic parameters. The determination of rate constants for solvent exchange, such as Marianelli[27] has done for gadolinium in H_2O, in D_2O and H_2O would be very important in answering the questions posed by the variation of $k_{23}(\text{H}_2\text{O})/k_{23}(\text{D}_2\text{O})$.

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