Inorganica Chimica Acta, 40 (1980) 91–98
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

The Rate and Mechanism for the Formation of Mixed Complexes between Lanthanoid EDTA and Pyridine-2-Carboxylate or 8-Hydroxyquinoline-5-sulfonate

CARL-GUSTAV EKSTRÖM, LENA NILSSON
Division of Physical Chemistry 1, Chemical Center, University of Lund, S-220 07 Lund, Sweden

IAN A. DUNCAN** and INGMAR GRENTHE*
Department of Inorganic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden

Received September 12, 1979

Equilibrium constants as well as the rate and mechanism of reactions of the type $MY(H_2O)_n + L \rightleftarrows MYL(H_2O)_{n-x} + xH_2O$ *have been studied. MY denotes EDTA complexes of various lanthanoids, while L is either pyridine-2-carboxylate (PIC) or 8-hydroxyquinoline-5 sulfonate (OXS). The PIC complexes were studied at 25 °C in 0.5* M $NaClO_4$, *while the experimental data for the OXS systems were taken from Furrer and recalculated. The equilibrium constants were determined by a standard potentiometric technique* viz. *the determination of the concentration of free hydrogen ion. The kinetic data were obtained by using the T-jump technique, with spectrophotometric detection. Two possible stoichiometric mechanisms were compared: (*i*) where the rate of ring closure or opening is of about the same magnitude as that of the other reaction steps, and (*ii*) where the former rate is much more rapid than any of the latter. Only the first mechanism, which consists of two consecutive steps, each with two parallel pathways, one of which is hydrogen ion dependent, was in agreement with the experimental observations. The rate constants for the unidentate association of L to MY were nearly independent of the entering ligand, indicating a dissociative interchange mechanism at least for the* pre-*Tb elements. The rate of chelate ring closure was dependent on both the ligand and the size of the lanthanoid ion.*

Introduction

A considerable amount of information about the thermodynamics of rare earth complexation reactions has been published over the last decades [1–4]. A popular theme among rare earth chemists has been to study how the chemical properties of rare earth complexes are influenced by the size of the central ion and the geometry of the ligands. Both thermodynamic and structural data have been used in investigations of this type. The rates and mechanisms of the complexation reactions are dependent on the coordination geometry. Kinetic data may thus be used to obtain additional information of this kind.

There are comparatively few studies published about the rates and mechanisms of ligand substitution reactions among the lanthanoids [5, 6]. Most investigations have been confined to measurements of rates of dissociation or rates of exchange of polydentate ligands. These are conjugate bases of weak acids, hence the rates are in general strongly pH dependent. The occurrence of parallel pathways in the substitution reaction and the fact that a polydentate ligand is involved makes it difficult to interpret the rate law in terms of elementary reactions. These points have been elaborated by Ekström [7] and Ryhl [8]. Consequently, uni- or bidentate ligands with low basicity should be preferred, if mechanistic information about lanthanoid(III) aquo ions as reaction centra is desired. However, complexes of this type are fairly weak and hence too labile to study with the conventional temperature jump equipment.

The kinetic and mechanistic data published are not always consistent. However, most authors agree that a complex formation reaction by a bidentate ligand is best described by the following dissociative or interchange mechanism, which was first suggested by Eigen [9, 10].

$$M(aq) + A\text{–}B(aq) \overset{\text{fast equilibrium}}{\rightleftarrows} M(H_2O)A\text{–}B(aq) \qquad (1)$$

---

*To whom correspondence should be addressed.

**Now at the Royal Institution, 21 Albemarle Street, London, U.K.

$$M(H_2O)A{-}B(aq) \underset{k_{-0}}{\overset{k_0}{\rightleftarrows}} M{-}A{-}B(aq) \qquad (2)$$

$$M{-}A{-}B(aq) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} M\left\langle\begin{array}{c} A \\ B \end{array}\right| \qquad (3)$$

M(aq) denotes the hydrated lanthanoid(III) ion and A–B a chelate forming ligand with A and B as donor atoms. Charges have been omitted for brevity. The reaction (1) is the fast formation of an outer sphere ion pair. The reaction (2) is the replacement of a coordinated water molecule by one of the donor atoms in the ligand. Reaction (3) describes the ring closure reaction when a chelate is formed. The stoichiometric mechanism is more complicated if the reactants are coupled to fast protolytic equilibria.

The rate constants k_+ and k_- for the overall process

$$M + A{-}B \underset{k_-}{\overset{k_+}{\rightleftarrows}} M(AB)$$

can be measured experimentally. They are equal to

$$k_+ = k_0 k_1 K_{os}\,(1 + K_{os}([M] + [A{-}B]))^{-1} \times$$

$$(k_1 + k_{-0})^{-1} \approx k_0 k_1 K_{os}(k_1 + k_{-0})^{-1} \qquad (4)$$

$$k_- = k_{-0} k_{-1}(k_1 + k_{-0})^{-1} \qquad (5)$$

if reaction (1) is much faster than the following reactions. The validity of this assumption has been discussed by Petrucci *et al.* [11].

The outer sphere equilibrium constant, K_{OS}, cannot be measured experimentally but can be estimated for instance from the Fuoss equation [12]. For a number of metal ions, including the rare earths, k_0 has been determined from the rate of water exchange determined by NMR methods [13] and also by other types of experiments [6]. The rate constants for ring closure/opening can be estimated from Eqns. (4) and (5) and from the known value of K_0, ($K_0 = k_0/k_{-0}$), which is the stability constant where only one donor atom of the ligand is bound to the complex (see Discussion).

One of the aims of the present investigation is to decide if and when the chelate ring closure is of importance for the overall rate of complex formation. For purely geometrical reasons the probability of a rate determining ring closure becomes larger the more crowded the complex and the more sterically demanding the ligand. This is the case in complexes having several coordinated ligands or where the ligands contain many donor atoms. The steric crowding in a complex is expected to increase as the size of the central atom decreases. In this and a subsequent study we have used lanthanoid EDTA complexes, denoted MY, as substrates in order to study the rates and mechanism of reactions of the type

$$MY(H_2O)_n + L \rightleftarrows MYL(H_2O)_{n-x} + xH_2O \qquad (6)$$

Reactions of this type have previously been studied by Furrer [14] using 8-hydroxyquinoline-5-sulfonate (OXS) or tetramethylmurexide as the ligand L. He describes the rate data using a mechanism of the Eigen type, where the rate determining step is the rate of water exchange. We have extended these studies to include two other bidentate ligands, *viz.* pyridine-2-carboxylate (picolinate) and 5-sulfosalicylate. The experimental work was carried out at 25 °C in solutions of constant ionic strength, $I = 0.5\ M$, using sodium perchlorate as the neutral salt. To calculate the rate constant the stability constant of the mixed complex must be known.

Determination of Stability Constants of Mixed Complexes

The stability constants of the mixed MY picolinate complexes were determined by a standard potentiometric method *viz.* the determination of the free hydrogen ion concentration. The stability constants were calculated from corresponding values of the average ligand number $\bar{n}$, and the free ligand concentration using standard methods.

Experimental

Chemicals

All chemicals used were of analytical grade. The lanthanoid oxides (Research Chemicals) had a purity greater than 99.9%. The purity of the picolinic acid (Fluka) was checked by an equivalent weight determination (found 123.0, calcd. 123.1). Stock solution of the various lanthanoid EDTA complexes were prepared in two ways, either by dissolving solid NaMY or from mixing standardized solutions of lanthanoid perchlorate, Na_2H_2EDTA, sodium hydroxide and sodium perchlorate.

Potentiometric Measurements

The protonation constant of the ligand and the equilibrium constants of the mixed complexes were determined by measuring the emf, *E*, of galvanic cells of the following type.

Ag, AgCl	$0.490\ M\ NaClO_4$ $0.010\ M$ NaCl	C_{MY}MY C_L Na-picolinate C_H picolinic acid $0.500\ M - (C_{MY} + C_L)$ $NaClO_4$	glass-electrode

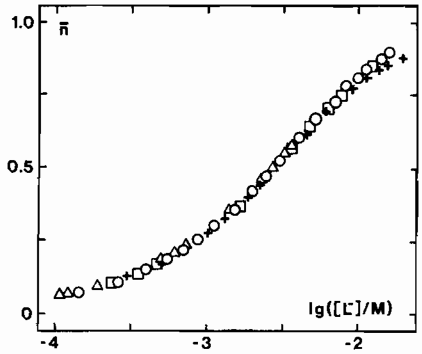


Fig. 1. $\bar{n}$ *vs.* lg[L^-] for ErEDTA picolinate where the symbols denote: ○ C_{MY} = 15 m*M* and C_L/C_H = 3:1, △ C_{MY} = 20 m*M* and C_L/C_H = 3:1, □ C_{MY} = 20 m*M* and C_L/C_H = 1:1, + C_{MY} = 10 m*M* and C_L/C_H = 1:1.

TABLE I. The Stability Constants for the Lanthanoid EDTA Picolinate Complexes. The protonation constant $\lg(\beta_{011}/M^{-1}) = 5.25 \pm 0.01$. All errors are equal to 3σ, where σ is the standard deviation determined in the least-squares refinement.

M	$\lg(\beta_{101}/M^{-1})$
Pr	2.36 ± 0.01
Nd	2.53 ± 0.01
Sm	2.77 ± 0.01
Gd	2.68 ± 0.01
Dy	2.53 ± 0.01
Er	2.59 ± 0.01
Yb	2.84 ± 0.02
Lu	3.11 ± 0.01

The protonation constant of picolinate, β_{011}, was determined in solutions with $C_{MY} = 0$. The other potentiometric titrations were made at two constant values of C_{MY} usually 10 and 20 m*M*. The concentration of picolinate ions was varied by a titration procedure using varying buffer concentrations (with ratios C_L/C_H equal to 3:1, 1:1, 1:3) for each value of C_{MY}. The experimental data for the ErY picolinate system in the form of $\bar{n}$ *vs.* lg [L^-] are shown in Fig. 1. These data and those for the other systems indicated that only one mixed complex MYL was formed. Most of the emf-titrations were made by using an automatic titration system [15].

Results

The stability constant for the reaction MY + L ⇄ MYL is denoted by β_{101}. The constant is evaluated from the corresponding values of the average ligand number $\bar{n}$ and the free ligand concentration L. The result of a least-squares refinement (Leta U Grop) is given in Table I. The protonation constant for picolinate is equal to $\beta_{011}/M^{-1} = (1.78 \pm 0.03)\ 10^5$. All errors limits are quoted to 3σ, where σ is the estimated standard deviation in the least-squares refinement.

Kinetic Studies

The complex formation reactions (6) are rapid. Hence a relaxation method was used, *viz.* the temperature-jump technique.

Experimental

The *T*-jump equipment was the SBA-7 model from Studiengesellschaft mbH Göttingen, Germany with spectrophotometric detection. The observed rate constants were evaluated from transmission *vs.* time curves obtained on a storage oscilloscope (Tektronix, Type 549). The main reaction was followed by using a suitable indicator. Three different indicators were used, methyl red, bromo cresol green, and bromo phenol blue. The total concentration of the reactants C_{MY} and C_L was in the range 3–10 m*M* and 5–90 m*M* respectively. The concentration of the indicator was 0.03–0.08 m*M*. The hydrogen ion concentration range was $3.5 < -\lg(h/\mathrm{M}) < 6$. The hydrogen ion concentration at equilibrium was measured using a galvanic cell of the type described in the preceding section.

Determination of Rate Constants for the Overall Reaction

The stoichiometry of the overall reaction with the coupled protolytic reactions and the indicator system is

$$\begin{array}{lllll} \mathrm{MYL} \rightleftharpoons \mathrm{MY} + & \mathrm{L} & & & \\ & \vdots & & & \\ & \mathrm{L} + & \mathrm{H} \rightleftharpoons \mathrm{HL} & & \\ & & \vdots & & \\ & & \mathrm{H} + \mathrm{In} \rightleftharpoons \mathrm{HIn} & & \end{array} \qquad (7)$$

where HIn/In is the indicator system with a protonation constant β_{In}. The observed rate constant k_{obs} for the overall process can be written as [7]

$$k_{obs} = f_c \cdot f_k \qquad (8)$$

where f_c is a function of the equilibrium concentrations and the equilibrium constants, but independent of the mechanism, while f_k is a function not only of the concentrations and the equilibrium constants but also of the rate constants (*cf.* eqn. 11 below). Information about the reaction mechanism may therefore be deduced from f_k. The experimental data consist of values of k_{obs} from solutions where the equilibrium concentrations h, [L], and [MY] have been systematically varied. The rate of reaction is much larger for the light lanthanoids than for the heavy ones and approaches the time resolution of the equipment for the Pr system. This results in fairly large experimental errors in the values of k_{obs} for the lighter lanthanoids.

Determination of the Function f_k

The function f_k is calculated from eqn. (8). For a series of coupled reactions of the type (7) the function f_c is equal to:

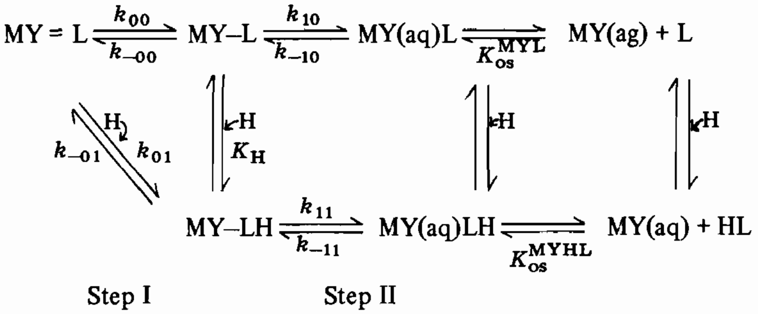
$$f_c = 1 + [L]\beta_{101} + [MY]\beta_{101}(1 + h\beta_{011})^{-1} + \\ + [MY]\,[L]\beta_{101}\delta \qquad (9)$$

where $\delta = [(h\beta_{011})^{-1} + 1]^{-2}[h + [L]h\beta_{011} + [In]h\beta_{In}]^{-1}$ and all concentrations are equilibrium concentrations. f_k turned out to be a function of h only. Plots of f_k *vs.* h. are shown in Fig. 2. From the function f_k the stoichiometric mechanism may be deduced as follows:

Deduction of Reaction Mechanism

Two possible stoichiometric mechanisms will be compared, (*i*) where the rate of ring closure/opening is of about the same magnitude as that of the other reactions and (*ii*) where the ring closure/opening is very rapid.

(*i*): The first mechanism can be written as



(10)

where the vertical arrows denote fast protonation reactions, the first one with an equilibrium constant, K_H. The formation of outer-sphere complexes MY(aq)L and MY(aq)HL are denoted by K_{os}^{MYL} and K_{os}^{MYHL} respectively. A rate constant in the stoichiometric mechanism is denoted by k_{ij} whence k_{ij}^* in eqn. (11) below denotes the corresponding formal rate constant calculated from the experimental rate equation. The mechanism in (10) consists of two consecutive steps, I and II, each of which contains two parallel reaction paths, *viz.* one pH dependent

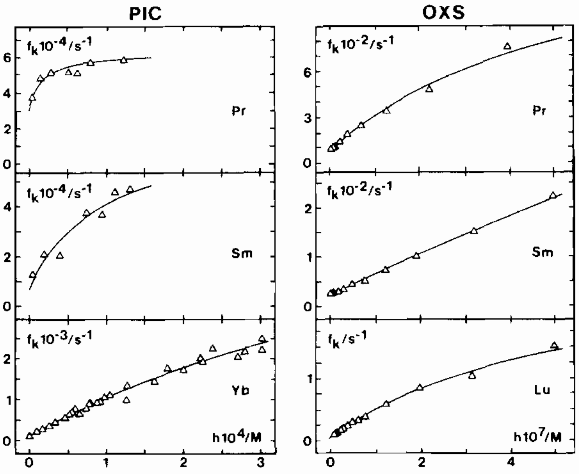


Fig. 2. The experimental data of f_k *vs.* h for some lanthanoid EDTA picolinates (PIC) to the left and some for OXS systems to the right. The full-drawn curves represent the calculated function f_k *vs.* h using mechanism *i*.

and one pH independent. This point will be further discussed in the following.

If the intermediates in (10) are in a steady state then the function f_k calculated from eqn. (8) for the above mechanism can be written as (*cf.*) [7]:

$$f_k^{-1} = (k_{00}^* + k_{01}^*\,h)^{-1} + (k_{10}^* + k_{11}^*\,h)^{-1} \qquad (11)$$

where $k_{00}^* = k_{00}$, $k_{10}^* = k_{10}K_{00}$, $k_{11}^* = k_{11}K_{00}K_H$, $k_{01}^* = k_{01}$. K_{00} denotes the equilibrium constant for the ring opening.

(*ii*) The second mechanism has been used by Furrer [14] to describe the kinetics of the lanthanoid EDTA OXS and tetramethylmurexide systems. Using the notations of Furrer the mechanism can be written:

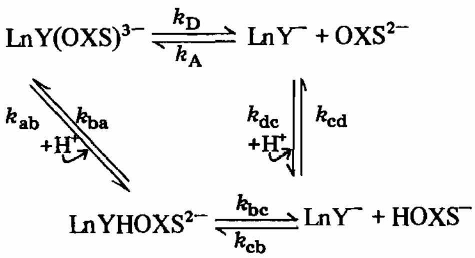


TABLE II. Values of $b\ a^{-1}$ for the OXS and the PIC Systems. Data for the OXS systems are from Ref. [14].

M	OXS lg ($b\ a^{-1}/M^{-1}$)	PIC lg ($b\ a^{-1}/M^{-1}$)
La	6.9	
Pr	7.6	5.0
Nd	7.3	5.3
Sm	7.3	5.0
Eu	7.0	
Gd	7.0	4.0
Dy	7.2	4.8
Er	7.6	5.0
Yb	7.7	5.1
Lu	8.0	5.6

This mechanism leads to the following expression for the observed rate constant for the association reaction.

$$\tau^{-1} = k_{\mathrm{obs}} = f_{\mathrm{c}}(k_{\mathrm{A}}/K_{\mathrm{LnYOXS}} + (k^{*}K_{\mathrm{HOXS}}/K_{\mathrm{LnYOXS}})h)$$

where $k^{*} = k_{\mathrm{cb}}k_{\mathrm{ba}}\,(k_{\mathrm{ba}} + k_{\mathrm{bc}})^{-1}$

The equation shows a linear relationship between f_{k} ($= k_{\mathrm{obs}}/f_{\mathrm{c}}$) and h from which the constant k_{A} and k^{*} may be determined. k_{A} is the product of an outer sphere equilibrium constant and the rate constant for water exchange, if the Eigen mechanism is valid. In the present case where both the reactants have negative charges, it might be expected that outer sphere complexes are of minor importance. If so, k_{A} may be regarded as a direct measure of the water exchange rate without any significant correction for individual K_{os} values, *cf.* the following discussion of the rate constants.

A choice between the two mechanisms can be made by plotting f_{k} *vs.* h. Such plots are given in Fig. 2 both for MY(PIC) and MY(OXS). The experimental errors in f_{k} are fairly large at the higher values of h but nevertheless the first mechanism (*i*) seems to be in closer agreement with the experimental observations in both cases, since *all* the plots are distinctly nonlinear (with the possible exception of SmY(OXS)).

Determination of Rate Constants

The experimental function f_{k} can be described in the form

$$f_{\mathrm{k}} = (a + bh)(1 + ch)^{-1} \qquad (12)$$

The constant a has been determined as the intercept in plots of f_{k} *vs.* h in a fairly small h-region, 10^{-6}–$10^{-4.5}$ M, (PIC), where the function does not deviate too much from a straight line. By rearranging eqn. (12) into

$$h(f_{\mathrm{k}} - a)^{-1} = (b - ac)^{-1} + hc(b - ac)^{-1} \qquad (13)$$

one can evaluate the constants b and c. This method was also used to determine a, b and c in the MY(OXS) systems from data in ref [14].

In the MY(PIC) systems the constant a could be obtained with a reasonable degree of accuracy, 5–10% only for M = Yb. The constant c, which is responsible for the non linear shape, could in general only be obtained with rather low accuracy. The experimental error is due to the high rates of reaction. This limited precision of the rate data for the PIC system makes it difficult to determine all three parameters a, b and c, especially for the lighter lanthanoids. However, the ratio b/a was found to be approximately constant throughout the lanthanoid

TABLE III. Values of the Parameters a, b and c for the OXS Systems and the PIC Systems.

	OXS			PIC		
	$10^{-1}\ a/s^{-1}$	$10^{-9}\ b/s^{-1}\ M^{-1}$	$10^{-6}\ c/M^{-1}$	$10^{-3}\ a/s^{-1}$	$10^{-8}\ b/s^{-1}\ M^{-1}$	$10^{-4}\ c/M^{-1}$
La	210 ± 8	17 ± 0.7	0.66 ± 0.34			
Pr	7.7 ± 0.1	2.9 ± 0.1	1.8 ± 0.4	31 ± 3	36 ± 3	5.7 ± 0.5
Nd	9.2 ± 0.2	1.9 ± 0.1	0.25 ± 0.18	13 ± 3	15 ± 3	3.1 ± 0.9
Sm	2.2 ± 0.1	0.44 ± 0.01	0.19 ± 0.12	6.7 ± 1.1	7.9 ± 1.3	1.1 ± 0.3
Eu	3.9 ± 0.1	0.35 ± 0.01	1.3 ± 0.5			
Gd	2.4 ± 0.1	0.21 ± 0.01	0.49 ± 0.14	7.5 ± 1.0	8.8 ± 1.1	4.5 ± 0.7
Dy	0.52 ± 0.02	0.089 ± 0.004	1.3 ± 0.4	3.3 ± 0.5	3.8 ± 0.6	3.0 ± 0.6
Er	0.080 ± 0.002	0.047 ± 0.001	3.2 ± 0.5	0.61 ± 0.07	0.72 ± 0.09	1.6 ± 0.3
Yb	0.010 ± 0.001	0.0056 ± 0.0004	2.0 ± 1.0	0.095 ± 0.006	0.11 ± 0.01	0.14 ± 0.02
Lu	0.0050 ± 0.0003	0.0054 ± 0.0003	1.8 ± 0.2	0.047 ± 0.002	0.055 ± 0.002	0.25 ± 0.03

series, see Table II. Hence, we preferred to use a two-parameter approximation in which the ratio b/a was assumed to be constant (equal to the value found in the Yb-system) for all lanthanoids in order to describe the rate data. A similar approximation has been used by Ekström [7] in his study of rare earth dipicolinates.

Rearrangement of eqn. (13) gives

$$(1 + (b/a)_{\mathrm{Yb}}h)f_{\mathrm{k}}^{-1} = 1/a + (c/a)h \tag{14}$$

By plotting the left hand side of (14) *vs.* h one can determine the constants a and c, while the constant b is calculated from the known ratio $(b/a)_{\mathrm{Yb}}$. The values of a, b and c are given in Table III.

The reason for the large uncertainty in c is that one of the consecutive steps, I or II in (10) has a much larger rate of reaction than the other. This makes it difficult to determine the rate constants for the rapid step. However, since plots of f_{k} *vs.* h are non linear there must be two consecutive steps in the mechanism. At least one of these steps must contain two parallel pathways, one of which is hydrogen ion dependent. The f_{k} *vs.* h plots have a non zero intercept for $h = 0$, which indicates that the protonated pathway does not exist in isolation. We also assume that the only measurable part of the rapid step is the non-protonated path and even this is determined with rather low accuracy.

Identification of the Experimental Parameters a, b *and* c

It remains to find out how a, b and c are coupled to the two consecutive steps in the mechanism. We tried to solve this problem by comparing the OXS and the PIC systems. The expression (11) can be written

$$f_{\mathrm{k}} = [k^{*}_{00}k^{*}_{10}D + (k^{*}_{00}k^{*}_{11} + k^{*}_{01}k^{*}_{10})Dh] \times [1 + (k^{*}_{01} + k^{*}_{11})Dh]^{-1} \tag{15}$$

where $D = (k^{*}_{00} + k^{*}_{10})^{-1}$ and the term $k^{*}_{01}\mathrm{k}^{*}_{11}h^{2}$ is neglected. This means that only one of the two protonated paths could be determined, *i.e.* one of the terms k^{*}_{01} or k^{*}_{11} is much smaller than the other. From a comparison of (12) and (15) it follows that $b/c = k^{*}_{00}$ or k^{*}_{10}, $a(1 - ac/b)^{-1} = k^{*}_{10}$ or k^{*}_{00} and $b(1 - ac/b)^{-1} = k^{*}_{11}$ or k^{*}_{01}. In each of these three pairs of alternatives the first one is true if $k^{*}_{01} \ll k^{*}_{11}$ and the second one if $k^{*}_{11} \ll k^{*}_{01}$. In order to make a choice between the two alternatives we compared the magnitude of the quantities β_{101} (b/c) and β_{101} $a(1 - ac/b)^{-1}$ and their variation through the lanthanoid series for both the PIC and the OXS systems. For a dissociative interchange (Eigen) mechanism we expect step II in (10) to be largely independent of the entering ligand, while the ring closure, step I, ought to be ligand dependent. This is only compatible with model 1, $k^{*}_{01} \ll k^{*}_{11}$ for the PIC systems and model 2, $k^{*}_{11} \ll k^{*}_{01}$ for the OXS systems.

The rate constants for the complex formation for the two alternatives of the mechanism (10) are given in Table IV, where lg $k^{*}_{-00} = \lg(\beta_{101}\cdot k_{00})$, lg $k^{*}_{-01} = \lg(\beta_{101}\ k_{01})$, lg $k^{*}_{-10} = \lg(\mathrm{K}_{\mathrm{os}}^{\mathrm{MYL}}\ k_{-10})$ and lg $k^{*}_{-11} = \lg(\mathrm{K}_{\mathrm{os}}^{\mathrm{MYHL}}k_{-11})$.

Reassessment of the Reaction Mechanism of the MY(OXS) Systems

Furrer [14] has studied the rate and mechanism of the MY(OXS) systems and interpreted his data according to the mechanism *ii*. He has used an expression for the observed rate constant derived by Karlen. This expression does not seem to be quite correct but the error has only a small influence on the rate constants calculated. Figure 2 shows some of the experimental values of f_{k} obtained by Furrer and curves calculated by using the mechanism *i* with the rate constants given in Table IV (both alternatives in mechanism *i* discussed above give identical values of f_{k}). The rate data in Figure 2 indicate that mechanism *i* is to be preferred to mechanism *ii.*

We suggest that a choice between models 1 and 2 (Table IV) in mechanism *i* can be made by the following reasoning: The association rate constants in model 1 differ substantially, up to 1.6 lg units between the OXS ligand and its protonated form. We do not think it likely that such large differences are due to differences in K_{os}. Furthermore model 1 results in values of the association rate constant (k^{*}_{-10} and k^{*}_{-11}) which differ substantially between the OXS and the PIC systems, while on the other hand the rate constants for ring closure (k^{*}_{-00}) for the two ligands are approximately the same. One expects a difference in geometry between the two ligands to cause differences in the rate constant for ring closure, (k^{*}_{-00}) rather than for the first step of complex formation (k^{*}_{-10} and k^{*}_{-11}). Model 2 on the other hand results in a value of k^{*}_{-10} for OXS which is in fairly good agreement with the values found in the PIC systems, while the rate of ring closure differs considerably between the two systems.

It is true that the experimental conditions of temperature and ionic strength are not the same in the two systems, nevertheless we feel that the facts above clearly indicate that model 2 should be preferred to model 1 in the OXS system.

Discussion

The largest equilibrium constants for the formation of MYPIC complexes are found for the smallest lanthanoids *viz.* Yb and Lu, indicating the absence of steric effects in the formation of mixed com-

TABLE IV. Values of the Association Rate Constants for Step I and II for the OXS and PIC Systems. The constants for the OXS systems have been recalculated from the experimental data of Furrer [14]. The constants k^*_{-10} and k^*_{-11} are equal to $k_{-10} \cdot K_{os}^{MYL}$ and $k_{-11} \cdot K_{os}^{MYHL}$, respectively. The errors are graphically estimated maximum errors in the various rate constants.

OXS				PIC		
Model 1	$(k^*_{01} \ll k^*_{11})$ $\lg(k^*_{-00}/s^{-1}\ M^{-1})$	$\lg(k^*_{-10}/s^{-1}\ M^{-1})$	$\lg(k^*_{-11}/s^{-1}\ M^{-1})$	*Model 1* $(k^*_{01} \ll k^*_{11})$ $\lg(k^*_{-00}/s^{-1}\ M^{-1})$	$\lg(k^*_{-10}/s^{-1}\ M^{-1})$	$\lg(k^*_{-11}/s^{-1}\ M^{-1})$
Model 2	$(k_{11} \ll k^*_{01})$ $\lg(k^*_{-10}/s^{-1}\ M^{-1})$	$\lg(k^*_{-00}/s^{-1}\ M^{-1})$	$\lg(k^*_{-01}/s^{-1}\ M^{-1})$	*Model 2* $(k^*_{11} \ll k^*_{01})$ $\lg(k^*_{-10}/s^{-1}\ M^{-1})$	$\lg(k^*_{-00}/s^{-1}\ M^{-1})$	$\lg(k^*_{-01}/s^{-1}\ M^{-1})$
La	7.8 ± 0.1	6.7 ± 0.1	5.1 ± 0.1			
Pr	7.2 ± 0.1	5.9 ± 0.1	4.9 ± 0.1	7.2 ± 0.2	7.1 ± 0.2	7.0 ± 0.2
Nd	7.9 ± 0.1	6.0 ± 0.1	4.8 ± 0.1	7.2 ± 0.2	6.8 ± 0.2	6.6 ± 0.2
Sm	7.7 ± 0.1	5.7 ± 0.1	4.4 ± 0.1	7.6 ± 0.2	6.6 ± 0.2	6.5 ± 0.2
Eu	6.8 ± 0.1	6.1 ± 0.1	4.5 ± 0.1			
Gd	7.0 ± 0.1	5.8 ± 0.1	4.1 ± 0.1	7.0 ± 0.1	6.8 ± 0.1	6.6 ± 0.1
Dy	6.4 ± 0.1	5.3 ± 0.1	4.0 ± 0.1	6.7 ± 0.1	6.2 ± 0.1	6.0 ± 0.1
Er	5.8 ± 0.1	4.6 ± 0.1	3.8 ± 0.1	6.3 ± 0.1	5.4 ± 0.1	5.3 ± 0.1
Yb	5.3 ± 0.1	3.9 ± 0.1	3.0 ± 0.1	6.7 ± 0.1	4.8 ± 0.1	4.6 ± 0.1
Lu	5.3 ± 0.1	3.5 ± 0.1	3.0 ± 0.1	6.5 ± 0.1	4.8 ± 0.1	4.6 ± 0.1

plexes [16]. This conclusion is further corroborated by stability constants for the M–PIC systems [18]. We have used the data published to calculate a value of $\beta_4 = (2.86 \pm 0.15)\ 10^{11}\ M^{-4}$, for the formation of the $HoPIC_4$ complex (the authors have reported values for only three stability constants, even though their experimental data clearly indicate that four complexes are formed). If charge and steric effects are absent, the fourth stepwise stability constant K_4, for the formation of $HoPIC_4$, should be smaller than the corresponding constant β_{101} for the formation of the mixed HoYPIC complex by a statistical factor of four. The ratio β_{101}/K_4 is equal to 360/45 = 8, where β_{101} is estimated from the values of the corresponding Dy and Er stability constants given in Table I. The mixed MYPIC complexes seem to be formed more easily than the corresponding $MPIC_4$ complexes, indicating that the steric hindrance of EDTA is smaller than that of three bidentate PIC ligands. On the other hand data published for the formation of the MYOXS [19, 20] systems indicate a steric hindrance to the formation of complexes with the smallest lanthanoid ions. The kinetic data to be discussed below are also consistent with this interpretation.

From the experimental kinetic data we can conclude that both the PIC and the OXS systems are best described by a two-step reaction mechanism which takes the rate of chelate ring closure/opening into account.

From data in Table IV and estimated [12] values of K_{os} one finds that k_{-10} and k_{-11} are nearly constant for a given lanthanoid, indicating a dissociative interchange (or Eigen) mechanism. The only rates of water exchange known from the literature (*e.g.* see Refs. 6, 13) refer to lanthanoid aquo ions. It is interesting to note that the values of the constants k^*_{-10} and k^*_{-11} do not differ much from these rates for the light lanthanoids (approx. a factor of ten). However, for the heavy elements, the rate of substitution is approximately three orders of magnitude smaller in MY than in M(aq). A possible explanation for this finding might be the change of structure of the MY complexes indicated by several other types of measurements [21, 22]. A decrease in the number of coordinated water molecules in the heaviest EDTA complexes thus results in a decreased lability of the remaining water molecules and possibly also to a charge in mechanism from dissociative to associative [14].

The rate constant for the ring-closure, k_{-00} is equal to $k^*_{-00}/(K_{OS} \cdot K_{-10})$, where K_{-10} is the equilibrium constant for the formation of a mixed complex where L is bonded through only *one* of its donor atoms. An estimate of the magnitude of $K_{OS} \cdot K_{-10}$ and its variation through the rare earth series may be obtained from stability constants for the formation of mixed MY–acetate complexes.

Reuben [22] *et al.* have reported values for the reaction

$$MY + Ac \rightleftarrows MY(Ac)$$

which are equal to 5, 10 and 2.5 M^{-1} for M = Pr, Gd, and Yb, respectively. These data together with the values of k^{*}_{-00} indicate that k_{-00} is considerably lower for the smaller lanthanoids than for the larger ones, presumably due to steric crowding in the mixed complex. Some additional information will be reported in a subsequent paper, dealing with the rates and mechanism for the formation of mixed complexes between MY and 5-sulfosalicylate.

Acknowledgements

The financial support of this work by grants from the Swedish Natural Science Research Council, British Council and Kungl. Fysiografiska Sällskapet is gratefully acknowledged. The authors also wish to thank Professor Ido Leden for stimulating discussions and helpful criticism of the manuscript.

Supplementary Material Available

A listing of experimental data in the form of $\bar{n}$ *vs.* lg $[L^{-}]$ (7 pages) and a listing of the primary experimental data of the kinetic measurements (4 pages).

References

1 I. Grenthe, *Acta Chem. Scand., 18,* 293 (1964).
2 D. G. J. Karraker, *Chem. Educ., 47,* 424 (1970).
3 G. R. Choppin, *Pure Appl. Chem., 27,* 23 (1971).
4 T. Moeller, E. R. Birnbaum, J. H. Forsberg & R. B. Gayhart, *Prog. in the Science and Technology of the Rare Earths,* Vol. 3, 61 (1968).
5 S. S. Yun & J. L. Bear, *J. Inorg. Nucl. Chem., 38,* 1041 (1976).
6 N. Puride & M. M. Farrow, *Coord. Chem. Rev., 11,* 189 (1973) and refs. therein.
7 C.-G. Ekström, *Kinetisk undersökning av lantanoidernas dipikolinatkomplex, Diss.,* University of Lund, Lund (1978).
8 T. Ryhl, *Studies on dissociation rates of some lanthanoid EDTA Complexes, Diss.,* University of Lund, Lund (1971).
9 H. Diebler and M. Eigen, *Z. Phys. Chem., 20,* 229 (1959).
10 M. Eigen, W, Kruse, G. Maass & L. DeMayer, 'Progress in Reaction Kinetics' (Edited by G. Porter), vol. 2, Chapter 6, Macmillan, New York (1964).
11 G. S. Darbari, F. Fittipaldi, S. Petrucci and P. Hemmes, *Acustica, 25,* 125 (1971).
12 R. M. Fuoss, *J. Am. Chem Soc., 80,* 5059 (1958).
13 J. Reuben & D. Fiat, *J. Chem. Phys., 51,* 4918 (1969).
14 M. Furrer, *Kinetik von schnellen Mischkomplexreaktionen der seltenen Erden,* Diss., Eidgenössischen Technischen Hochschule Zürich (1974).
15 T. Wallin. To be published.
16 I. Grenthe, *J. Am. Chem. Soc., 83,* 360 (1961).
17 T. F. Gritmon, M. P. Goedken and G. R. Choppin, *J. Inorg. Nucl. Chem., 39,* 2021 (1977).
18 B. F. Freasier, A. G. Oberg and W. W. Wendtlandt, *J. Phys. Chem., 62,* 700 (1958).
19 G. Geier and U. Karlen, *Helv. Chim. Acta, 54,* 135 (1971).
20 G. Geier, U. Karlen and A. v. Zelewsky, *Helv. Chim. Acta, 52,* 1967 (1969).
21 H. Ots, *Acta Chem. Scand., 27,* 2351 (1973).
22 G. A. Elgavish and J. Reuben, *J. Am. Chem. Soc., 98,* 4755 (1976).