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Kinetic Studies of Mixed Complexes between Lanthanoid EDTA and 5-Sulfosalicylate

CARL-GUSTAV EKSTRÖM, LENA NILSSON

Division of Physical Chemistry 1, Chemical Center, University of Lund, S-220 07 Lund, Sweden

and INGMAR GRENTHE*

Department of Inorganic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden

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The Eigen–Diebler mechanism has been tested for mixed complexes between lanthanoid EDTA (ethylenediaminetetraacetate) and 5-sulfosalicylate denoted by MY(SULF). The measurements were made at 25 °C and with the ionic strength of 0.5 M *using sodium perchlorate as the ionic medium. T-jump technique with spectrophotometric detection was used to obtain the kinetic data. The stability constants for the mixed complexes were determined by a spectrophotometric method. The mechanism contains two consecutive steps, a ligand–water exchange step and a ring closure/opening step. The kinetics of the studied complexes was dependent both on the hydrogen ion concentration and the acid part of the buffer concentration. Two stoichiometric mechanisms were tested:* i *where the rate of ring closure/opening is of the same magnitude as the water–ligand exchange rate, and* ii *where the rate of ring closure/opening is much more rapid than the other. Only mechanism* i *was in agreement with the experimental data. The rate constants of ligand–water exchange have almost the same values as the corresponding constants for other mixed complexes such as MEDTA forms with picolinate and 8-hydroxyquinoline-5-sulfonate. Hence a dissociative Eigen-Diebler mechanism is indicated, at least for the lighter lanthanoids.*

Introduction

In a previous communication [1], the rate and mechanism of the formation of ternary complexes MYL, between some lanthanoid EDTA complexes, MY, and 8-hydroxyquinoline-5-sulfonate or picolinate, L, were described. The stoichiometric mechanism proposed, consists of two parallel pathways, one of which is hydrogen ion dependent. The rate constants for the unidentate association of L to MY were found to be nearly independent of the entering ligand, indicating a dissociative inter-change mechanism at least for the pre-Tb elements. For the heavier elements a change to an associative mechanism may occur. The rate of chelate ring closure, which is of the same order of magnitude as the association rate constant, was dependent both on the ligand L and on the lanthanoid ion.

The present study has been extended to a third bidentate ligand, 5-sulfosalicylate (SULF). This ligand was selected because it has a different basicity and a different set of donor atoms (two oxygens) as compared with the ones in the previous study (one nitrogen and one oxygen). The three different ligands investigated in these two studies, thus offer a good possibility to test the Eigen–Diebler [2] mechanism on substitution reactions at various lanthanoid reaction centra.

Determination of Stability Constants of Mixed Complexes

The stability constants of the mixed lanthanoid EDTA 5-sulfosalicylate complexes, in the following denoted MYL, were determined by a spectrophotometric method.

The stability constants were calculated from the known total concentrations of MY, the ligand, the free hydrogen ion concentration and the measured absorbance of the mixed complexes and the ligand.

Experimental

Chemicals: All chemicals used were of analytical grade. The lanthanoid oxides (Research Chemicals) had a purity greater than 99.9%. Stock solution of the various MY complexes were prepared by dissolving the solid NaMY in aqueous sodium perchlorate. For the spectrophotometric measurements a Zeiss PMQII spectrophotometer was used. All the measurements were made in 1 cm sample cells at

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*Author to whom correspondence should be addressed.

25 °C and at an ionic strength of 0.5 *M*, using sodium perchlorate as the ionic medium.

Spectrophotometric Measurements

The stability constants for the mixed complexes were determined by measuring the light absorbance at the wavelength 258 nm of solutions of MY and SULF. The free hydrogen ion concentration was measured by using galvanic cells of the type:

Ag, AgCl	0.490 M NaClO$_4$ 0.010 M NaCl	c_{MY} MY c_L SULF c_B base part of buffer c_{BH} acid part of buffer 0.500 M – (c_{MY} + 3c_L + c_{BH})NaClO$_4$	Glass Electrode

TABLE I. The Stability Constants of the MY(SULF) Complexes. All Errors are equal to 3σ, where σ is the Standard Deviation obtained in the Least-squares Refinement.

M	$\lg(\beta_{101}/M^{-1})$
La	3.77 ± 0.02
Nd	4.17 ± 0.02
Gd	4.40 ± 0.02
Er	4.31 ± 0.02
Lu	4.42 ± 0.02

Two series of measurements were made. In one c_{MY} was zero, and in the other c_{MY} was equal to 5 m*M*. In both series the hydrogen ion concentration was varied from $0.8 \cdot 10^{-10}$ *M* to $15 \cdot 10^{-10}$ *M*, while the total ligand concentration was kept constant, 0.05 m*M*. The experiments showed that only one mixed complex, MYL, was formed in the concentration range studied.

The stability constant for the reaction MY + L $\rightleftarrows$ MYL is denoted by β_{101}, charges are omitted for brevity. The protonation constant for SULF, L + H $\rightleftarrows$ LH, is denoted by β_{011}, where $\lg(\beta_{011}/M^{-1}) = 11.54$ [3]. The stability constant of the mixed complex can be obtained from an expression deduced in the following way:

$$c_{MY} = [MY] + [MYL] \quad (1)$$

$$c_L = [L] + [LH] + [MYL] \quad (2)$$

The total absorbance A is equal to

$$A = \epsilon_{MYL}[MYL] + \epsilon_{LH}[LH] + \epsilon_L[L] \quad (3)$$

where ϵ_X denotes the molar absorptivity of the species X. The absorbance in the solution where $c_{MY} = 0$ is denoted by A_L, where

$$A_L = \epsilon_{LH}[LH] + \epsilon_L[L] \quad (4)$$

Equations (1)–(4) can be rearranged into

$$(A - A_L)(\beta_{011}h + 1)/[MY]c_L =$$

$$= \beta_{101} \cdot \epsilon_{MYL} - \beta_{101} \cdot A/c_L \quad (5)$$

Here [MY] can be approximated with c_{MY}, because $c_{MY} \gg c_L$. Hence the stability constant of the mixed complex will be obtained as the slope of the left hand side of the expression (5) *vs.* A/c_L. Figure 1 shows a plot of this function for the Nd system. The stability constants are given in Table I.

Kinetic Studies

Experimental

As the complexation reactions are rapid, a relaxation method was used, *viz.* the temperature-jump technique. 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 studying the change of the spectrum of the mixed complex. The concentration of c_{MY},

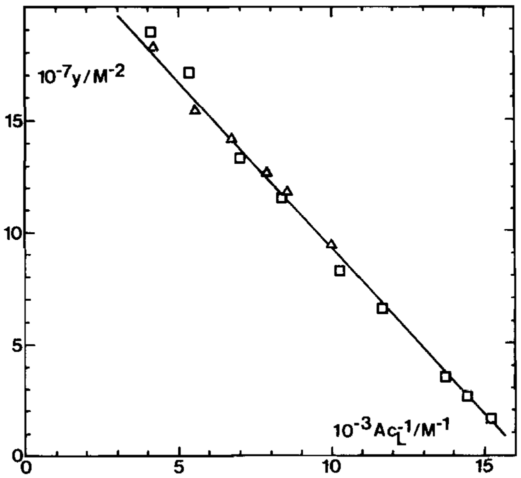


Fig. 1. The function $(A - A_L)(\beta_{011}h + 1)/[MY]c_L$ denoted by y in the Figure *vs.* A/c_L, for the NdY(SULF) system, where the concentrations of MY and the ligand are △: 5.00 m*M* and 0.05 m*M*, respectively, □: 10.0 m*M* and 0.05 m*M*, respectively.

c_L, and h was in the range 2–10 mM, 0.05–0.5 mM, and $0.8\cdot10^{-10}$–$50\cdot10^{-10}$ M, respectively. A temperature of 25 °C was maintained in all measurements. The ionic strength was 0.5 M, using sodium perchlorate as the ionic medium. The galvanic cell described in the preceding section was used to determine the hydrogen ion concentration of the solutions. The hydrogen ion concentration was kept constant in each run by using suitable buffers, *viz*. ammonia (am $pK_a = 9.34$), ethanolamine (et $pK_a = 9.44$), trimethylamine (trim $pK_a = 9.92$), and triethanolamine (triet $pK_a = 7.85$), in such concentrations that both c_B and c_{BH} were large enough so that h remained constant for the small changes of [L] and [LH] occurring during the kinetic run. The concentration of the acid part of the buffer, BH, was kept constant at 8, 10, 18, 30, 50, or 100 mM in each kinetic series. At least three different concentrations of BH were investigated for each buffer.

Determination of the Rate Constants for the Overall Reaction

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

$$\begin{array}{lr} \mathrm{MYL} \rightleftarrows \mathrm{MY} + \mathrm{L} & \\ \qquad\qquad\quad \vdots & \\ \qquad\qquad\quad \mathrm{L} + \mathrm{H} \rightleftarrows \mathrm{LH} & (6) \\ \qquad\qquad\qquad\quad \vdots & \\ \qquad\qquad\qquad\quad \mathrm{H} + \mathrm{B} \rightleftarrows \mathrm{BH} & \end{array}$$

where BH/B is the buffer system with protonation constant β_B. The observed rate constant, k_{obs}, for the overall process can be written as [4]

$$k_{obs} = f_c \cdot f_k$$

The mechanism is deduced from f_k, which is a function of the rate constants, the equilibrium constants and the concentrations. The function f_c is only dependent on the equilibrium concentrations and the equilibrium constants and thus independent of the mechanism.

The experimental data consist of values of k_{obs} from solutions were the equilibrium concentrations of h, LH, MY, and BH have been systematically varied. These data may be obtained from the authors.

For a series of coupled reactions [4] of the type (6) f_c is equal to

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

where

$$\delta = [(h\beta_{011})^{-1} + 1]^{-2}[h + [\mathrm{L}]h\beta_{011} + [\mathrm{B}]h\beta_{\mathrm{B}}]^{-1}$$

In this case f_k turned out to be a function of h and [BH] only. Plots of f_k *vs.* h for a given concentration of BH, were described with a function of the type

$$f_k = ah/(1 + bh) \qquad (7)$$

where a and b are constants at constant [BH]. The constants were determined by the graphical methods described below, and were subsequently refined by a least-squares method using the program 'STEPIT'.

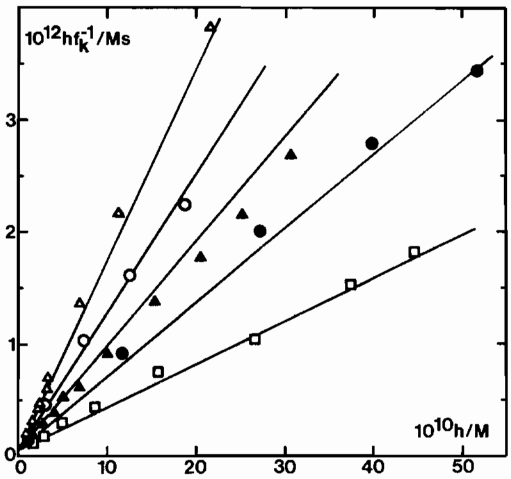


Fig. 2. The function h/f_k *vs.* h for the GdY(SULF) system with different ammonium ion concentrations denoted by △: 8 mM, ○: 18 mM, ▲: 30 mM, ●: 50 mM, and □: 100 mM. Full drawn curves are calculated by using the buffer concentrations, the pH and the rate constants given in Table II.

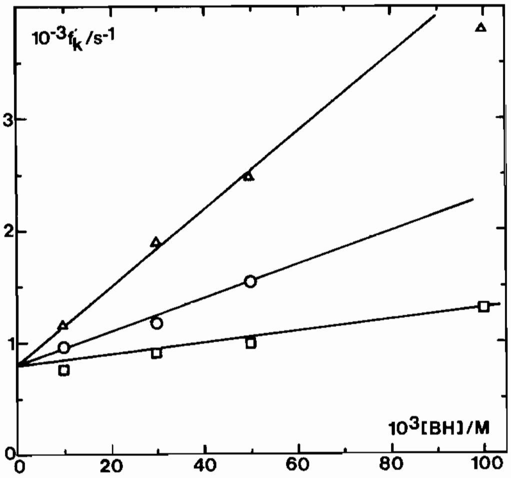


Fig. 3. The function $h/(h/f_k - 1/a)$ denoted by f'_k in the Figure *vs.* [BH], for the NdY(SULF) system, for the three buffers, △: am, ○: et, and □: trim. Full drawn curves are calculated by using the rate constants given in Table II.

Graphical determination of the parameters a *and* b

To evaluate the parameters a and b, the eqn. (7) was rearranged into

$$h/f_k = 1/a + hb/a \tag{8}$$

From the plots of h/f_k *vs.* h for each buffer concentration, it was obvious that the intercept $1/a$ was independent of the buffer concentration and the buffer used, while the slopes, b/a, varied with the buffer and its concentration, Fig. 2. In order to determine this concentration dependency, the function $h/(h/f_k - 1/a)$ was plotted *vs.* [BH] for each buffer used. These plots were linear and on the form

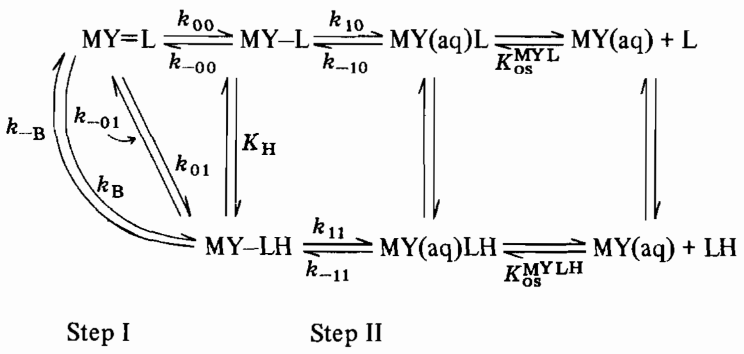
$$h/(h/f_k - 1/a) = a/b = A + B[\mathrm{BH}] \tag{9}$$

The intercept A was independent of the kind of buffer used, while the slope B was buffer dependent, Fig. 3.

Deduction of f_k *for various stoichiometric reaction mechanisms*

Stoichiometric mechanisms similar to those tested in the previous study [1] will be tested also on this system. One of these mechanisms (*i*) includes two consecutive steps with parallel hydrogen ion dependent and hydrogen ion independent pathways. The two consecutive steps are a ring closure/opening step, I, and a unidentate association/dissociation step, II. The dependency of k_{obs} with [BH] found in this system indicates there is an additional pathway, most probably placed in step I as will be discussed later. The other mechanism, (*ii*), proposed by Furrer [5], is a mechanism where the ring closure/opening step is much faster than the other reactions, in this case with an additional buffer catalyzed pathway.

i:



The vertical arrows denote fast protonation reactions. The equilibrium constants K_H, K_{os}^{MYL}, and K_{os}^{MYLH} are defined in the mechanistic scheme presented above. The rate constants in the stoichiometric mechanism are denoted k_{ij}. If the intermediates in the mechanism are in a steady state, then f_k can be written as [4]

$$f_k = [(k_{00}^* + k_{01}^* h + k_B^*[\mathrm{BH}])^{-1} + (k_{10}^* + k_{11}^* h)^{-1}]^{-1} \tag{10}$$

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

The buffer dependency in the mechanism gives three possible buffer pathways, namely in step I as proposed in the scheme above, in step II or in both steps. The expression for f_k will be different for each of these possibilities.

A buffer dependent pathway in steps I and II, respectively, leads after rearrangement of eqn. (10) to the following f_k functions

$$f_k = \frac{\dfrac{k_{10}^* k_{00}^* + k_{10}^* k_B^*[\mathrm{BH}]}{\mathrm{N}} + \dfrac{k_{10}^* k_{01}^* + k_{11}^* k_{00}^* + k_{11}^* k_B^*[\mathrm{BH}]}{\mathrm{N}} h + \dfrac{k_{11}^* k_{01}^*}{\mathrm{N}} h^2}{1 + \dfrac{(k_{11}^* + k_{01}^*)}{\mathrm{N}} h} \tag{11}$$

and

$$f_k = \frac{\dfrac{k_{00}^* k_{10}^* + k_{00}^* k_B^*[\mathrm{BH}]}{\mathrm{N}} + \dfrac{k_{00}^* k_{11}^* + k_{10}^* k_{01}^* + k_{01}^* k_B^*[\mathrm{BH}]}{\mathrm{N}} h + \dfrac{k_{01}^* k_{11}^*}{\mathrm{N}} h^2}{1 + \dfrac{(k_{11}^* + k_{01}^*)}{\mathrm{N}} h} \tag{12}$$

where $N = k^*_{10} + k^*_{00} + k^*_B[BH]$

If buffer dependent pathways occur in both steps, the following function will be obtained:

$$f_k = \frac{\dfrac{k^*_{10}k^*_{00} + k^*_{10}k^*_{B1}[BH] + k^*_{B2}[BH] + k^*_{B1}k^*_{B2}[BH]^2}{N'}}{1 + \dfrac{k^*_{11} + k^*_{01}}{N'}h} + \frac{\dfrac{k^*_{10}k^*_{01} + k^*_{11}k^*_{00} + k^*_{11}k^*_{B1}[BH] + k^*_{B2}k^*_{01}[BH]}{N'}h + \dfrac{k^*_{11}k^*_{01}}{N'}h^2}{1 + \dfrac{k^*_{11} + k^*_{01}}{N'}h} \tag{13}$$

where $N' = k^*_{10} + k^*_{00} + k^*_{B1}[BH] + k^*_{B2}[BH]$

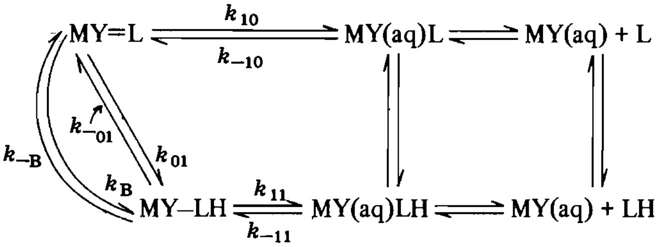
A choice between the different stoichiometric mechanisms and an identification of the rate constants can be made by comparing the theoretical expressions (11)–(13) with the experimental function (7).

In (11) the hydrogen independent term must be zero, *viz.* k^*_{10} is equal to zero. The hydrogen dependent term h^2 is equal to zero if k^*_{01} or k^*_{11} is zero, in this case k^*_{01} must be zero, otherwise the h dependent term in the numerator will disappear. Expression (12) will be consistent with experimental data if k^*_{00} and k^*_{11} are equal to zero. Both (11) and (12) now have the same mathematical form as the experimental function (7). A choice between the two can only be made by comparing the magnitude of the different rate constants with data for similar systems. This will be discussed later.

Both k^*_{11} and k^*_{01} can not be zero in eqn. (13). Hence the h dependent term in the numerator must depend on the buffer concentration [BH]. This is not in agreement with the experimental observations and the mechanism which leads to (13) can thus be disregarded.

ii:

The Furrer type pseudo one-step mechanism with a buffer pathway added can be written as



where the buffer pathway may be either parallel to the k_{01}/k_{-01} or the k_{11}/k_{-11} pathway. The function f_k for these two cases is equal to

$$f_k = k^*_{10} + \frac{1}{\dfrac{1}{k^*_{01}h + k^*_B[BH]} + \dfrac{1}{k^*_{11}h}} \tag{14}$$

and

$$f_k = k^*_{10} + \frac{1}{\dfrac{1}{k^*_{11}h + k^*_B[BH]} + \dfrac{1}{k^*_{01}h}} \tag{15}$$

respectively. The true rate constants are $k^*_{10} = k_{10}$, $k^*_{01} = k_{01}$, $k^*_B = k_B$, and $k^*_{11} = k_{11}K_{01}$. The equilibrium constant for the ring opening is denoted by K_{01}.

The expressions (14) and (15) have the same mathematical form and may now be compared to the experimental function (7). After rearrangement eqn. (14) becomes

$$f_k = \frac{k^*_{10} + ((k^*_{10}k^*_{01} + k^*_{10}k^*_{11})/k^*_B[BH] + k^*_{11})h + (k^*_{01}k^*_{11}/k^*_B[BH])h^2}{1 + ((k^*_{01} + k^*_{11})/k^*_B[BH])h} \tag{16}$$

By comparison of this expression with (7), it follows that k^*_{10} and k^*_{01} must be equal to zero. Hence,

$$f_k = \frac{k^*_{11}h}{1 + (k^*_{11}/k^*_B[BH])h} \tag{16'}$$

A transformation of (16′) gives

TABLE II. Values of Association Rate Constants for the SULF Systems.

Model 1:	$\lg(k^*_{-00}/s^{-1}\ M^{-1})$	$\lg(k^*_{-B}/s^{-1}\ M^{-1})$	$\lg(k^*_{-11}/s^{-1}\ M^{-1})$
Model 2:	$\lg(k^*_{-10}/s^{-1}\ M^{-1})$	$\lg(k^*_{-B}/s^{-1}\ M^{-1})$	$\lg(k^*_{-01}/s^{-1}\ M^{-3})$
La	7.5 ± 0.1		7.3 ± 0.1
am		−2.7 ± 0.1	
et		−2.9 ± 0.1	
Nd	7.1 ± 0.1		6.5 ± 0.1
am		−2.8 ± 0.1	
et		−3.1 ± 0.1	
trim		−3.6 ± 0.1	
Gd	7.0 ± 0.1		6.2 ± 0.1
am		−2.8 ± 0.1	
et		−3.1 ± 0.1	
trim		−3.7 ± 0.1	
triet		−2.7 ± 0.1	
Er	6.3 ± 0.1		5.1 ± 0.1
am		−3.6 ± 0.1	
et		−3.8 ± 0.1	
trim		−4.4 ± 0.1	
Lu	6.2 ± 0.1		4.3 ± 0.1
am		−3.8 ± 0.1	
et		−4.0 ± 0.1	

$$h/(h/f_k - 1/k^*_{11}) = k^*_B[BH] \qquad (16'')$$

This function will have an intercept equal to zero, while the corresponding experimental function (9) has a non zero intercept. Hence the Furrer type mechanism is not in agreement with the experimental data and can be disregarded.

In the previous discussion, a number of rate constants have been put equal to zero. This does not mean that they are exactly zero, only that the terms in which they occur are small enough to be neglected.

Identification of the rate constants in mechanism i

The experimental data indicate that the mechanism consists of two consecutive steps, one of which contains only a hydrogen ion dependent pathway, while the other contains two parallel paths, *viz.*, one hydrogen ion independent and one buffer catalyzed. The hydrogen ion dependent pathway could then be either k_{11} or k_{01}, mechanism (11) or (12). To make a choice between the two, we compared the values of the association rate constants, Model 1 and Model 2 in Table II, with the previously determined association rate constants for the PIC and OXS systems [1].

In Model 1, $k^*_{10} = 0$ and the buffer dependent pathway is in step I. We then have $k^*_{11} = a$, $k^*_{00} = A$, and $k^*_B = B$. The corresponding association rate constants are $k^*_{-11} = a\beta_{101}/\beta_{011}$, $k^*_{-00} = A\beta_{101}$, and $k^*_{-B} = B\beta_{101}/\beta_{011}$.

In Model 2, $k^*_{00} = 0$ and the buffer dependent pathway is in step II. We then get $k^*_{01} = a$, $k^*_{10} = A$, and $k^*_B = B$. The corresponding association rate constants are equal to $k^*_{-01} = a\beta_{101}/\beta_{011}$, $k^*_{-10} = A\beta_{101}$, and $k^*_{-B} = B\beta_{101}/\beta_{011}$.

The experimental constants *a*, *A*, and *B* are given in Table III. The association rate constants for Models 1 and 2 are given in Table II where $k^*_{-B} = k_{-B}K_{os}^{MYL}K_{11}^{-1}\beta_B^{-1}$, $k^*_{-00} = k_{-00}K_{os}^{MYL}/K_{10}$, and $k^*_{-11} = k_{-11}K_{os}^{MYLH}$ for Model 1.

For an Eigen–Diebler mechanism, the rate constant k_{-11} should be independent of the ligand. There is no reason why the outer sphere stability constants should differ much between the ligands PIC, OXS, and SULF. From Table II, it is obvious that only Model 1 with the buffer catalyzed pathway in step I is consistent with the previous observations in the PIC and OXS systems, hence this Model was chosen.

Buffer dependent pathways in the reaction mechanism

A buffer dependency in the rate of metal complexation has been noticed also in other investigations [5, 6]. Acetate buffers are known to accelerate complex formation reactions [7, 8]. This effect has been interpreted in terms of the formation of a mixed metal ligand acetate complex, where the acetate coordination may affect the strength of the metal

TABLE III. The Experimental Parameters a, A, B_{am}, B_{et}, B_{trim}, and B_{triet} for the SULF Systems. The Errors are equal to 3σ, where σ is the Standard Deviation.

M	$a/s^{-1}\ M^{-1}$	$A\ 10^{-2}/s^{-1}$	$B_{am}\ 10^{-4}/s^{-1}\ M^{-1}$	$B_{et}\ 10^{-3}/s^{-1}\ M^{-1}$	$B_{trim}\ 10^{-3}/s^{-1}\ M^{-1}$	$B_{triet}\ 10^{-4}/s^{-1}\ M^{-1}$
La	$(1.2 \pm 0.5)10^{15}$	58 ± 2	12 ± 1	71 ± 6		
Nd	$(6.6 \pm 0.7)10^{13}$	8.0 ± 0.2	3.5 ± 0.1	15 ± 1	5.1 ± 0.5	
Gd	$(2.1 \pm 0.2)10^{13}$	4.1 ± 0.1	2.2 ± 0.1	9.9 ± 0.7	2.7 ± 0.3	2.6 ± 0.1
Er	$(2.3 \pm 0.1)10^{12}$	0.98 ± 0.03	0.43 ± 0.02	2.5 ± 0.2	0.61 ± 0.08	
Lu	$(2.5 \pm 0.1)10^{11}$	0.65 ± 0.04	0.20 ± 0.02	1.2 ± 0.1		

ligand bonds. Catalysis by ammonia buffers have been noticed *e.g.*, in the reactions between alcaline earth ions and *trans*-1,2-diaminocyclohexanetetraacetate [9].

Four different buffers were used in this study. The values of the rate constants for the buffer dependent pathway, k_B^* (*cf.* Table III) show that the strongest acid triet gives the strongest catalytic effect and the weakest acid trim the weakest. These findings indicate that the buffer functions as a proton transfer agent to the ligand, *cf.* ref. 10.

Discussion

There are a number of complex formation reactions with the lanthanoid ions where a hydrogen dependent pathway could not be identified in the pH range studied. This is the case *e.g.* with mixed complexes formed between lanthanoid EDTA and 7-nitro-8-oxyquinoline-5-sulfonate [6] or tetra methylmurexide [5]. In these cases measurements have been made around pH = 8 and the pK_a values for the ligands are so low that no perceptible amounts of LH was present. If no hydrogen dependent or buffer dependent pathways exist in the reaction mechanism one has simply a set of consecutive reactions and the overall rate constant can be written as

$$k_{obs} = f_c(\Sigma(k_i)^{-1})^{-1}$$

if the intermediates are in a steady state.

From this function it is not possible to calculate the rate constants, separately. Investigations of this type will therefore only give an indirect test of the Eigen-Diebler mechanism. The advantage of having hydrogen dependent or buffer dependent pathways parallel to the hydrogen independent ones is thus that they make it possible to calculate the rate constants separately. There are other lanthanoid systems studied, *e.g.* MEDTA tropolonate [6] and MHDTA (N-2-hydroxyethylethylenediamine-N,N′,N′,triacetate) 8-oxyquinoline-5-sulfonate [6], where hydrogen dependent pathways have been found. These are further discussed in another communication [11]. The two last systems were tested with the two mechanisms, *i* and *ii*. The tropolonate system was in agreement with Furrer's mechanism and the other with a two-step mechanism.

As the values of the rate constants, k_{-10}^* and k_{-11}^*, for the three systems PIC, SULF, and OXS, have about the same magnitude for a given lanthanoid the Eigen–Diebler mechanism seems to be valid for the formation of these mixed complexes. However, for the heavy lanthanoids there are indications [5] for a gradual change in mechanism from dissociative to associative. The rate constants involved in the ring opening/closure step for a given lanthanoid are substantially different for the ligands OXS and PIC, while the SULF systems have about the same values as the PIC systems. This can perhaps be explained by the similar geometry of these two ligands, although there is a six-membered ring in the SULF complexes compared to a five-membered ring in the PIC systems. The OXS ligand is a much bulkier complexing agent, with the chelate ring involved in both the six rings of the ligand. This might explain the much slower rate for the smallest lanthanoids. The mechanistic discussion presented in this paper should have been more stringent if information on the rate of water exchange in the lanthanoid EDTA complexes were available.

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