

## Kinetic Studies of Lanthanoid Carboxylate Complexes

### I. The Dissociation Rates of Ytterbium, Lanthanum and Copper EDTA Complexes

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The dissociation rates of the ytterbium, lanthanum, and copper EDTA complexes in slightly acid media have been investigated. The rate constants of these dissociations have been determined from reactions in which the ligand is exchanged between two different metal ions. The measurements have been made at 25.0°C and at an ionic strength of 0.5 M, using potassium chloride as neutral salt. The solutions were buffered with 12.5 mM sodium acetate and varying amounts of acetic acid. The dissociation was found to be catalyzed by hydrogen ions, according to the equation  $f = k_0 + \bar{k}_1[\text{H}^+] + \bar{k}_2[\text{H}^+]^2$  for the rate constant  $f$ .

The lanthanoid ions form strong complexes with many multidentate ligands. The stability constants of the complexes with ethylenediaminetetraacetate, EDTA, range from  $10^{15} \text{ M}^{-1}$  for lanthanum to  $10^{20} \text{ M}^{-1}$  for lutetium.<sup>1-3</sup>

Hoard *et al.*<sup>4,5</sup> have found from X-ray studies of salts of lanthanoid EDTA complexes that the ligand is hexadentate. It is bound to the central ion by four oxygen and two nitrogen atoms. The ligand is located at one side of the central ion, whereas the opposite side is occupied by coordinated water molecules. As the radius of the central ion decreases along the lanthanoid series, the central ion presumably sinks deeper into the "basket" formed by the ligand molecule which results in a shortening of the metal-nitrogen distances.

It is also possible that a change of the number of coordinated water molecules occurs. Thermodynamic data<sup>6</sup> indicate a change in the coordination number, possibly from nine to eight, somewhere in the middle of the lanthanoid series. On thermodynamic, spectroscopic, and kinetic grounds, Geier and Karlen<sup>7-10</sup> have claimed that two kinds of LnEDTA complexes, *viz.*  $\text{Ln}(\text{EDTA})(\text{OH}_2)_3^-$  and  $\text{Ln}(\text{EDTA})(\text{OH}_2)_2^-$ , are in equilibrium in solution. For the first members of the series up to samarium, the complex with three water molecules predominates, whereas after dysprosium, the two-water complex is favoured.

Some investigations have been reported on the kinetics of lanthanoid EDTA complexes.<sup>11-19</sup> They are based on radioisotope exchange studies in slightly acid solutions. The ligand exchange of lanthanum and lutetium EDTA complexes has been studied by NMR line broadening by Merbach and Gnägi.<sup>20</sup> A few studies of mixed EDTA lanthanoid complexes have also been reported.<sup>8,21</sup>

Several different rate laws and mechanisms have been suggested in the investigations cited. Most of the papers give only one reaction path, *viz.* a path catalysed by hydrogen ions in such a way, that the rate constant becomes proportional to the concentration of these ions. Furthermore, a decrease in the rate constant along the lanthanoid series has been related to the increasing stability constant.

The aim of the present investigation is to determine the dissociation rates and possible reaction mechanisms of some lanthanoid EDTA complexes with methods other than isotope exchange reactions. The suggested existence of two types of EDTA complexes, containing two or three water molecules, might be reflected in the rate constants of the dissociation. One would also expect a hydroxide ion catalysis of the dissociation, since mixed complexes are known which contain EDTA and hydroxide as ligands. This has not been examined in the previous studies.

The present investigation will be reported in this and two forthcoming papers.

#### THE KINETIC MODEL

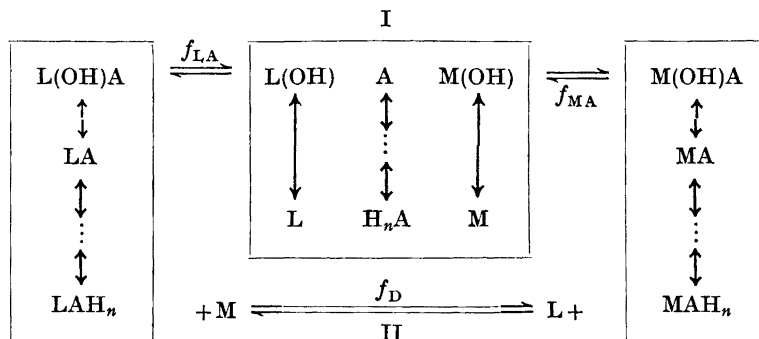
This model, which is in accordance with the reactions of EDTA complexes discussed by Margerum,<sup>22</sup> has been developed together with Ekström.<sup>23</sup> It describes possible reactions of a ligand exchange between two different metal ions, according to the over-all reaction



where A denotes the ligand and L and M the two metal ions. Catalysis by hydrogen and hydroxide ions has been included in the model. The ligand is supposed to have a multidentate character. Mixed complexes, *e.g.* formed by species used as buffers, are excluded in this short description.

Two different reaction paths are taken into account, *viz.* (i) a primary dissociation of the complex LA, followed by an association of the ligand A to the metal ion M, and (ii) a direct substitution reaction between M and the complex LA to the products L and MA.

If the metal ion L has a high coordination number compared to the multidentate ligand A, which itself has possibilities to form species of the type HA, H<sub>2</sub>A, ..., H<sub>n</sub>A, there exist several possibilities to form mixed complexes, such as L(OH)<sub>n</sub>A, LAH, LAH<sub>n</sub>. The distribution of L over these species depends on the acidity of the solution. The metal ion M may also have similar possibilities to form mixed complexes. The situation is described in the following reaction scheme.

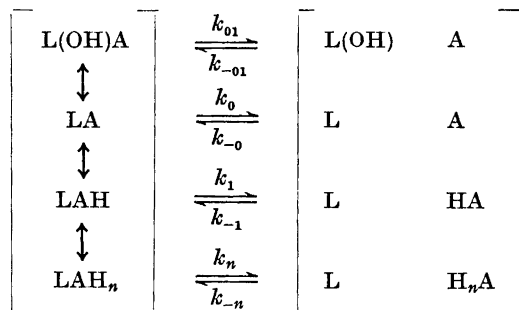


All equilibria in which only hydrogen ions are exchanged are assumed to be rapid compared to the rates of paths I and II. This assumption will be discussed in a forthcoming paper. In this scheme,  $\rightleftharpoons$  denotes a fast equilibrium.  $f_{\text{LA}}$  is a function of the hydrogen ion concentration and of the rate constants for the various LA complexes. The corresponding function for the MA complexes is  $f_{\text{MA}}$ .  $f_{\text{D}}$  is a function of the hydrogen ion concentration and of the rate constants for the direct substitution reaction.

#### DEDUCTION OF THE RATE LAW

The total rate of disappearance of the LA complex together with species formed from LA by fast protonations or deprotonations is the sum of the rates along the parallel paths I and II.

*The rate along path I.* The following reaction scheme is regarded:



As mentioned earlier, all species enclosed in the left brackets are supposed to be in fast equilibrium with each other. Each of them dissociates to a product within the right brackets. Thus, the rate of disappearance by path I of all complexes containing both L and A is

$$\begin{aligned}
 - \frac{d([\text{L(OH)A}] + [\text{LA}] + \dots + [\text{LAH}_n])}{dt} &= - \frac{dC_{\text{LA}}'}{dt} \quad (2) \\
 &= k_{01}[\text{L(OH)A}] - k_{-01}[\text{L(OH)}][\text{A}] + k_0[\text{LA}] - k_{-0}[\text{L}][\text{A}] + \\
 &+ \dots + k_n[\text{LAH}_n] - k_{-n}[\text{L}][\text{H}_n\text{A}]
 \end{aligned}$$

where  $C_{LA}'$  denotes the sum of concentrations of all types of complexes containing both L and A at the time  $t$ . The following equilibrium constants are introduced

$$K_{LAH_n} = \frac{[LAH_n]}{[LA][H]^n}; \quad K_{L(OH)A} = \frac{[L(OH)A][H]}{[LA]}; \quad (3)$$

$$K_{L(OH)} = \frac{[L(OH)][H]}{[L]}; \quad \beta_L = \frac{[LA]_\infty}{[L]_\infty[A]_\infty};$$

$$\gamma_n = \frac{[H_nA]}{[A][H]^n}$$

The relations between the forward and backward rate constants are then given by

$$\frac{k_n}{k_{-n}} = \frac{\gamma_n}{\beta_L K_{LAH_n}} \quad \text{and} \quad \frac{k_{01}}{k_{-01}} = \frac{K_{L(OH)}}{K_{L(OH)A} \beta_L} \quad (4)$$

If the hydrogen ion concentration is constant during the reaction, *i.e.*

$$d[H]/dt = 0 \quad (5)$$

eqn. (2) can be written as

$$(-d[LA]/dt) \alpha_0 = f_{LA}([LA] - \beta_L[L][A]) \quad (6a)$$

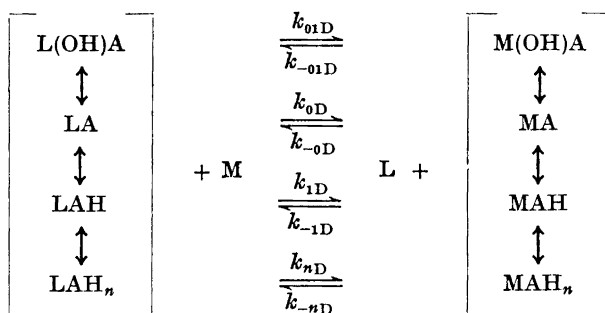
where

$$\alpha_0 = 1 + K_{L(OH)A} \frac{1}{[H]} + \dots + K_{LAH_n} [H]^n \quad (6b)$$

and

$$f_{LA} = k_{01} K_{L(OH)A} \frac{1}{[H]} + k_0 + \dots + k_n K_{LAH_n} [H]^n \quad (6c)$$

*The rate along path II.* The reaction scheme for this path is



If notations for the equilibrium constants corresponding to those used in path I are introduced, the rate of disappearance by path II of all complexes containing both L and A is

$$-\frac{d[\text{LA}]}{dt} \alpha_0 = f_D([\text{LA}][\text{M}] - \frac{\beta_L}{\beta_M} [\text{MA}][\text{L}]) \quad (7a)$$

where

$$f_D = k_{01D} K_{L(\text{OH})A} \frac{1}{[\text{H}]} + k_{0D} + \dots + k_{nD} K_{L\text{A}H_n} [\text{H}]^n \quad (7b)$$

*The complete rate law.* The total rate of disappearance of complexes containing both L and A is then given by

$$\begin{aligned} -\frac{dC_{\text{LA}}'}{dt} &= -\frac{d[\text{LA}]}{dt} \alpha_0 = \\ &= f_{\text{LA}}([\text{LA}] - \beta_L[\text{L}][\text{A}]) + f_D([\text{LA}][\text{M}] - \frac{\beta_L}{\beta_M} [\text{MA}][\text{L}]) \end{aligned} \quad (8)$$

In a steady state, the rate of formation of all types of MA complexes is equal to the rate of disappearance of all types of LA complexes

$$\begin{aligned} -\frac{dC_{\text{LA}}'}{dt} = \frac{dC_{\text{MA}}'}{dt} &= -f_{\text{MA}}([\text{MA}] - \beta_M[\text{M}][\text{A}]) + f_D([\text{LA}][\text{M}] - \\ &- \frac{\beta_L}{\beta_M} [\text{MA}][\text{L}]) \end{aligned} \quad (9)$$

This approximation means that

$$d[\text{A}]/dt = 0 \quad (10)$$

Thus

$$f_{\text{LA}}([\text{LA}] - \beta_L[\text{L}][\text{A}]) = -f_{\text{MA}}([\text{MA}] - \beta_M[\text{M}][\text{A}]) \quad (11)$$

where  $f_{\text{MA}}$  is analogous to  $f_{\text{LA}}$ . Combination of eqns. (11) and (8) gives

$$\begin{aligned} -\frac{d[\text{LA}]}{dt} \alpha_0 &= \left( \frac{f_{\text{LA}} f_{\text{MA}} \beta_M}{f_{\text{LA}} \beta_L [\text{L}] + f_{\text{MA}} \beta_M [\text{M}]} + f_D \right) \times \\ &\times \left( [\text{LA}][\text{M}] - \frac{\beta_L}{\beta_M} [\text{L}][\text{MA}] \right) \end{aligned} \quad (12)$$

At equilibrium, the total concentration of all species containing both L and A is

$$C_{\text{LA}} = [\text{LA}]_{\infty} \alpha_{\text{LA}} \quad (13)$$

and the corresponding concentration of all species containing L but not A is

$$C_{\text{L}} = [\text{L}]_{\infty} \alpha_{\text{L}} \quad (14)$$

where  $\alpha_{\text{LA}}$  and  $\alpha_{\text{L}}$  are functions of the hydrogen ion concentration (analogous to  $\alpha_0$ ).  $C_{\text{MA}}$  and  $C_{\text{M}}$  are defined analogously. At a time  $t$ , the total concentrations differ from their equilibrium values by a quantity  $x$ , defined by

$$\begin{aligned} C_{\text{LA}}' &= C_{\text{LA}} + x; \quad C_{\text{MA}}' = C_{\text{MA}} - x; \\ C_{\text{L}}' &= C_{\text{L}} - x; \quad C_{\text{M}}' = C_{\text{M}} + x \end{aligned} \quad (15)$$

Combinations of eqns. (12) to (15) results in

$$-\frac{dx}{dt} = \left( \frac{f_{LA}f_{MA}}{f_{LA}\beta_L \frac{C_L}{\alpha_L} \left(1 - \frac{x}{C_L}\right) + f_{MA}\beta_M \frac{C_M}{\alpha_M} \left(1 + \frac{x}{C_M}\right)} + \frac{f_D}{\beta_M} \right) \times \\ \times \left( \beta_M \frac{C_{LA} + C_M}{\alpha_{LA}\alpha_M} + \beta_L \frac{C_L + C_{MA}}{\alpha_L\alpha_{MA}} + x \frac{\beta_M}{\alpha_M\alpha_{LA}} \left(1 - \frac{C_M C_{LA}}{C_L \cdot C_{MA}}\right) \right) x \quad (16)$$

This equation is integrated to

$$\ln \frac{x}{x_0} + \frac{Q_1 - Q_2}{Q_2 - Q_3} \ln \frac{1 + Q_2 x}{1 + Q_2 x_0} - \frac{Q_1 - Q_3}{Q_2 - Q_3} \ln \frac{1 + Q_3 x}{1 + Q_3 x_0} = \\ = -k_{\text{obs}} t \quad (17)$$

where

$$k_{\text{obs}} = \left( \frac{f_{LA}[f_{MA}(\beta_M/\beta_L)]}{f_{LA}(C_L/\alpha_L) + [f_{MA}(\beta_M/\beta_L)](C_M/\alpha_M)} + f_D \right) \left( \frac{C_M + C_{LA}}{\alpha_M\alpha_{LA}} + \frac{\beta_L}{\beta_M} \frac{C_L + C_{MA}}{\alpha_L\alpha_{MA}} \right) \quad (18)$$

$$Q_1 = \frac{f_{MA}\beta_M\alpha_L - f_{LA}\beta_L\alpha_M}{f_{MA}\beta_M\alpha_L C_M + f_{LA}\beta_L\alpha_M C_L} \quad (19a)$$

$$Q_2 = \frac{\alpha_L\alpha_{MA}\alpha_M - \alpha_M\alpha_{LA}\beta_L}{\alpha_{MA}\alpha_L\beta_M(C_M + C_{LA}) + \alpha_{LA}\alpha_M\beta_L(C_L + C_{MA})} \quad (19b)$$

and

$$Q_3 = \frac{(f_{MA}\beta_M\alpha_L - f_{LA}\beta_L\alpha_M)f_D}{f_{MA}\beta_M\alpha_L C_M + f_{LA}f_D\beta_L\alpha_M C_L + f_{LA}f_{MA}\alpha_M\alpha_L\beta_M} \quad (19c)$$

When  $x$  is small, eqn. (17) reduces to the general relation for a first order reaction:

$$\ln \frac{x}{x_0} = -k_{\text{obs}} t \quad (20)$$

As already mentioned, all these equations are valid only with the assumption of constant hydrogen ion concentration and a steady state concentration of the free ligand during the reaction.

Reaction path I consists of two consecutive reactions, *viz.* the dissociation of the LA complexes followed by an association of A and M to the MA complexes. If the dissociation is rate determining, then

$$f_{LA}C_L/\alpha_L \ll (f_{MA}\beta_M/\beta_L)c_M/\alpha_M$$

and  $f_{LA}$  can be determined from eqn. (18). If, on the other hand, the association is rate determining, then  $f_{LA}C_L/\alpha_L \gg (f_{MA}\beta_M/\beta_L)c_M/\alpha_M$ . In this case  $f_{MA}$ , *i.e.* the dissociation rate of the MA complexes, can be determined. When  $f_{LA}$  and  $f_{MA}\beta_M/\beta_L$  are of the same order of magnitude, either  $f_{LA}$  or  $f_{MA}$  can be determined from reaction (1), depending on the relative concentrations of L and M.

It is convenient to rearrange eqn. (18) in two different ways, depending on which one of the two reactions along path I is rate determining. When the dissociation is rate determining, the following relations are useful:

$$k_{\text{obs}} = \left( \frac{f_{\text{LA}}}{1 + (f_{\text{LA}}/f_{\text{MA}})\delta_1} + f_{\text{D}} \frac{C_{\text{M}}}{\alpha_{\text{M}}} \right) \delta_2 \quad (21a)$$

where

$$\delta_1 = \frac{\beta_{\text{L}} C_{\text{L}} \alpha_{\text{M}}}{\beta_{\text{M}} C_{\text{M}} \alpha_{\text{L}}} \quad (21b)$$

and

$$\delta_2 = \frac{1}{\alpha_{\text{LA}}} \left( 1 + \frac{C_{\text{LA}}}{C_{\text{M}}} + \frac{\beta_{\text{L}}}{\beta_{\text{M}}} \times \frac{C_{\text{L}} + C_{\text{MA}} \alpha_{\text{M}} \alpha_{\text{LA}}}{C_{\text{M}} \alpha_{\text{L}} \alpha_{\text{MA}}} \right) \quad (21c)$$

When the association is rate determining, the corresponding relations are

$$k_{\text{obs}} = \left( \frac{f_{\text{MA}}}{1 + (f_{\text{MA}}/f_{\text{LA}})\delta_1} + \frac{\beta_{\text{L}}}{\beta_{\text{M}}} f_{\text{D}} \frac{C_{\text{L}}}{\alpha_{\text{L}}} \right) \delta_2 \quad (22a)$$

where

$$\delta_1 = \frac{\beta_{\text{M}} C_{\text{M}} \alpha_{\text{L}}}{\beta_{\text{L}} C_{\text{L}} \alpha_{\text{M}}} \quad (22b)$$

and

$$\delta_2 = \frac{1}{\alpha_{\text{MA}}} \left( 1 + \frac{C_{\text{MA}}}{C_{\text{L}}} + \frac{\beta_{\text{M}} C_{\text{M}} + C_{\text{LA}} \alpha_{\text{L}} \alpha_{\text{MA}}}{C_{\text{L}} \alpha_{\text{M}} \alpha_{\text{LA}}} \right) \quad (22c)$$

One set of measurements is carried out to determine  $k_{\text{obs}}([\text{H}^+])$  for the dissociation of LA and then another set to determine  $k_{\text{obs}}([\text{H}^+])$  for the dissociation of MA. Then it is possible to calculate the rate constants in the functions  $f_{\text{LA}}$ ,  $f_{\text{MA}}$ , and  $f_{\text{D}}$  by an iterative procedure.

## EXPERIMENTAL

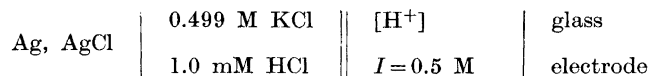
*Chemicals.* All chemicals were of analytical grade. Standard solutions of  $\text{YbCl}_3$ ,  $\text{LaCl}_3$ , and  $\text{CuCl}_2$  were prepared by dissolving the corresponding oxides (from Potash & Chemical Corp.) in hydrochloric acid. The solutions were standardized with EDTA, using xylenol orange for the lanthanoids and thymol blue for the copper as indicators. Ethylenediaminetetraacetic acid was prepared from a solution of the disodium salt, acidified by hydrochloric acid. The precipitate was washed and dried. A stock solution was prepared by dissolving a weighed amount of the acid in a sodium hydroxide solution (*cf.*, *e.g.*, Schwarzenbach and Flaschka<sup>24</sup>). Buffer solutions were prepared from acetic acid and sodium hydroxide. A stock solution of potassium chloride was made by dissolving a weighed amount of dried salt.

*Measurements.* All measurements were made at  $25.0 \pm 0.1^\circ\text{C}$  and at the ionic strength 0.5 M. The ionic strength for each of the solutions S and T (see below) was adjusted to 0.5 M by potassium chloride.

The lanthanoid EDTA complexes have a rather marked affinity to hydrogen ions. The association constants range from  $100 \text{ M}^{-1}$  to  $1000 \text{ M}^{-1}$ .<sup>18,25</sup> To avoid large concentrations of protonated complexes, the investigation has to be carried out at  $\text{pH} > 3$ . In order to achieve controlled pH values in this region, a buffer must be used. A mixture of 12.5 mM sodium acetate and varying amounts of acetic acid was chosen as buffer. Such a buffer has only a small effect on the rate of the reaction (p. 3964).

The reactions were performed by mixing two solutions. As a rule, only one of the solutions contained the buffer. No differences in the observed rate constants could be detected, whether the buffer was in only one of the solutions or in both of them before mixing.

The hydrogen ion concentration of the solutions was determined by measuring the emf of the cell



Before and after each determination, a standard solution, containing a known hydrogen ion concentration around 1 mM, was measured. The diffusion potentials were negligible.

*The copper (a) and ytterbium systems.* The rates of dissociation of the copper and ytterbium EDTA complexes were measured by a spectrophotometric method.

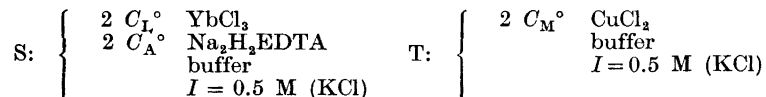
Two solutions, S and T, were thermostated at 25.0°C and mixed rapidly. (The mixing time was less than 5 s.) For the copper system, the two solutions were mixed with two calibrated syringes directly into a thermostated cuvette, whereas for the lanthanoid system the solutions were mixed into a reaction vessel. Samples from this vessel were taken at different time intervals and measured with a Zeiss PMQ II spectrophotometer, equipped with a Solatron digital voltmeter LM 142.02, from which the transmittance of the copper EDTA complex was read.

Because of the small total concentration, it was necessary to perform the measurements in the UV region (wave length 280–300 nm), where the molar light absorptivity is high. In the lanthanoid system, with an excess of copper ions, a marked photocatalytic effect was observed. It is well known that many copper complexes exhibit photolysis in the UV region.<sup>26</sup> The transmittance of each sample was generally measured after 10 s in the light path. In order to check that this procedure gave  $k_{\text{obs}}$ -values unaffected by the photocatalytic effect, the following procedure was applied for some runs. By means of a recorder connected to the spectrophotometer, the transmittance for each sample was followed for about 30 s and extrapolated to zero time, *i.e.* the time when the sample had been placed into the light beam of the spectrophotometer.  $k_{\text{obs}}$  was then evaluated from extrapolated values.

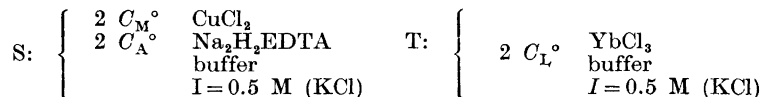
The same rate constants were obtained with and without this correction. Some experiments were carried out at both 285 and 600 nm. Those at 600 nm were in the light path during the entire run. At this wavelength no photocatalytic effect was found. In the copper system, with an excess of ytterbium ion, no photocatalytic effect could be observed either. These runs were therefore carried out in the cuvette.

The rate law has been deduced by assuming a steady state concentration for the hydrogen ions. The validity of this assumption was tested for some of the reactions in the ytterbium system by measuring the emf of the cell given above. By this procedure it was verified that the pH of the solution remained constant during the reaction.

The solutions S and T had the following compositions:  
for the ytterbium system



and for the copper (a) system



Equal volumes of the solutions S and T were mixed. The reactions were followed during approximately three half-lives. The first reading was taken after about one half of a half-life. In these cases, the rate determining step along path I is the dissociation of the



Table 1. Rate data for the ytterbium system. L=Yb and M=Cu.

$[H^+] \times 10^5/M$ ,  $k_{\text{obs}} \times 10^4/s^{-1}$ ,  $100(k_{\text{obs}} - k_{\text{calc}})/k_{\text{calc}}$ ,  $f_{\text{LA,exp}} \times 10^4/s^{-1}$ ;  
 $C_{\text{L}}^\circ = 2.99 \times 10^{-4}$  M,  $C_{\text{A}}^\circ = 2.00 \times 10^{-4}$  M,  $C_{\text{M}}^\circ = 4.99 \times 10^{-3}$  M:  
 4.27, 0.639, -4.3, 0.560; 5.76, 1.02, -1.1, 0.901; 7.23, 1.54, 6.5, 1.38; 8.75, 1.91, -1.9,  
 1.73; 10.3, 2.52, 0.6, 2.30; 11.8, 3.49, 11.6, 3.23; 13.3, 3.78, -0.6, 3.51; 15.0, 4.60, -1.1;  
 4.32; 16.3, 5.56, 4.1, 5.27; 19.2, 7.07, 0.8, 6.80; 22.2, 8.97, 0.4, 8.77; 25.1, 10.7, -3.3,  
 10.6; 28.3, 13.4, -0.4, 13.6; 31.4, 15.7, -2.1, 16.1;

$C_{\text{L}}^\circ = 2.99 \times 10^{-4}$  M,  $C_{\text{A}}^\circ = 2.00 \times 10^{-4}$  M,  $C_{\text{M}}^\circ = 9.97 \times 10^{-3}$  M:  
 9.20, 1.84, -6.6, 1.78;

$C_{\text{L}}^\circ = 4.55 \times 10^{-4}$  M,  $C_{\text{A}}^\circ = 4.00 \times 10^{-4}$  M,  $C_{\text{M}}^\circ = 9.97 \times 10^{-3}$  M:  
 2.04, 0.243, -0.1, 0.214; 18.1, 6.17, -1.5, 5.98; 30.2, 15.4, 3.7, 15.9;

$C_{\text{L}}^\circ = 7.00 \times 10^{-4}$  M,  $C_{\text{A}}^\circ = 2.00 \times 10^{-4}$  M,  $C_{\text{M}}^\circ = 9.97 \times 10^{-3}$  M:  
 6.15, 1.07, -4.2, 0.965; 18.5, 6.24, -3.8, 6.09; 26.8, 12.5, 3.3, 12.8;

$C_{\text{L}}^\circ = 2.99 \times 10^{-4}$  M,  $C_{\text{A}}^\circ = 2.00 \times 10^{-4}$  M,  $C_{\text{M}}^\circ = 1.50 \times 10^{-2}$  M  
 1.11, 2.79, 8.1, 2.80;

$C_{\text{L}}^\circ = 4.00 \times 10^{-4}$  M,  $C_{\text{A}}^\circ = 3.00 \times 10^{-4}$  M,  $C_{\text{M}}^\circ = 1.50 \times 10^{-2}$  M:  
 2.01, 0.231, 2.1, 0.215; 14.3, 3.85, -4.3, 3.86; 22.6, 8.09, -6.1, 8.44; 30.8, 14.7, 0.2, 15.9;

$C_{\text{L}}^\circ = 2.99 \times 10^{-4}$  M,  $C_{\text{A}}^\circ = 2.00 \times 10^{-4}$  M,  $C_{\text{M}}^\circ = 1.99 \times 10^{-2}$  M:  
 11.2, 2.73, 5.4, 2.78; 20.0, 7.58, 10.6, 8.05; 26.5, 11.0, 0.1, 12.1; 30.2, 13.2, -4.5, 14.7.

ytterbium and copper EDTA complexes, respectively. The data in Tables 1 and 2 are averages of three independent measurements.

*The copper (b) and lanthanum systems.* In order to check the kinetic model, when the association of the ligand to the central ion is rate determining along path I, the copper system was used. In this experiment a small amount of copper ions was mixed with a large amount of both lanthanum ions and lanthanum EDTA complex.

Table 2. Rate data for the copper (a) system. M=Cu and L=Yb.

$[H]^+ \times 10^5/M$ ,  $k_{\text{obs}} \times 10^3/s^{-1}$ ,  $100(k_{\text{obs}} - k_{\text{calc}})/k_{\text{calc}}$ ,  $f_{\text{MA,exp}} \times 10^3/s^{-1}$ ;

$C_{\text{M}}^\circ = 4.36 \times 10^{-4}$  M,  $C_{\text{A}}^\circ = 2.02 \times 10^{-4}$  M,  $C_{\text{L}}^\circ = 5.03 \times 10^{-3}$  M:  
 7.05, 0.558, -1.8, 0.702; 17.1, 1.69, -1.4, 2.18; 27.2, 3.20, -0.5, 4.38; 37.2, 4.64, -7.3,  
 6.70;

$C_{\text{M}}^\circ = 5.98 \times 10^{-4}$  M,  $C_{\text{A}}^\circ = 1.00 \times 10^{-4}$  M,  $C_{\text{L}}^\circ = 7.47 \times 10^{-3}$  M:  
 5.55, 0.432, -0.7, 0.551; 17.0, 1.73, 3.0, 2.26; 33.8, 4.60, 6.4, 6.69; 44.9, 6.46, 0.0, 9.99;  
 56.0, 9.23, 4.7, 15.4;

$C_{\text{M}}^\circ = 5.98 \times 10^{-4}$  M,  $C_{\text{A}}^\circ = 1.00 \times 10^{-4}$  M,  $C_{\text{L}}^\circ = 1.01 \times 10^{-2}$  M:  
 2.51, 0.216, 1.9, 0.281; 5.46, 0.437, -2.2, 0.532; 8.73, 0.738, -2.2, 0.896; 11.6, 1.09,  
 2.7, 1.35; 14.9, 1.53, 5.2, 1.93; 17.6, 1.85, 2.3, 2.36; 21.1, 2.24, -2.9, 2.90; 24.1, 2.60,  
 -5.7, 3.43; 29.2, 3.61, 0.2; 4.96; 35.4, 4.62, -1.7, 6.59; 41.8, 5.70, -4.1, 8.47; 47.2,  
 6.87, -2.3, 10.6; 52.8, 8.05, -2.3; 12.9; 58.7, 9.93, 4.0, 16.5; 64.4, 10.9, 0.2, 18.7;

$C_{\text{M}}^\circ = 8.02 \times 10^{-4}$  M,  $C_{\text{A}}^\circ = 3.29 \times 10^{-4}$  M,  $C_{\text{L}}^\circ = 1.27 \times 10^{-2}$  M:  
 7.03, 0.585, -0.7, 0.711; 12.0, 1.11, -0.5, 1.37; 22.1, 2.55, 3.6, 3.34; 32.1, 3.93, -4.6, 5.44;

$C_{\text{M}}^\circ = 2.00 \times 10^{-3}$  M,  $C_{\text{A}}^\circ = 2.02 \times 10^{-4}$  M,  $C_{\text{L}}^\circ = 1.27 \times 10^{-2}$  M:  
 7.24, 0.513, -0.2, 0.739; 17.6, 1.69, 4.6, 2.44; 27.9, 3.26, 6.0, 4.96; 38.2, 5.09, 5.5, 8.17.

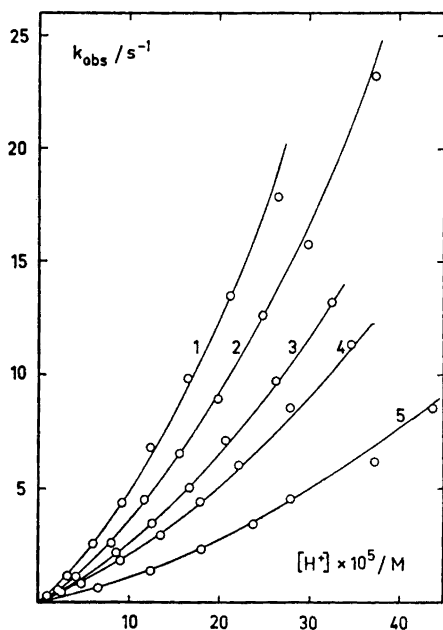


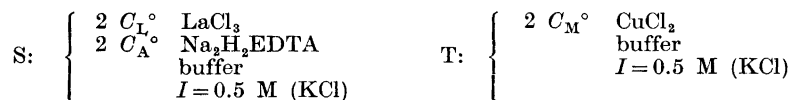
Fig. 1. The observed rate constant,  $k_{\text{obs}}$  for the copper (b) system as a function of the hydrogen ion concentration. In all cases,  $C_{\text{Cu}}^{\circ} = 2.00 \times 10^{-4}$  M and  $C_{\text{A}}^{\circ} = 5.00 \times 10^{-3}$  M. The concentration of lanthanum ions,  $C_{\text{La}}^{\circ}$ , is (1)  $8.58 \times 10^{-3}$  M, (2)  $1.00 \times 10^{-2}$  M, (3)  $1.24 \times 10^{-2}$  M, (4)  $1.50 \times 10^{-2}$  M, and (5)  $2.50 \times 10^{-2}$  M. The full-drawn curves have been calculated from the obtained rate constants of  $f_{\text{MA}}$ ,  $f_{\text{LA}}$ , and  $f$ . Some experimental points close to the origin have been omitted for clarity.

From a plot of the observed rate constant *vs.* the hydrogen ion concentration (Fig. 1), it is seen that a separate curve is obtained for each lanthanum ion concentration at a constant concentration of lanthanum complex. At a given pH, the rate decreases for increasing lanthanum ion concentration. This behaviour is exactly what is expected from the kinetic model for large  $\delta$ -values.

The measurements on the lanthanum system were performed in such a way that the dissociation of the complex became rate determining.

The shortest half-lives for the studied reactions of these two systems are in the ms range. They were studied with a Durrum-Gibson stopped-flow spectrophotometer. The wavelength range used was 600–820 nm. To check that no photochemical effects were present, some runs were studied at different wavelengths and slit widths. No differences in the observed rate constants could be detected.

The solutions S and T, which were mixed in equal volumes, had the following compositions both for the copper (b) and for the lanthanum systems:



To remove dissolved air, the solutions were boiled for two minutes at decreased pressure at room temperature.

The effect of the acetate concentration on the rate was investigated in the copper (b) system. Some solutions with varying concentrations of acetate at constant pH were measured. A moderate increase of the observed rate constant with increasing acetate concentration was found (Table 3). This result is consistent with that of Gientworth *et al.*<sup>17</sup> for the cerium system. The rate data are given in Tables 3 and 4 and in Figs. 1 and 2.

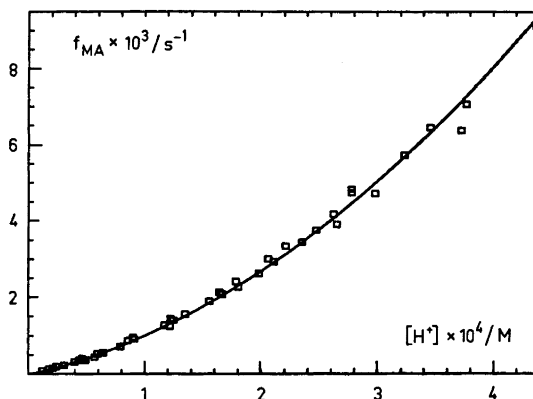


Fig. 2. The resulting dissociation rate constant of the copper EDTA complex,  $f_{MA}$ , from the copper (b) system as a function of the hydrogen ion concentration. The full-drawn curve has been calculated from the obtained rate constants.

Table 3. Rate data for the copper (b) system. M = Cu and L = La.

$[H^+] \times 10^5 / M$ ,  $k_{obs} / s^{-1}$ ,  $100(k_{obs} - k_{calc}) / k_{calc}$ ,  $f_{MA,exp} \times 10^4 / s^{-1}$ ,  $f_{D,exp} \times 10^{-1} / s^{-1} M^{-1}$ ;

$C_M^\circ = 2.00 \times 10^{-4} M$ ,  $C_A^\circ = 5.00 \times 10^{-3} M$ ,  $C_L^\circ = 8.58 \times 10^{-3} M$ :  
0.830, 0.281, -3.9, 0.572, 0.242; 3.07, 1.13, -4.4, 2.32, 0.699; 5.93, 2.57, 1.9, 5.37, 4.40;  
9.09, 4.35, 1.7, 9.19, 6.78; 12.3, 6.83, 8.1, 14.6, 17.9; 16.4, 9.88, 4.9, 21.3, 19.2; 21.1, 13.5,  
0.2, 29.3, 12.9; 26.5, 17.9, -5.8, 39.1, -8.38;

$C_M^\circ = 2.00 \times 10^{-4} M$ ,  $C_A^\circ = 5.00 \times 10^{-3} M$ ,  $C_L^\circ = 1.00 \times 10^{-2} M$ :  
0.338, 0.0892, 2.5, 0.244, 0.241; 0.940, 0.244, -1.7, 0.667, 0.454; 2.10, 0.559, -3.4,  
1.54, 0.799; 3.98, 1.16, -1.7, 3.22, 1.88; 4.86, 1.36, -8.4, 3.76, 0.188; 7.90, 2.58, -3.0,  
7.29, 2.89; 11.7, 4.50, 2.2, 12.9, 8.77; 15.6, 6.57, 1.5, 19.1, 11.0; 19.8, 8.96, -1.3, 26.3,  
8.91; 24.7, 12.7, 0.8, 37.6, 16.3; 29.8, 15.8, -5.3, 47.2, -1.87; 37.7, 23.3, -2.9, 70.7, 6.75;

$C_M^\circ = 2.00 \times 10^{-4} M$ ,  $C_A^\circ = 5.00 \times 10^{-3} M$ ,  $C_L^\circ = 1.24 \times 10^{-2} M$ :  
1.25, 0.242, 1.0, 0.931, 0.774; 4.37, 0.954, 2.5, 3.76, 3.00; 8.56, 2.20, 5.7, 8.89, 7.46; 12.5,  
3.46, 2.1, 14.2, 8.73; 16.7, 5.02, 0.8, 20.8, 10.4; 20.6, 7.13, 5.9, 30.1, 20.3; 26.2, 9.78, 2.1,  
41.8, 19.3; 32.4, 13.3, 0.7, 57.4, 20.6;

$C_M^\circ = 2.00 \times 10^{-4} M$ ,  $C_A^\circ = 5.00 \times 10^{-3} M$ ,  $C_L^\circ = 1.50 \times 10^{-2} M$ :  
0.531, 0.0853, 10.1, 0.424, 0.469; 1.22, 0.193, 5.4, 0.953, 0.912; 2.39, 0.396, 6.1, 1.98, 1.85;  
4.62, 0.819, 5.6, 4.17, 3.59; 8.99, 1.85, 7.8, 9.70, 8.02; 13.5, 2.97, 2.7, 15.8, 9.41; 17.8,  
4.45, 5.1, 24.2, 14.9; 22.1, 6.04, 5.6, 33.4, 19.6; 27.8, 8.59, 7.2, 48.3, 28.5; 34.6, 11.3, 1.8,  
64.6, 24.2;

$C_M^\circ = 2.00 \times 10^{-4} M$ ,  $C_A^\circ = 5.00 \times 10^{-3} M$ ,  $C_L^\circ = 2.50 \times 10^{-2} M$ :  
1.82, 0.174, 4.9, 1.47, 1.22; 6.46, 0.654, -2.0, 5.69, 3.45; 12.2, 1.39, -4.6, 12.6, 5.64;  
18.0, 2.37, -1.9, 22.7, 9.41; 23.5, 3.47, -0.3, 34.4, 13.3; 27.8, 4.63, 4.9, 47.4, 20.6; 37.2,  
6.18, -9.2, 63.8, 7.92; 43.7, 8.52, -1.9, 91.2, 21.7;

$C_M^\circ = 2.00 \times 10^{-4} M$ ,  $C_A^\circ = 1.00 \times 10^{-2} M$ ,  $C_L^\circ = 1.50 \times 10^{-2} M$ :  
4.90, 2.70, -11.6, 3.65, -0.799;

$C_M^\circ = 2.00 \times 10^{-4} M$ ,  $C_A^\circ = 1.50 \times 10^{-2} M$ ,  $C_L^\circ = 2.02 \times 10^{-2} M$ :  
5.70, 4.74, -11.2, 4.40, -0.785.

Variation with acetate concentration:  
 $[H^+] = 0.85 \times 10^{-5} M$ ,  $C_M^\circ = 2.00 \times 10^{-4} M$ ,  $C_A^\circ = 5.00 \times 10^{-3} M$ ,  $C_L^\circ = 8.58 \times 10^{-3} M$ :  
 $[Ac^-] / mM$ ,  $k_{obs} / s^{-1}$ : 12.5, 0.276; 25.0, 0.284; 37.5, 0.293; 50.0, 0.296; 62.5, 0.310.

Table 4. Rate data for the lanthanum system. L=La and M=Cu.

$[H^+] \times 10^5/M$ ,  $k_{\text{obs}} \times 10/s^{-1}$ ,  $100(k_{\text{obs}} - k_{\text{calc}})/k_{\text{calc}}$ ,  $f_{\text{LA,exp}} \times 10/s^{-1}$ ;

$C_L^\circ = 2.06 \times 10^{-4}$  M,  $C_A^\circ = 2.00 \times 10^{-4}$  M,  $C_M^\circ = 4.99 \times 10^{-3}$  M:

1.95, 0.923, -0.9, 0.932; 3.69, 1.64, 2.7, 1.65; 12.0, 5.15, 5.4, 5.24; 20.8, 9.09, 5.4, 9.32; 33.4, 15.2, 5.6, 15.7;

$C_L^\circ = 3.26 \times 10^{-4}$  M,  $C_A^\circ = 3.00 \times 10^{-4}$  M,  $C_M^\circ = 9.98 \times 10^{-3}$  M:

3.12, 1.46, 6.0, 1.47; 3.83, 1.70, 3.1, 1.72; 4.54, 1.90, -1.3, 1.92; 7.41, 3.29, 7.8, 3.30; 10.6, 4.13, -4.7, 4.19; 13.7, 5.82, 4.1, 5.92; 17.2, 7.07, 0.2, 7.22; 20.5, 8.42, -1.1, 8.62; 23.9, 10.0, 0.5, 10.3; 27.4, 11.3, -2.3, 11.7; 33.3, 14.8, 3.4, 15.4; 41.3, 19.4, 6.6, 20.2; 47.3, 21.2, -0.1, 22.3; 55.0, 25.7, 1.8, 27.2;

$C_L^\circ = 3.26 \times 10^{-4}$  M,  $C_A^\circ = 3.00 \times 10^{-4}$  M,  $C_M^\circ = 1.50 \times 10^{-2}$  M:

2.80, 1.21, -4.1, 1.22; 3.61, 1.51, -3.9, 1.52; 4.12, 1.82, 2.9, 1.83; 5.27, 2.16, -2.6, 2.18; 8.92, 3.59, -1.8, 3.64; 13.1, 5.15, -4.1, 5.23; 15.8, 6.12, -5.4, 6.23; 21.6, 8.49, -5.7, 8.69; 24.3, 9.91, -2.5, 10.2; 27.9, 11.8, -0.6, 12.1; 32.1, 13.9, 0.9, 14.4; 38.2, 17.0, 1.8, 17.7; 47.2, 20.7, -2.1, 21.8; 54.4, 24.0, -3.7, 25.4; 62.0, 28.5, -2.0, 30.3.

## CALCULATIONS AND RESULTS

The errors in the observed rate constants were approximately  $\pm 5\%$ . The precision of the emf's was about  $\pm 0.1$  mV, corresponding to an error of about 1% in the hydrogen ion concentration.

The stability constants used for the lanthanoid EDTA complexes were those of Betts and Dahlinger.<sup>1</sup> However, these constants are valid at 25°C and at an ionic strength of 0.1 M (potassium chloride). The stability constant for the copper EDTA complex has been determined by Schwarzenbach *et al.*<sup>3</sup> at 20°C and in a 0.1 M potassium chloride medium. The corresponding constant at 25°C was calculated by using the enthalpy value, given by Case and Stavelly.<sup>27</sup> However, all measurements in the present work were carried out at the ionic strength 0.5 M. The 0.1 M medium constants were used in the calculations, since in most cases the rate constants are rather insensitive to changes of the stability constants.

The constants for formation of acid complexes were those of Kolat and Powell<sup>25</sup> for the lanthanoids, and of Schwarzenbach *et al.*<sup>3</sup> for copper. The constants used are given in Table 5.

The rate constants were evaluated from eqns. (20), (21a - c) for the copper (a), ytterbium, and lanthanum systems, and from eqns. (20), (22a - c) for the

Table 5. Stability constants used in the calculations.

System	$\log \beta$	Ref.	$\log K_{\text{LAH}}$	Ref.
Cu (a)	18.68	3	3.0	3
Cu (b)	18.71	—	3.0	
La	15.19	1	2.4	25
La-Cu (b)	15.16	—	2.4	
Yb	18.99	1	2.7	25

copper (b) system. In the copper (b) system, a few  $k_{\text{obs}}$ -values were also calculated from eqns. (17) – (19a – c). The differences in  $k_{\text{obs}}$ -values obtained from the two sets of equations were negligible compared with the experimental errors. The  $\delta_1$ -values are in the range 0.03 – 0.16, whereas  $\delta_2$  varies from  $1 \times 10^3$  to  $9 \times 10^3$ . The resulting values of  $f_{\text{MA}}$  and  $f_{\text{D}}$  then become inversely proportional to the  $\delta_2$ -values, but they are rather insensitive to  $\delta_1$  because  $\delta_1$  in eqn. (22) is multiplied with  $f_{\text{MA}}/f_{\text{LA}}$ . Since the rate of dissociation of the copper complex is much slower than that of the lanthanum complex, it follows that  $\delta_1 f_{\text{MA}}/f_{\text{LA}} \ll 1$ .

By minor changes of the stability constants, *viz.*  $\log \beta_{\text{CuA}}$  from 18.68 to 18.71 and  $\log \beta_{\text{LaA}}$  from 15.19 to 15.16, a good agreement of the rate constants of the dissociation of the copper EDTA complex from the copper (a) and copper (b) experiments could be obtained (Table 6). This reveals that the approximation of using stability constants valid at an ionic strength of 0.1 M in a 0.5 M medium is a good one. From the experiments with the copper (b) system, it was not possible to determine the rate constant in path I for the uncatalysed dissociation step, owing to its low value. In this experiment, a hydrogen ion catalysed reaction along path II was also detected. However, the corresponding rate constant is rather inaccurate, since only a small fraction (in most cases less than 20 %) of the total reaction proceeds along this path.

Table 6. The obtained rate constants for the dissociation of the EDTA complexes. The errors are the confidence limits at the 99 % level.

System	$k_0/\text{s}^{-1}$	$k_1/\text{s}^{-1} \text{ M}^{-1}$	$k_2/\text{s}^{-1} \text{ M}^{-2}$	Ref.
Cu (a)	$(9.0 \pm 5.1)10^{-5}$	$6.5 \pm 1.0$	$(3.5 \pm 0.3)10^4$	this
Cu (b)	—	$6.9 \pm 0.3$	$(3.3 \pm 0.3)10^4$	this
La	$(2.0 \pm 1.0)10^{-2}$	$(3.7 \pm 0.3)10^3$	$(1.9 \pm 0.7)10^6$	this
	—	$7.0 \times 10^3$	—	11
Yb	—	$0.76 \pm 0.08$	$(1.43 \pm 0.07)10^4$	this
	—	0.70	$2.3 \times 10^4$	11

The calculations were performed by a digital computer, using a program written by Ekström and Rühl.<sup>28</sup> In order to check the error limits of the constants, especially of  $f_{\text{D}}$ , the following procedure was used. New values of  $k_{\text{obs}}$  were produced from the experimental values by means of normally distributed random errors, using  $\sigma = 0.05k_{\text{obs}}$ , which corresponds to the accuracy of the observed rate constants. With these new  $k_{\text{obs}}$ -values, a new set of parameters in the rate functions was calculated. The results remained within the different confidence limits, as often as was statistically expected. Hence, the weighting procedures used seem to have given realistic standard deviations.

The rate constant of the dissociation of the copper, lanthanum, and ytterbium EDTA complexes in the media used is given by

$$f = \bar{k}_0 + \bar{k}_1[\text{H}^+] + \bar{k}_2[\text{H}^+]^2$$

For the copper (b) system, a direct substitution reaction, path II, was found together with path I. This corresponds to the reaction



with  $f_D = \bar{k}_{1D}[\text{H}^+]$  and  $\bar{k}_{1D} = (5.7 \pm 1.8)10^5 \text{ s}^{-1} \text{ M}^{-2}$ . The apparent rate constants  $k_1$  are products of the rate constants and the corresponding equilibrium constants for the formation of acid complexes (eqn. 6c). The results, together with the results of other authors, are given in Table 6.

*Acknowledgements.* This work has been supported by a grant from *Statens Naturvetenskapliga forskningsråd*. I express my sincere gratitude to Fillic. Carl-Gustav Ekström for invaluable help during this research. I also thank Professor Ido Leden for his constant support and constructive criticism and Docent Ingmar Grenthe for many helpful discussions and suggestions. My thanks are also due to Dr. Peter Sellers for linguistic criticism.

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Received April 25, 1972.

*Acta Chem. Scand.* **26** (1972) No. 10