Exchange Reactions of *trans*-1,2-Diaminocyclohexane-tetraacetate Complexes of Magnesium, Calcium, Strontium, and Lanthanum Ions in Aqueous Alkaline Solution

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The rate of transfer of magnesium, calcium, strontium, and lanthanum ions from D-(−)-*trans*-1,2-diaminocyclohexane-N,N,N',N'-tetra-acetate ≡ D-CDTA^{4-} to D,L-CDTA^{4-} has been studied in alkaline solution. The rate of reaction is independent of the HCDTA^{3-} and CDTA^{4-} concentrations for all the ions studied with the exception of the lanthanum ion for which a first order dependence on the CDTA^{4-} concentration is observed. The [H$^+$] profile of the rate constants of the dissociation reactions has been determined and a mechanism consistent with the observed [H$^+$] profile is given. This mechanism is valid for the CDTA complexes of both the alkaline earth ions and the lanthanum ion. The activation parameters for the resolved rate constants have also been determined and support the stated mechanism.

The kinetics of the dissociation of the alkaline earth ion complexes of *trans*-1,2-diaminocyclo-hexane-N,N,N',N'-tetraacetate (CDTA) have in a previous paper [1] been shown to be dependent on [H$^+$] in a complex way. Glentworth *et al.*,[2] Brücher and Szarvas,[3] and Nyssen and Margerum [4] have studied the kinetics of the dissociation of the lanthanide ion complexes of CDTA in neutral or acidic solution. Glentworth *et al.* and Nyssen and Margerum have shown that the [H$^+$] independent term in the rate law for the dissociation is too large to be equal to the direct dissociation of the complexes to Ln^{3+} and CDTA^{4-}; however, the mechanisms proposed for the reaction path independent of [H$^+$] are not in agreement (*cf.* Ref. 2b).
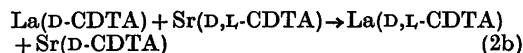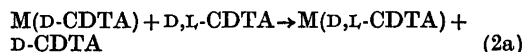
The present studies deal with the kinetics of dissociation at hydrogen ion concentrations where the usual first order dependence on [H$^+$]

is not observed. The dissociation refers to the reaction scheme in (1).

$$\text{MCDTA} \underset{\text{H}^+}{\overset{k_d}{\longrightarrow}} \text{M} + \text{CDTA} \qquad (1)$$
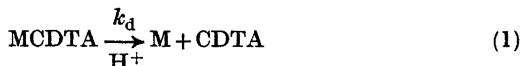
The [H$^+$] range has been expanded and studies on the dissociation of LaCDTA have been included (*cf.* Ref. 1). The mechanism of dissociation of MCDTA at low [H$^+$] is found to be similar for M = Mg, Ca, Sr, or La. The stated mechanism agrees with that suggested by Nyssen and Margerum [4] for the dissociation of the lanthanide complexes of CDTA.

The overall reactions studied are shown in (2a) (M = Mg, Ca, Sr or La) and (2b). Reaction (2b) has been included in the investigation since a pronounced dependence on [CDTA^{4-}] exists for La(D-CDTA) in reaction (2a). The charges, protons, and nomenclature for the optical rota-

$$\text{M(D-CDTA)} + \text{D,L-CDTA} \rightarrow \text{M(D,L-CDTA)} + \text{D-CDTA} \qquad (2a)$$

$$\text{La(D-CDTA)} + \text{Sr(D,L-CDTA)} \rightarrow \text{La(D,L-CDTA)} + \text{Sr(D-CDTA)} \qquad (2b)$$

tion have been omitted for clarity in (2a) and (2b). Each one of the enantiomers L-CDTA and D-CDTA forms only one of the two possible isomeric complexes due to the stereospecificity of this ligand.[5,6]

EXPERIMENTAL

Chemicals. D,L-H$_4$CDTA, the racemic form of *trans*-1,2-diaminocyclohexane-N,N,N',N'-tetra-acetic acid (Fluka *p.a.*) was recrystallized by

dissolving in dilute NaOH followed by the addition of HNO$_3$. D-H$_4$CDTA (D(−)H$_4$CDTA) was contributed by Professor K. H. Pearson, Cleveland State University, Cleveland, Ohio, U.S.A., and was used without further purification. The metal salts used were the nitrates of analytical grade. D,L-H$_4$CDTA and nitrates of Mg, Ca, Sr, and La were quantitatively analyzed by complexometric titrations.

Weighed amounts of the metal nitrate and H$_4$CDTA were dissolved to give the desired concentrations of the reactants. 2,6-Lutidin, tris(hydroxymethyl)methylamine, borate, and N-ethylpiperidine of the highest available purity were used and the solutions were adjusted to the desired pH by adding a solution of CsOH to the acidic form of these bases. CsOH was prepared by ion exchange of CsNO$_3$ on an IRA 400 resin (BDH). [CO$_3^{2-}$] constituted less than 1 % of [OH$^-$] in the CsOH solutions, as determined by titration with acid. The ionic strength was adjusted using CsNO$_3$ instead of nitrates of Li$^+$, Na$^+$ or K$^+$ as it has been shown that complexes are formed between these metal ions and CDTA, whereas Cs$^+$ has not been observed to form CDTA complexes in the pH ranges used.[7,8]

Apparatus. A Perkin-Elmer Model 141 photoelectric polarimeter (with potentiometric readout) in combination with a "Servograph REC 51" recorder equipped with a high sensitivity unit "REA 112" (Radiometer, Copenhagen) was used to monitor the change in optical rotation as a function of time during the reactions. The polarimeter had the following five wavelengths available: 589, 578, 546, 436, and 365 nm. However, in this work, 365 nm was used exclusively because of the greater change in optical rotation at this wavelength during reaction (2). The 1 dm polarimeter cell with quartz windows was thermostated to a precision of ± 0.1 °C. The "rapid" reactions were followed by means of a simple mixing device consisting of a Y-formed glass tube which was connected to two calibrated glass syringes containing the reactants. A water bath of the desired temperature was used to thermostate the glass syringes and the Y-formed glass tube. The mixing of the reactants was completed within 5 s, and the response time of the polarimeter and recorder was about 10 s following the initial mixing.

The pH of the reaction mixture was measured after the completion of the reaction with a "pH Meter 4" equipped with a calomel electrode, K 401, and a glass electrode, G 202 B (Radiometer, Copenhagen).

Rate measurements. The pH ranges used in the study of reaction (2) are shown in Figs. 2, 3, 4, and 6. Titrations of the complexes to be discussed have shown that protonated forms as well as the hydroxo forms of these complexes are found in negligible concentrations in the pH ranges studied (*cf.* Ref. 1). The formula for the investigated CDTA complexes is therefore MCDTA$^{(4-n)-}$ where n is the charge of the metal ion.

Table 1. Molar rotations (deg. M^{-1} cm^{-1}) of D-CDTA and the D-CDTA complexes investigated.[a]

CDTA	MgCDTA	CaCDTA	SrCDTA	LaCDTA
−5.4	5.3	2.5	1.3	8.7

[a] pH 10.0; N-ethylpiperidine buffer 5×10^{-3} M; 25 °C; 365 nm.

Table 1 shows the values of the molar rotations of the optically active species employed in reaction (2). The molar rotations are calculated from measurements performed on 10^{-3} M solutions with pH adjusted to 10.0 with CsOH. The total change in rotation during reaction (2) is $0.07 - 0.11°$ for the concentrations used. Different initial concentrations of the decomposing species were used; in each case a tenfold to fiftyfold excess of entering ligand was present, which was found to be sufficient to make the overall reaction go to completion.

As opposed to the exchange reactions with Cu(II) ion in NH$_4^+$/NH$_3$ solutions,[1] changes in [H$^+$] do not occur for reaction (2). Buffer concentrations of 5×10^{-3} M are therefore sufficient for maintaining the desired pH in the present investigation. For M = La in reaction (2a) at low pH, no buffer is required since the excess of CDTA supplies the solution with a buffer capacity in this pH range. In some kinetic runs, it is possible to maintain a given pH with different buffers, all of which yield identical rate constants, *i.e.*, no buffer effect is observed. The hydrogen ion concentration is calculated as log [H$^+$] = −pH; that is, the activity coefficient which is a constant at the ionic strength maintained here has been omitted.

A least squares analysis performed on a "Wang" desk computer was used to obtain the best linear dependence.

The stability constants used in the present work are given in Table 2.

Table 2. Stability constants.

Complex	log K (M^{-1})
H$_2$CDTA	(6.1)[a]
HCDTA	(13.2)[b]
MgCDTA	(11.0)[a]
CaCDTA	(13.1)[a]
SrCDTA	(10.5)[a]
LaCDTA	(16.9)[a]

[a] Ref. 10; $\mu = 0.1$ (KNO$_3$); corrected to 25 °C by the thermodynamic values from Ref. 10. [b] Ref. 7; $\mu = 0.1$ (CsNO$_3$); 25 °C.
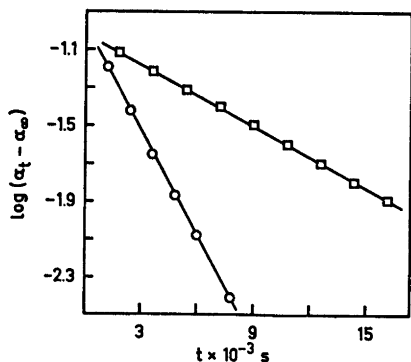
Fig. 1. First order plots. $\bigcirc$ reaction (2a); $[Mg(D\text{-}CDTA)]_0 = 1.0 \times 10^{-3}$ M; $[D,L\text{-}CDTA]_0 = 5.0 \times 10^{-2}$ M; pH 8.29; 25.0 °C; $\mu = 0.5$. $\square$ reaction (2b); $[La(D\text{-}CDTA)]_0 = 1.0 \times 10^{-3}$ M; $[Sr(D,L\text{-}CDTA)]_0 = 1.0 \times 10^{-2}$ M; pH 9.38; 25.0 °C; $\mu = 0.1$.

The exchange reactions studied are all carried out under conditions which make them pseudo first order. Two first order plots representing, respectively, reactions (2a) and (2b) are shown in Fig. 1. $[]_0$ indicates initial concentration.

RESULTS

Magnesium, calcium, strontium. The kinetics of dissociation for the CDTA complexes according to reaction (2a) have been examined as a function of hydrogen ion concentration as well as temperature.

The results are shown in Figs. 2, 3, and 4 where k_d is the observed first order rate constant. The log k_d versus pH plot is chosen in order to be able to include all the experimental results for the dissociation reactions of a given complex in one figure. Log k_d shows a linear dependence on pH at low values of pH with a slope of approximately -1 thereby indicating that a first order dependence on hydrogen ion concentration dominates in this pH range. Furthermore, zero order dependence on [D,L-HCDTA^{3-}] or [D,L-CDTA^{4-}] is observed as illustrated from the experiments with different concentrations of D,L-CDTA. k_d is accordingly the rate constant of the dissociation reaction, k_d being a function only of [H$^+$] and the medium.

Figs. 2, 3, and 4 give, on the other hand, no distinct information on the [H$^+$] profile at high values of pH. Plots of k_d versus [H$^+$] for high
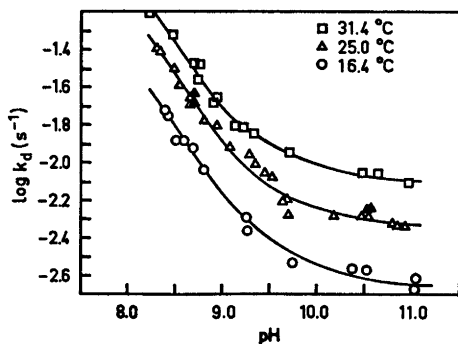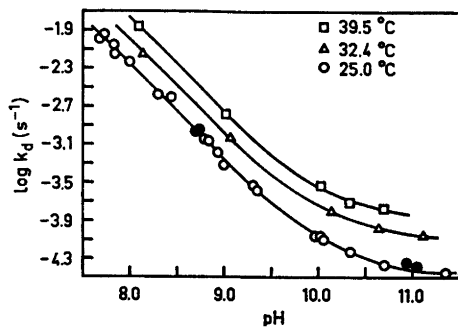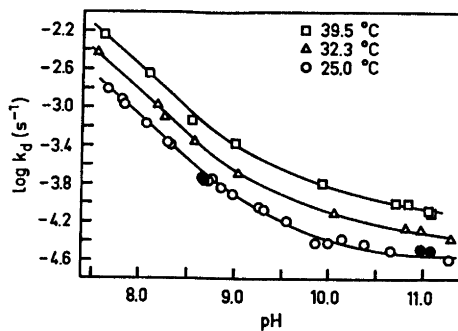
Figs. 2 – 4. Log k_d versus pH for M = Mg, Ca, and Sr, respectively. $[M(D\text{-}CDTA)]_0 = 1.0 \times 10^{-3}$ M; $[D,L\text{-}CDTA]_0 = 5.0 \times 10^{-2}$ M. The symbols, $\bullet$ and $\blacktriangle$, indicate $[D,L\text{-}CDTA]_0 = 1.0 \times 10^{-2}$ M; 25.0 °C. $\mu = 0.5$.

values of pH (*cf.* Fig. 5) yield profiles similar to those found in Ref. 1.

The straight lines in Fig. 5 display the results of a linear regression analysis of k_d versus [H$^+$] at higher [H$^+$] (*cf.* the following section, "Discussion").

Lanthanum. The observed first order rate constants for reaction (2a) (M = La) and (2b) are designated k_c and k_s, respectively. The deter-
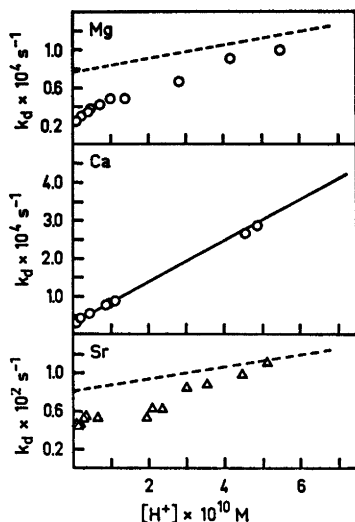
Fig. 5. Dependence of k_d on $[H^+]$ for pH 9.2 − 11.4 for M = Mg, Ca, and Sr respectively; 25.0 °C; $\mu = 0.5$.

mination of k_s from the double exchange in reaction (2b) is feasible only if k_d for the dissociation of SrCDTA is much larger than k_s. Otherwise, k_s will necessarily be dependent on the rate of dissociation of the scavenger, SrCDTA. From Figs. 4 and 6 it is seen that k_d for SrCDTA is indeed much larger than k_s. Reaction (2b) will proceed to completion only if [D,L-CDTA] is considerably higher than [D-CDTA]. This condition is fulfilled when using an excess of Sr(D,L-CDTA) since the ratio between the stability constants for SrCDTA and
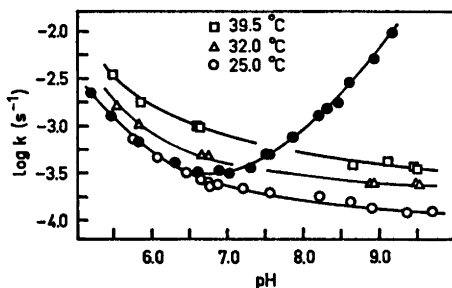

Fig. 6. Log k_s and log k_c *versus* pH for M = La. The symbols □△○ are used for k_s; [La(D-CDTA)]$_0$ = 1.0 × 10^{-3} M; [Sr(D,L-CDTA)]$_0$ = 1.0 × 10^{-2} M. The symbol ● is used for k_c; [La(D-CDTA)]$_0$ = 5.0 × 10^{-4} M; [D,L-CDTA]$_0$ = 1.0 × 10^{-2} M; 25.0 °C. $\mu = 0.1$.

LaCDTA are of the correct order of magnitude (*cf.* Table 2).

From Fig. 6 it is seen that for LaCDTA the reactions approach first order in $[H^+]$ at low values of pH and that the exchange reaction of the ligand is faster than the double exchange reaction with SrCDTA at pH > 6.5. The plot of log k_c *versus* pH in Fig. 6 indicates that k_c depends specifically on [D,L-CDTA^{4-}] and is independent of [D,L-HCDTA^{3-}] and [D,L-H$_2$CDTA^{2-}]. That k_c has this particular form for dependence is evident from the fact that k_c is equal to k_s for pH < 6.5 and from the fact that k_s, for steric reasons, must be independent of [SrCDTA] (*cf.* Margerum [9]). Furthermore, k_c and k_s must be equal to k_d for pH < 6.5, k_d being the rate constant of dissociation analogous to the similar rate constant of dissociation of the alkaline earth complexes. k_d is included in both k_c and k_s, the concentration of D,L-CDTA^{4-} being negligible in the experiments with the double exchange of SrCDTA as compared with the experiments with the ligand exchange (*cf.* the magnitude of the stability constant of SrCDTA in Table 2). Furthermore, the exchange reaction between La(D-CDTA) and D-CDTA^{4-} does not give rise to a change in rotation which means that the exchange reaction between La(D-CDTA) and L-CDTA^{4-} is the only one being observed.

The difference between k_c and k_s is calculated according to eqn. (3). $k_{CDTA}{}^{LaCDTA}$ is the rate constant of the reaction between La(D-CDTA) and L-CDTA^{4-} where c indicates [L-CDTA^{4-}] in the ligand exchange.

$$k_c - k_s = k_{CDTA}{}^{LaCDTA}[\text{L-CDTA}^{4-}]_c \qquad (3)$$

[L-HCDTA^{3-}]$_c$ can, in the pH range 7.5 − 9.2, be set equal to the total concentration of free L-CDTA (*cf.* Table 2); *i.e.*, [L-HCDTA^{3-}]$_c$ is half the free ligand concentration. $k_c - k_s$ may then be stated as in eqn. (4).

$$k_c - k_s = k_{CDTA}{}^{LaCDTA} \frac{[\text{L-HCDTA}^{3-}]_c}{K_{HCDTA}[H^+]} \qquad (4)$$

Fig. 7 shows a plot of $k_c - k_s$ *versus* $[H^+]^{-1}$ where the slope of the straight line obtained is used for the calculation of $k_{CDTA}{}^{LaCDTA}$. For the calculation of $k_c - k_s$ the observed values of k_c are used whereas an estimated value for k_s at the same $[H^+]$ as k_c is obtained by interpolation between the observed values of k_s. The vanish-
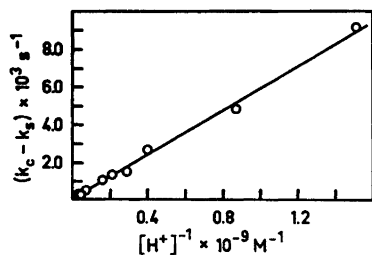
Fig. 7. $k_c - k_s$ *versus* $[H^+]^{-1}$ for the calculation of k_{CDTA}^{LaCDTA}; 25.0 °C; $\mu = 0.1$.

ing intercept for the straight line in Fig. 7 corroborates eqn. (4). The low $[Sr^{2+}]$ in connection with reaction (2b) does not result in a contribution to k_s since a dependence of k_s on $[Sr^{2+}]$ would give rise to a negative intercept and non-linearity in Fig. 7. k_{CDTA}^{LaCDTA} is calculated from the slope to be 1.9×10^4 M^{-1} s^{-1} when using $K_{HCDTA} = 10^{13.2}$ M^{-1} (*cf.* Table 2) and $[L\text{-}HCDTA^{3-}]_c = 5.0 \times 10^{-3}$ M. The value of k_{CDTA}^{LaCDTA} is surprisingly large compared with the rate constant of the reaction between Pb(L-CDTA) and D-CDTA^{4-} which according to Carr and Baker [8] is equal to 3.77×10^{-2} M^{-1} s^{-1}. Otherwise, the work done by these authors and that done in the present study agree inasmuch as no dependence on [HCDTA^{3-}] is observed. The observed rate of both the ligand and double exchange reaction is expressed by eqn. (5) where the bracket is equal to the observed first order rate constants k_c or k_s.

$$-\frac{d[LaCDTA]}{dt} =$$
$$\{k_{CDTA}^{LaCDTA}[L\text{-}CDTA^{4-}] + k_d\}[LaCDTA] \qquad (5)$$

$[L\text{-}CDTA^{4-}]$ in the double exchange, indicated by s, is calculated from eqn. (6) which is valid in the pH range $7.5 - 9.7$.

$$[L\text{-}CDTA^{4-}]_s = \left(\frac{[Sr(L\text{-}CDTA)]}{K_{SrCDTA}K_{HCDTA}[H^+]}\right)^{\frac{1}{2}} \qquad (6)$$

The rate constant k_d for the dissociation of LaCDTA is calculated from k_s using eqns. (5) and (6) (*cf.* Table 3).

Table 3 shows k_d as being negative at pH 9.71. This inconsistency may be attributed to the fact that the value of the stability constant for SrCDTA ($10^{10.5}$ M^{-1}) is too low. This value has been determined with K$^+$ present. The presence of K$^+$ causes an error since this ion is known to coordinate with CDTA (*cf.* Ref. 7). It can, however, be stated with certainty that k_d extrapolated to $[H^+] = 0$ is negligible. Qualitatively both k_s and k_d have the same dependence on $[H^+]$ as that of k_d in the dissociation reaction of the alkaline earth complexes. Furthermore, k_s is equal to k_d at pH < 7.5.

DISCUSSION

Fig. 8 shows qualitatively the dependence of k_d on $[H^+]$ for MCDTA in the pH range investigated (M = Mg, Sr or La). A similar $[H^+]$ profile of k_d for BaCDTA has also been found (*cf.* Jensen and Larsen [1]). The $[H^+]$ profile of k_d for CaCDTA is, on the other hand, found to be a straight line. The mechanism of the dissociation reaction for CaCDTA is, however, assumed to be the same as that for the dissociation reactions of the other alkaline earth and lanthanum complexes. This assumption is main-

Table 3. Calculation of k_d for M = La in the pH range $7.5 - 9.7$.[a]

pH	$k_s \times 10^4$ s^{-1}	$k_{CDTA}^{LaCDTA}[L\text{-}CDTA^{4-}]_0 \times 10^4$ s^{-1}[b]	$k_d \times 10^4$ s^{-1}
7.56	1.92	0.11	1.81
8.21	1.75	0.24	1.51
8.62	1.56	0.38	1.18
8.91	1.33	0.53	0.80
9.38	1.17	0.91	0.26
9.71	1.22	1.33	(−0.11)

[a] 25.0 °C; $\mu = 0.1$. [b] $[L\text{-}CDTA^{4-}]_0$ is calculated from eqn. (6); $[Sr(L\text{-}CDTA)]_0 = 5.0 \times 10^{-3}$ M; K_{SrCDTA} and K_{HCDTA} from Table 2.
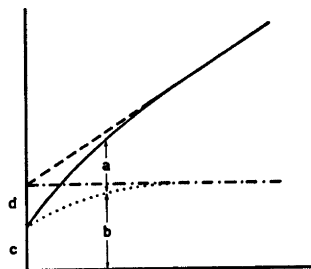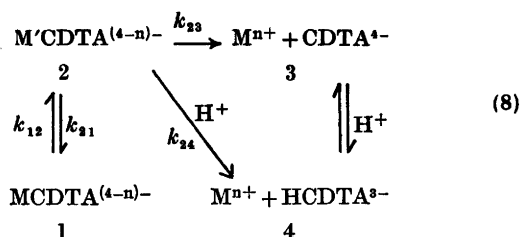
Fig. 8. Typical form of the curve of k_d *versus* [H$^+$]; for M = Ca see text. a = k_H^{MCDTA}[H$^+$]; b = $k_d - k_H^{MCDTA}$[H$^+$];   c = k_1^{MCDTA};   d = k_2^{MCDTA}; $k^{MCDTA} = k_1^{MCDTA} + k_2^{MCDTA}$. The solid curve is the observed k_d. − − − is the extrapolated straight line for the observed first order [H$^+$] dependence at low values of pH. · · · is the [H$^+$] profile for the reaction rate according to the proposed mechanism in (8). − · − · − shows how this mechanism is independent of [H$^+$] for [H$^+$] greater than a given value corresponding to the straight line for k_d.

ly based upon the magnitude of the activation parameters.

Fig. 8 shows both that k_d is given by eqn. (7) at low values of pH, and that this equation is invalid at higher pH values; at high pH the difference between k_d and k_H^{MCDTA}[H$^+$] is

$$k_d = k^{MCDTA} + k_H^{MCDTA}[H^+] \qquad (7)$$

smaller than k^{MCDTA}. The deviation from the straight line in Fig. 8 is explained by the mechanism depicted in scheme (8) where the rate determining step is 1→2. Mechanism (8) gives the direct dissociation of MCDTA$^{(4-n)-}$

$$
\begin{array}{ccc}
\text{M'CDTA}^{(4-n)-} & \xrightarrow{k_{23}} & \text{M}^{n+} + \text{CDTA}^{4-} \\
2 & & 3 \\
k_{12} \Big\Updownarrow k_{21} & \searrow^{\text{H}^+}_{k_{24}} & \Big\Updownarrow \text{H}^+ \\
\text{MCDTA}^{(4-n)-} & \text{M}^{n+} + \text{HCDTA}^{3-} \\
1 & 4
\end{array}
\qquad (8)
$$

along the paths 1→2→3. Furthermore, this mechanism also explains the k^{MCDTA} part of k_d (*i.e.*, paths 1→2→3 and 1→2→4) and, as regards this aspect, is in accordance with the mechanism assumed by Nyssen and Margerum.[4]

Jensen and Larsen [1] concluded that k_H^{MCDTA} is [H$^+$] dependent and accordingly interpreted k^{MCDTA} as the rate constant for the direct dissociation of the CDTA complexes. Both k_H^{MCDTA}

and k^{MCDTA} are assumed to be [H$^+$] independent in the present investigation.

The difference between k_d and k_H^{MCDTA}[H$^+$] may be expressed as in eqn. (9) when applying the "Steady State" approximation to species 2 in mechanism (8).

$$k_d - k_H^{MCDTA}[H^+] = \frac{k_{23} + k_{24}[H^+]}{k_{21} + k_{23} + k_{24}[H^+]} k_{12} \qquad (9)$$

Basolo and Pearson [11] have treated complexes of the chelate type in an analogous fashion and have arrived at a mechanism similar to (8).

The dependence of the reaction rate on [H$^+$] is, according to mechanism (8), determined by the magnitude of k_{21} relative to k_{24}[H$^+$]. Eqn. (9) is reduced to eqn. (10) if k_{21} is negligible compared with k_{24}[H$^+$]. Eqn. (7) shows that in this case k_{12} is identical to k^{MCDTA}.

$$k_d - k_H^{MCDTA}[H^+] = k_{12} = k^{MCDTA} \qquad (10)$$

Eqn. (9) is, on the other hand, reduced to eqn. (11) if k_{24}[H$^+$] is negligible as compared to k_{21}.

$$k_d - k_H^{MCDTA}[H^+] = \frac{k_{23} + k_{24}[H^+]}{k_{21} + k_{23}} k_{12} \qquad (11)$$

If [H$^+$] is small, a first order dependence on the hydrogen ion concentration is to be expected. Upon extrapolating to the k_d-axis in the plot of k_d *versus* [H$^+$] (*cf*. Fig. 8), it is seen that k_d can be expressed as in eqn. (12).

$$k_d = \frac{k_{23}k_{12}}{k_{21} + k_{23}} \equiv k_1^{MCDTA} \qquad (12)$$

It is furthermore seen from this figure that $k^{MCDTA} = k_1^{MCDTA} + k_2^{MCDTA}$.

k_H^{MCDTA}, k^{MCDTA}, k_1^{MCDTA}, and k_2^{MCDTA} are thus determined from the experimental results. k_H^{MCDTA} and k^{MCDTA} are − as shown in previous sections − the slope and the intercept, respectively, of the straight line found at low values of pH when plotting k_d *versus* [H$^+$]. k_1^{MCDTA} is the intercept of the straight line obtained when plotting k_d *versus* [H$^+$], *but* only at high values of pH. k_2^{MCDTA} is calculated as described in the preceding paragraph. It has to be emphasized, however, that [H$^+$] must be one to two orders of magnitude greater when determining k^{MCDTA} than when determining k_1^{MCDTA}. This condition arises as a consequence of the approximations leading to eqns. (10) and (12).

Table 4. The resolved rate constans for the dissociation of MCDTA complexes.[a]

M	t °C	k^{MCDTA} s^{-1}	k_H^{MCDTA} $M^{-1}s^{-1}$	pH range	k_1^{MCDTA} s^{-1}	k_2^{MCDTA} s^{-1}	pH range
Mg	25.0	7.7×10^{-5} $(5.2 \times 10^{-4})^b$ $(0)^c$	7.1×10^4 $(3.8 \times 10^4)^b$ $(6.33 \times 10^4)^c$	$7.7 - 8.4$ $(8.5 - 9.2)^b$ $(5.5 - 7.6)^c$	2.4×10^{-5}	5.3×10^{-5}	$10.4 - 11.0$
	32.3	1.2×10^{-4}	1.3×10^5	$7.6 - 8.6$	3.6×10^{-5}	8.1×10^{-5}	$11.0 - 11.3$
	39.5	1.9×10^{-4}	2.4×10^5	$7.6 - 9.0$	5.7×10^{-5}	1.3×10^{-4}	$10.8 - 11.1$
Ca							
	25.0	3.1×10^{-5} $(2.1 \times 10^{-4})^b$ $(0)^c$	5.4×10^5 $(4.2 \times 10^5)^b$ $(4.14 \times 10^5)^c$	$7.6 - 11.4$ $(8.5 - 10.5)^b$ $(5.5 - 7.6)^c$			
	32.4	7.1×10^{-5}	1.0×10^5	$8.2 - 11.1$			
	39.5	1.1×10^{-4}	1.7×10^5	$8.0 - 10.7$			
Sr							
	16.4	3.9×10^{-3}	3.5×10^6	$8.4 - 8.8$	2.2×10^{-3}	1.7×10^{-3}	$10.4 - 11.0$
	25.0	8.0×10^{-3} $(1.4 \times 10^{-2})^b$ $(3.0 \times 10^{-2})^c$	6.4×10^6 $(6.7 \times 10^6)^b$ $(6.06 \times 10^6)^c$	$8.3 - 8.9$ $(8.5 - 9.2)^b$ $(5.5 - 7.6)^c$	4.2×10^{-3}	3.8×10^{-3}	$10.5 - 10.9$
	31.4	1.5×10^{-2}	8.4×10^6	$8.2 - 8.9$	7.9×10^{-3}	6.6×10^{-3}	$10.5 - 11.0$
La							
	25.0	2.1×10^{-4} $(0)^d$ $(0)^e$	2.8×10^2 $(1.66 \times 10^2)^d$ $(2.34 \times 10^2)^e$	$5.7 - 7.7$ $(3.9 - 5.3)^d$ $(4.6 - 5.5)^e$	(0)	2.1×10^{-4}	
	32.0	3.8×10^{-4}	4.1×10^2	$5.5 - 7.7$	(0)	3.8×10^{-4}	
	39.5	7.9×10^{-4}	7.5×10^2	$5.5 - 7.6$	(0)	7.8×10^{-4}	

[a] $\mu = 0.5$ ($CsNO_3$) for M= Mg, Ca, and Sr; $\mu = 0.1$ ($CsNO_3$) for M= La. [b] Ref. 1; $\mu = 0.5$ (NH_4NO_3). [c] Ref. 15; $\mu = 0.5$ (Na-acetate). [d] Ref. 4; $\mu = 0.1$ ($NaClO_4$). [e] Ref. 3; $\mu = 0.1$ ($NaClO_4$).

Table 4 shows the resolved rate constants calculated in accordance with the procedure described in the previous paragraphs as well as the corresponding rate constants from the literature. Satisfactory agreement is found for k_H^{MCDTA} even in the event that the pH range in the present investigation is not the same as that in the cited studies. k_1^{MCDTA} and k_2^{MCDTA} cannot be calculated in the case of CaCDTA since no deviation from eqn. (7) is observed in the investigated pH range. The dissociation reaction of CaCDTA, on the other hand, may well follow mechanism (8). It is a possibility that the deviation from eqn. (7) appears at a higher value of pH which would indicate that k_{21} is larger than k_{23} but relatively small compared with $k_{24}[H^+]$. It is remarkable that k^{MCDTA} for the exchange reactions between the CDTA complexes of the alkaline earth ions and metal ions is considerably larger than the corresponding rate constants obtained in the present investigation (cf. Jensen and Larsen [1]). This fact may be related to a dependence on the metal ion concentration similar to the dependence on $[H^+]$ in mechanism (8) (cf. Nyssen and Margerum [4]). Another explanation for the difference between the values obtained for k_M^{CDTA} in the present work and the work by Jensen and Larsen [1] may involve the NH_4^+/NH_3 buffer used in that investigation in a manner similar to an effect observed with ammonium acetate in a study on isotopic Ce(III)exchange in Ce(III)polyaminocarboxylic acid chelates by Balcombe and Wiseall.[12]

The direct dissociation of the CDTA complexes according to mechanism (8) proceeds along reaction path $1 \to 2 \to 3$. A necessary condition for this dissociation mechanism is that the rate of the reverse reaction be slower than the diffusion controlled rate of the reaction between two ions, i.e., about 10^{10} $M^{-1}s^{-1}$ (cf. Caldin [13]). Furthermore, the rate of the reverse reaction where the rate determining step (rds) is $2 \to 1$ must be slower than the rate of formation for the water exchange mechanism of the aquo metal ion.[14]

Eqn. (13) shows how the rate constant

Table 5. Comparison of calculated rate constants for the formation of MCDTA from M^{n+} and $CDTA^{4-}$ at 25 °C with values predicted from the rate constants of water exchange.

M	k_M^{CDTA} $M^{-1}s^{-1}$	$k_M^{-H_2O}$ s^{-1}	$K_{OS}k_M^{-H_2O}$ $M^{-1}s^{-1}$
Mg	2.5×10^6	$(1.4 \times 10^5)^b$	7.0×10^6
Ca	$(3.9 \times 10^8)^a$	$(3.0 \times 10^8)^c$	1.5×10^{10}
Sr	1.3×10^8	$(3.5 \times 10^8)^c$	1.8×10^{10}
La		$(5.2 \times 10^8)^d$	$> 2.6 \times 10^{10}$

^{a} k_1^{CaCDTA} is assumed equal to k^{CaCDTA}. ^{b,c,d} Ref. 16, 17, and 18, respectively.

k_M^{CDTA} for the formation of $MCDTA^{(4-n)-}$ from M^{n+} and $CDTA^{4-}$ has been calculated from k_1^{MCDTA} and the stability constant for the corresponding complex $MCDTA^{(4-n)-}$.

$$k_M^{CDTA} = k_1^{MCDTA}K_{MCDTA} \tag{13}$$

Table 5 shows values for k_M^{CDTA} calculated from eqn. (13) as well as the values predicted from the water exchange rate of the outer sphere complex. K_{OS} is the outer-sphere association constant; a value of 50 M^{-1} has been used for the $2+$ metal and the $4-$ ligand [15] whereas a value larger than 50 M^{-1} has been used for the $3+$ metal ion (La^{3+}) and the $4-$ ligand (*cf.* Table 5). It is seen that the values of $K_{OS}k_M^{-H_2O}$ are larger than the values of k_M^{CDTA}. k_1^{LaCDTA} is found to be negligible (*cf.* Table 4). A calculation by means of eqn. (13) using the diffusion controlled value, $k_{La}^{CDTA} = 10^{10}$ M^{-1} s^{-1}, yields a $k_1^{LaCDTA} \leq 10^{-7}$ s^{-1}. The values of k_1^{MCDTA}, as calculated in the preceding section, are therefore consistent with mechanism (8).

Activation parameters. The rds in mechanism (8) is assumed to be $1 \rightarrow 2$. Accordingly, the activation parameters for k_1^{MCDTA} and k_2^{MCDTA} must be the same. The dependence of the resolved rate constants on temperature is shown in Table 4. Arrhenius plots of log k *versus* T^{-1} show satisfactory linearity, even in the case of $k = k_2^{MgCDTA}$ or k_2^{SrCDTA} where k is determined with some uncertainty because of the rather large values of k_d. $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ are calculated using the Arrhenius plots (*cf.* Table 6). Table 6 indicates that the requirements for identical activation parameters for k_1^{MCDTA} and k_2^{MCDTA} is fulfilled. The value of $\Delta G^{\ddagger}$ and the pronounced negative value of $\Delta S^{\ddagger}$ for k^{CaCDTA}

Table 6. Activation parameters for the resolved rate constants; 25 °C.

M	$\Delta H^{\ddagger}$ kJ mol^{-1}	$\Delta S^{\ddagger}$ J (deg mol)$^{-1}$	$\Delta G^{\ddagger}$ kJ mol^{-1}
Mg			
k_1	44	-187	100
k_2	46	-172	97
k_H	66	61	46
Ca			
k^a	72	-92	99
k_H	62	72	41
Sr			
k_1	61	-88	87
k_2	65	-74	87
k_H	41	24	34
La			
k_2	83	-45	96
k_H	53	-20	59
	$(54)^b$	$(-22)^b$	$(61)^b$
	$(80)^c$	$(79)^c$	$(56)^c$

^{a} k^{CaCDTA}. ^{b,c} Ref. 4 and 3, respectively.

resemble the parameters obtained for the corresponding reactions with magnesium, strontium, and lanthanum complexes. Mechanism (8) would therefore appear to account for all the reactions examined in a very convincing manner.
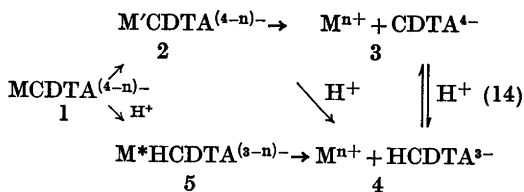
It is seen from Table 6 that all the reactions related to (8) show a pronounced negative entropy of activation which may be related to a solvation of the transition state. Solvation could come about if step $1 \rightarrow 2$ in mechanism (8) involves the breaking of a metal ion chelate bond followed by the solvation of the free coordination site of the metal ion. Such a solvation gives rise to a change of the solvation of the complex as a whole.

The free energies of activation are remarkably constant for step $1 \rightarrow 2$ for the MCDTA complexes investigated. Nyssen and Margerum [4] have proposed that step $1 \rightarrow 2$ is a slow distortion of the complex which is consistent with an angular displacement instead of a linear displacement in preparation for opening the chelate rings (*cf.* Margerum [19]). Assuming the angular displacement theory, the free energy of activation is related to the rotational barriers of the chelate which again is related to the type of ligand. Furthermore, Day and Reilley [21] have

used an NMR technique in their studies on these complexes and suggest that the relatively long lifetime of the $N-M$ bond is correlated with the steric hindrance caused by this ligand. This hindrance would make the support of a water molecule in the bond breaking impossible. The constant free energy of activation may then be rendered comprehensible in terms of these theories.

The rate constant of dissociation k_d is given by eqn. (7) at low values of pH. k_H^{MCDTA} has been accurately determined in the studies by Margerum et al. [20] and Nyssen and Margerum.[4] The activation parameters found in the present investigation for this pathway of the dissociation reaction of LaCDTA agree with the values found by Nyssen and Margerum,[4] whereas Brücher and Szarvas [21] find different values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, but the same value for $\Delta G^{\ddagger}$.

It has been found that k_H^{MCDTA} represents an rds which involves a proton attack on one of the nitrogen atoms. This attack results in an intermediate with the metal ion outside the coordination cage of the ligand (cf. Margerum et al.[20] and Nyssen and Margerum [4]). Mechanism (8) has accordingly to be extended to that shown in (14) which is valid at both the low and high values of pH used in this work. M*HCDTA in mechanism (14) has been observed by Nyssen

$$
\begin{array}{ccc}
& M'CDTA^{(4-n)-} \rightarrow & M^{n+} + CDTA^{4-} \\
& 2 & 3 \\
MCDTA^{(4-n)-} & & \searrow H^+ \quad \Big\Vert H^+ \quad (14) \\
1 \quad \searrow H^+ & & \searrow \\
& M*HCDTA^{(3-n)-} \rightarrow & M^{n+} + HCDTA^{3-} \\
& 5 & 4
\end{array}
$$

and Margerum [4] in their study on the rate of formation of LaCDTA. Studies [1] on the rate of dissociation of this type of complexes all show a similar $[H^+]$ profile for these reactions with $M = Mg$, Sr, or Ba; the present study shows this same $[H^+]$ profile for $M = Mg$, Sr, or La.

The dissociation reaction for these MCDTA complexes is therefore assumed to follow mechanism (14) in the investigated pH range and for $M = Mg$, Ca, Sr, Ba, or La (cf. the preceding discussion). The rds are $1 \rightarrow 2$ and $1 \rightarrow 5$ for the spontaneous and the H^+ activated dissociation, respectively. The rds $1 \rightarrow 5$ dominates at low values of pH and rds $1 \rightarrow 2$ dominates at relatively high values of pH.

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