Exchange Reactions of trans-1,2-Diaminocyclohexanetetraacetate Complexes of Alkaline Earth Ions in the pH Range 8.5—10.5

ARNE JENSEN and NIELS RHOD LARSEN
The Royal Danish School of Pharmacy, Chemical Laboratory A, DK-2100 Copenhagen Ø, Denmark

The exchange reactions between the alkaline earth complexes of trans-1,2-diaminocyclohexane-N,N',N'-tetraacetate (CDTA) and Cu(II) or Pb(II) have been studied by Margerum et al.¹ and Pausch and Margerum.² The reaction rate was shown to be independent of the Cu(II) and Pb(II) concentrations. Furthermore, a linear relation was found between the reaction rate constant and the hydrogen ion concentration. The pH range investigated was 5.5—7.6 for Mg, Ca and SrCDTA and 7.0—7.6 for BaCDTA.

The present communication describes the exchange reaction between the alkaline earth complexes of CDTA and Cu(II) in the pH range 8.5—10.5. The overall reaction is shown in (1). The rate of reaction was measured at 380 or 800 nm on a Durrum-Gibson stopped flow spectrophotometer for M = Ba²⁺ or Sr²⁺ and on a Beckman DK-2 spectrophotometer for M = Ca²⁺ or Mg²⁺. The initial concentration of MCDTA⁻ was 10⁻³ M, and the ionic strength and pH were adjusted using NH₄NO₃ and NH₃.

The rate of reaction (1) is independent of the concentration of Cu(NH₃)₄²⁺ when Cu²⁺ is used in an excess of 50—100. Reaction (1) is accordingly pseudo first order at constant pH with the rate constant k₄.

A plot of k₄ versus [H⁺] for M = Ca²⁺ (cf. Fig. 1) indicates in the investigated pH range a linear relationship between k₄ and [H⁺] which agrees with eqns. (2) and (3) as stated by Margerum et al.¹ and Pausch and Margerum.³ Furthermore, titration curves of MCDTA⁻ (M = Mg²⁺, Ca²⁺, Sr²⁺ or Ba²⁺) show that MCDTA⁻ and M(OH)CDTA⁺ are not found in the solutions used in the present investigation where the hydrogen ion concentration is low.

\[
\frac{d[MCDTA⁺]}{dt} = k₄[MCDTA⁺] = k_{MCDTA} \]

\[
[MCDTA⁺] + k_{MCDTA}[H⁺][MCDTA⁺] \quad (2)
\]

\[
k₄ = k_{MCDTA} + k_{H}[H⁺] \quad (3)
\]

Figs. 2, 3, and 4 show plots of k₄ versus [H⁺] for M = Mg²⁺, Sr²⁺, and Ba²⁺, respectively. From these plots it is seen that eqn. (2) is quantitatively correct only in the pH range 8.5—9.2.

k₄ and k₄ in Table 1 have been calculated from Figs. 1, 2, 3, and 4 using the relationship given in eqn. (3). The calculation for M = Mg²⁺, Sr²⁺, and Ba²⁺ has been carried out in the pH range mentioned above where the linear

Table 1. Rate constants for the dissociation of MCDTA⁻ complexes.

<table>
<thead>
<tr>
<th>M⁺⁺</th>
<th>k_{MCDTA} sec⁻¹</th>
<th>k_{H}[MCDTA] sec⁻¹</th>
<th>pH range sec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>5.2 x 10⁻⁴</td>
<td>(3.8 x 10⁴)</td>
<td>8.5—9.2</td>
</tr>
<tr>
<td>Ca</td>
<td>2.1 x 10⁻⁴</td>
<td>(4.2 x 10⁴)</td>
<td>8.5—10.5</td>
</tr>
<tr>
<td>Sr</td>
<td>1.4 x 10⁻²</td>
<td>(6.7 x 10⁴)</td>
<td>8.5—9.2</td>
</tr>
<tr>
<td>Ba</td>
<td>1.3</td>
<td>(1.1 x 10⁵)</td>
<td>8.5—9.2</td>
</tr>
</tbody>
</table>

¹ Calculated from eqn. (3) by a least squares method; for the calculation of k_{MCDTA} see text; initial [MCDTA⁺] = 10⁻³ M; [Cu(NH₃)₄²⁺] = 10⁻¹ M; NH₄⁺/NH₃ buffer; μ = 0.5; 25.0°C.
² From Ref. 2; μ = 0.5; 25.0°C.
Figs. 2, 3, and 4 also show that the plots of $k_d$ versus $[H^+]$ deviate from the straight line in the pH range 9.2–10.5 for $M=Mg^{2+}$, $Sr^{2+}$ or $Ba^{2+}$. Eqn. (3) is therefore not correct. $k_{H^{MCDTA}}$, when interpreted as the rate constant for the direct dissociation of the CDTA complex, is accordingly smaller than stated in Table 1. From the observed $[H^+]$ profile, it is reasonable to conclude that $k_{H^{MCDTA}}$ is probably a complex function of the hydrogen ion concentration. The $[H^+]$ dependence of $k_{H^{MCDTA}}$ is negligible for $pH < 9.2$; cf. Table 1.

Nyssen and Margerum have studied the kinetics of both dissociation and formation of $LaCDTA^-$ in the pH range 4.2–6.0. Eqn. (3) was found to be valid for the dissociation. These authors have shown that the rate-determining step for the formation of $LaCDTA^-$ had to be placed after a fast formation of a reaction intermediate. The rate-determining step of formation of $LaCDTA^-$, as well as of the alkaline earth complexes of CDTA, is not the characteristic water exchange rate of the hydrated metal ion. Furthermore, the rate of formation of $LaCDTA^-$ was found to increase with decreasing $[H^+]$.

The $[H^+]$ profile in Figs. 2, 3, and 4 may possibly be explained by assuming the same kinetics of formation for $LaCDTA^-$ and for $MCDTA^-$ ($M^{2+}=Mg^{2+}$, $Sr^{2+}$ or $Ba^{2+}$). The complexity of $k_{H^{MCDTA}}$ in this investigation may then be rendered more comprehensible by using a “Steady State” approximation for the reaction intermediate similar to that described for $LaCDTA^-$. Parallel studies on the rate of dissociation of these complexes are being carried out in this laboratory using the exchange of optically active CDTA instead of metal ion exchange. The studies confirm the $[H^+]$ profile of these reactions for $M^{2+}=Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$ or $Ba^{2+}$.

Figs. 1–4. Hydrogen ion dependence on the observed first-order rate constants $k_d$ for, respectively, $CaCDTA^-$, $MgCDTA^-$, $SrCDTA^-$, and $BaCDTA^-$. 

Relation between $k_d$ and $[H^+]$ exists. These two rate constants have also been determined by Pausch and Margerum. Satisfactory agreement was found between their values and the constants calculated in the present work (Table 1).


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