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Short Communications

The Influence of Ammonium Ion on Dissociation Reactions of *trans*-1,2-Diaminocyclohexanetetraacetate Complexes of Alkaline Earth Ions in the pH Range 8—10

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The exchange reactions between the alkaline earth complexes of *trans*-1,2-diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetraacetate (CDTA) and Cu(II) or Pb(II) have been studied by several authors.[1–3] Furthermore, the rate of dissociation of these complexes has been studied using the exchange of optically active CDTA instead of metal ion exchange.[4,5] It has been shown in the studies mentioned that the rate of dissociation k_d in the pH range 7 – 9 can be calculated from eqn. (1)

$$k_\mathrm{d} = k^\mathrm{MCDTA} + k_\mathrm{H}{}^\mathrm{MCDTA}[\mathrm{H}^+] \qquad (1)$$

A deviation from this equation is observed at pH > 9 for $\mathrm{M} = \mathrm{Mg}^{2+}$, Sr^{2+}, or Ba^{2+}, but *not* for $\mathrm{M} = \mathrm{Ca}^{2+}$.[3,4] The mechanism shown in (2) is stated for the dissociation of $\mathrm{MCDTA}^{(4-n)-}$, and it is believed that this mechanism is also valid for $\mathrm{M} = \mathrm{Ca}^{2+}$ (rds ≡ rate determining step).

Considerably higher values of k^MCDTA, but not of $k_\mathrm{H}{}^\mathrm{MCDTA}$, were obtained in the exchange between the MCDTA complex and Cu(II) than in the exchange between the MCDTA complex and CDTA, *cf.* eqn. (1) and Ref. 4. A cause for this difference in the obtained values of k^MCDTA has been the use of an ammonium/ammonia buffer when investigating the exchange reactions between the MCDTA complexes and the Cu(II) ion.[3]

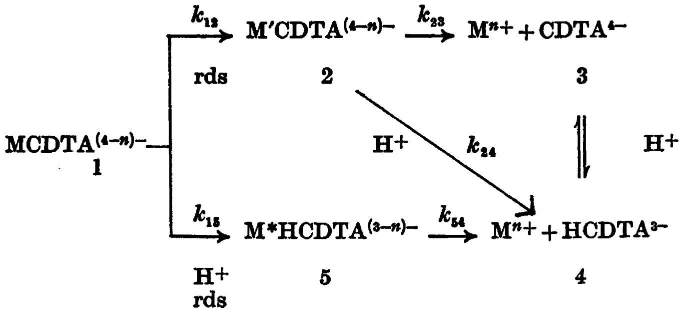
The present communication indicates conclusively that the rate of dissociation of the magnesium, calcium, and strontium complexes of CDTA is influenced in a pronounced way by the ammonium ion concentration – and *not* by the ammonia concentration. The overall reactions studied are shown in (3a) ($\mathrm{M} = \mathrm{Mg}^{2+}$) and (3b) ($\mathrm{M} = \mathrm{Ca}^{2+}$ or Sr^{2+}). The reactions are pseudo first order with rate constants k_d. The charges, protons, and nomenclature for the optical rotation have been omitted for clarity.

$$\mathrm{M(D\text{-}CDTA)} + \mathrm{Ba(D,L\text{-}CDTA)} \rightarrow \mathrm{M(D,L\text{-}CDTA)} + \mathrm{Ba(D\text{-}CDTA)} \qquad (3a)$$

$$\mathrm{M(D\text{-}CDTA)} + \mathrm{Li(D,L\text{-}CDTA)} \rightarrow \mathrm{M(D,L\text{-}CDTA)} + \mathrm{Li(D\text{-}CDTA)} \qquad (3b)$$

The double exchange reactions in eqn. (3) insure a concentration of free CDTA sufficiently low so that ammonium complexes do not in any way interfere in the reaction.

Ba(D,L-CDTA) can be used only in (3a) ($\mathrm{M} = \mathrm{Mg}^{2+}$) as the change in optical rotation observed with this complex is too small for $\mathrm{M} = \mathrm{Ca}^{2+}$ or Sr^{2+}. Li(D,L-CDTA) has been used in (3b) since a readily observable change in rotation is obtained. The determination of k_d



(2)

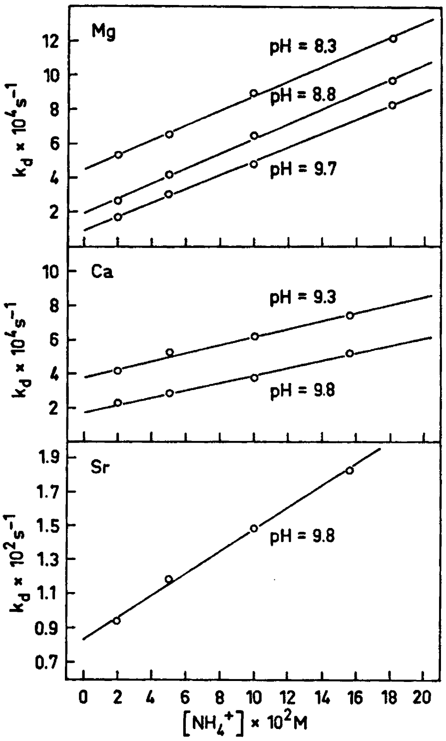


Fig. 1. Ammonium ion dependence on the observed first-order rate constants k_d for, respectively, $MgCDTA^{2-}$, $CaCDTA^{2-}$, and $SrCDTA^{2-}$.

in (3a) and (3b) is feasible only if the rate constants of dissociation of Ba(D,L-CDTA) and Li(D,L-CDTA), respectively, are much larger than k_d, a condition which is shown to be fulfilled. The ionic strength and pH are adjusted using $CsNO_3$ and CsOH.[4] A tenfold excess of the racemic species is used to make the overall reactions go essentially to completion.

A "Perkin-Elmer Model 141" photoelectric polarimeter (with potentiometric read-out) in combination with a "Radiometer Servograph REC 51" recorder equipped with a high sensitivity "Radiometer REA 112" unit was used to monitor the change in optical rotation as a function of time during the reactions.[4]

A plot of k_d *versus* $[NH_4^+]$ for $M = Mg^{2+}$, Ca^{2+}, or Sr^{2+} at constant pH (*cf.* Fig. 1) indicates a linear relationship between k_d and $[NH_4^+]$ for the investigated range of ammonium ion concentration and pH values. Furthermore the results of a linear regression analysis indicate a slope for Mg^{2+} or Ca^{2+} independent of the pH value used. Variations in $[NH_3]$ occurring in conjunction with variations in $[NH_4^+]$ are therefore without effect upon the linear relation between k_d and $[NH_4^+]$. The linear relationships can be expressed by eqn. (4) where C is the pH dependent rate constant of dissociation obtained without NH_4^+ present and $k_{NH_4}^{MCDTA}$ is the rate constant of the ammonium ion assisted dissociation.[4]

Table 1. Rate constants for the dissociation of $MCDTA^{2-}$ complexes.

M^{2+}	pH	C s^{-1} [a]	$k_{NH_4}^{MCDTA} M^{-1} s^{-1}$ [a]
Mg	9.7	8.9×10^{-5}	4.1×10^{-3}
Mg	8.8	1.9×10^{-4}	4.3×10^{-3}
Mg	8.3	4.5×10^{-4}	4.3×10^{-3}
Ca	9.8	1.8×10^{-4}	2.2×10^{-4}
Ca	9.3	3.8×10^{-4}	2.4×10^{-4}
Sr	9.8	8.3×10^{-3}	6.5×10^{-2}

[a] Calculated from eqn. (4) by a least squares method; initial $[M(D\text{-}CDTA)] = 2.5 \times 10^{-3}$ M; $[M(D,L\text{-}CDTA)] = 2.5 \times 10^{-2}$ M; NH_4^+/NH_3 buffer; $\mu = 0.5$ ($CsNO_3$); 25.0 °C.

$$k_d = C + k_{NH_4}^{MCDTA}[NH_4^+] \qquad (4)$$

It may be concluded that NH_4^+ acts on step 1→2 in mechanism (2). This is a consequence of the facts that k_H^{MCDTA} is independent of $[NH_4^+]$ [3,4] and that the relative deviation from the straight line in the $[H^+]$ profile for k_d is the same whether carrying out a metal ion exchange in an ammonium/ammonia buffer or a ligand exchange without ammonium ion. The deviation from the straight line is caused by step 2→4 in mechanism (2).[3,4]

Fig. 1 and Table 1 also show that $k_{NH_4}^{SrCDTA} > k_{NH_4}^{MgCDTA} > k_{NH_4}^{CaCDTA}$ which agrees with $k_{12}^{SrCDTA} > k_{12}^{MgCDTA} > k_{12}^{CaCDTA}$ and *not* with $k_H^{SrCDTA} > k_H^{CaCDTA} > k_H^{MgCDTA}$.[3,4] The accordance between the sequences of $k_{NH_4}^{MCDTA}$ and k_{12}^{MCDTA} therefore supports the conclusion that step 1→2 is influenced by ammonium ion. The sequences of $k_{NH_4}^{MCDTA}$ and k_{12}^{MCDTA} are not on the other hand in accordance with the sequence of the ionic radii of Mg^{2+}, Ca^{2+}, and Sr^{2+}. This discrepency and the special course of the dissociation of the CaCDTA complex described previously [3,4] may be attributed to a different structure of the CaCDTA complex as compared to the structures of the Mg^{2+} and Sr^{+2} complexes as well as those of the BaCDTA and LaCDTA complexes.[3,4] However, circular dichroism measurements and absorption measurements of aqueous solutions of $Mg(D\text{-}CDTA)^{2-}$, $Ca(D\text{-}CDTA)^{2-}$, $Sr(D\text{-}CDTA)^{2-}$, $Ba(D\text{-}CDTA)^{2-}$, $La(D\text{-}CDTA)^{-}$, and $H(D\text{-}CDTA)^{3-}$ in the wavelength range 200 – 325 nm did not demonstrate that

Ca(D-CDTA)$^{2-}$ possesses a structure of its own, since the effects observed were very small.

It is difficult to explain how the ammonium ion influences step 1→2 in the stated mechanism. It seems reasonable though to assume that this step is very complex consisting perhaps of several steps where an intermediate such as M''NH_4CDTA is found in one of the steps.

It is necessary to control the factors that affect the reaction rates when making use of the kinetic properties of the CDTA complexes of the alkaline earth ions in analytical chemistry.[2] The present investigation has shown that [NH_4^+] has such pronounced influence on the values of k_d that a prior knowledge of [NH_4^+] in the sample to be analysed is essential for the method. Further studies[6] on the differential kinetic analysis of the alkaline earth ions are being carried out with particular emphasis on the use of classical spectrophotometry in automated analyses.

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Analysis of the 100 MHz ^{1}H NMR Spectrum and Conformation of *trans*-2-*t*-Butyl-*cis*-2-methyl-1,3-dithiane 1-Oxide

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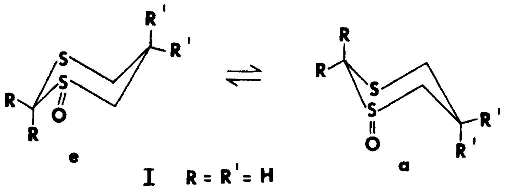
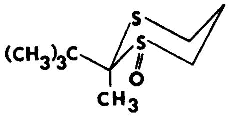
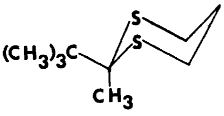


I R = R' = H
II R = Me, R' = H
III R = H, R'R' = O



IV



V

Recent studies from our laboratories[1-3] and elsewhere[4,5] have demonstrated that the S = O bond of 1,3-dithiane 1-oxides I, II, III favours the equatorial site. In contrast thiane 1-oxide,[6] 1,3-oxathiane 3-oxide,[4,7] and thiane-3-one 1-oxide[3] adopt preferentially the axial S = O conformer. The origin of the equatorial S = O preference in I – III is somewhat unclear but a suggestion[1] that dipolar interactions are involved has recently received support in the form of force field calculations performed by Allinger and Kao.[8] These workers also calculated that conformer Ie is 4.2 kcal mol^{-1} more stable than the lowest energy twist form.

In the present paper we report the analysis of the 100 MHz spectrum of the 2-*t*-butyl-2-

Table 1. 100 MHz spectral parameters (in Hz) of IV and V in $CDCl_3$.

Chemical shift [a]			Coupling constants		
	IV	V [b]		IV	V [b]
4a	266.60	303.11	4a5a	12.75	11.85
4e	239.38	271.80	4e5e	3.00	4.35
5a	215.07	178.73	4a5e	2.92	3.28
5e	228.88	205.47	4e5a	3.97	3.96
6a	267.13	303.11	5a6a	14.21	11.85
6e	301.85	271.80	5e6e	3.82	4.35
			5a6e	3.39	3.96
			5e6a	3.23	3.28
			4a4e	– 14.49	– 14.46
			5a5e	– 14.54	– 13.56
			6a6e	– 13.31	– 14.46
			4e6e	1.57	0.65
			4a6a	– 0.18	0.03
			4a6e	– 0.23	– 0.05
			4e6a	– 0.41	– 0.05

[a] Downfield from TMS. [b] Data taken from Ref. 11.