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Kinetics of the Ligand Exchange Reaction of Propylenediaminetetraacetate Ion with Ethylenediaminetetraacetatonickel(II)

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Ligand exchange reactions of PDTA (1,2-propylenediaminetetraacetate ion) with a metal complex of EDTA (ethylenediaminetetraacetate ion) where the metal ion (M) was lead [1], cadmium [2], or copper [3] have been investigated previously (Eq. 1):

$$\mathrm{PDTA^{4-} + M(EDTA)^{2-} \leftrightarrows M(PDTA)^{2-} + EDTA^{4-}} \qquad \text{(Eq. 1)}$$

The present study describes the kinetics of the reaction shown in equation 1 in which the metal is nickel.

Experimental

Kinetic measurements were made employing both nuclear magnetic resonance (NMR) and polarimetry. Previously prepared and recrystallized d, l-PDTA and d-PDTA [4] were used in the NMR and polarimetry measurements respectively. A Ni(EDTA) stock solution was prepared using equal moles of a standardized nickel nitrate solution and a standardized H_4EDTA solution. Tetramethylammonium hydroxide (TMAOH) and reagent grade nitric acid were used for pH adjustment. The decrease in area of the methyl doublet from PDTA (referenced to TMAOH) was monitored with a Varian A-60D NMR (Figure 1). The $\mathrm{Ni(PDTA)^{2-}}$ complex cannot be detected due to the large paramagnetic contact shift associated with nickel ion [5]. Reactant concentrations were equal at about 0.2*M*.

The change in rotation of d-PDTA as it becomes complexed to nickel was measured on a Perkin–Elmer 141 polarimeter as described elsewhere [6]. All measurements were made at 365 nm since preliminary measurements had shown this to be optimal of the wavelengths available. The molar rotation [α] of Ni(l-PDTA) was measured to be 14.95 l-deg/cm-mol at u = 0.5 and 25 °C at 365 nm. Molar rotations of l-PDTA species have been previously reported [6]. The reactant concentration of $\mathrm{Ni(EDTA)^{2-}}$ was 2×10^{-3} for all measurements while the concentration of d-PDTA was at least a factor of 10 greater. Reaction halftimes varied from about 15 hours at high pH (12–13) to 200 hours at low pH (7–8).

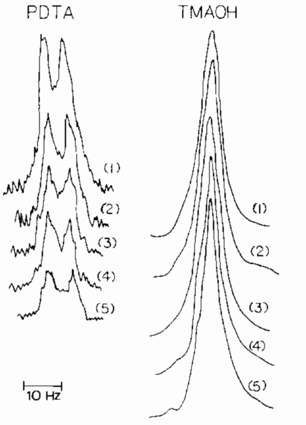

Figure 1. NMR traces of PDTA methyl doublet and TMAOH as a function of time. pH = 11.36; $\mu \approx 2$; T = 24 °C; (PDTA) = (NiEDTA) = 0.198 *M*. Elapsed time for trace 1) 1 hr 10 min; 2) 8 hr 23 min; 3) 14 hr 55 min; 4) 25 hr 29 min; and 5) 45 hr 57 min. Spectrum Amplitude for PDTA doublet = 80. Spectrum Amplitude for TMA singlet = 4.

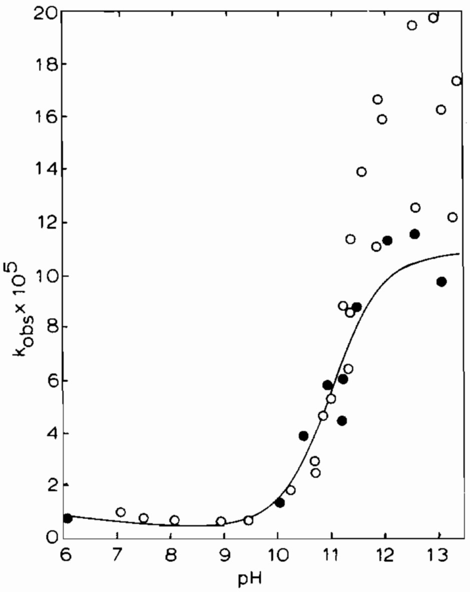

Figure 2. pH profile of the rate constant for PDTA substitution of Ni(EDTA). The open circles correspond to the NMR data taken at $\mu \approx 2$ and T = 24 °C. The closed circles correspond to the polarimetry data taken at $\mu = 0.5$ and T = 25 °C. The solid line corresponds to the best fitting line calculated from the resolved rate constants of equation 4.

Results and Discussion

Reactions monitored by NMR were run under second-order, equal-concentration conditions. A linear plot of $1/C_{PDTA}$ *versus* time can be constructed giving a slope equal to k_{obs}, the observed rate constant (Eq. 2), if the equilibrium constant is sufficiently large to force the reaction essentially to completion. The actual plots used were of (A_{TMA}/A_{CH_3}) *vs.* time (Eq. 2). Selected reactions were also calculated on the basis of reversible, second-order, equal-concentration. Linear plots were obtained which yielded rate constants virtually the same numerically as resulted from Eq. 2:

$$(1/C_{PDTA})_t = m(A_{TMA}/A_{CH_3}) = k_{obs}t \qquad \text{(Eq. 2)}$$

where A_{TMA} and A_{CH_3} are areas of the TMAOH and CH_3 peaks, respectively, and m = proportionality constant = $(A_{CH_3}/A_{TMA})_0/[PDTA]_0$. Reactions monitored by polarimetry were run under irreversible pseudo-first-order conditions. By plotting $-\ln(\alpha_{eq} - \alpha_{obs})$ *versus* time, a straight line is obtained having a slope equal to k'_{obs} (Eq. 3).

$$-\ln(\alpha_{eq} - \alpha_{obs}) = -\ln(\alpha_{eq} - \alpha_0) + k'_{obs}t \qquad \text{(Eq. 3)}$$

where α_0 = initial rotation, α_{obs} = observed rotation, α_{eq} = rotation at equilibrium, and $k'_{obs} = k_{obs}\text{-}(PDTA)_{xs}$.

The hydrogen ion dependence of the reaction is explained in equation 4.

$$\begin{aligned} k_{obs}(\text{NiEDTA})C_{PDTA} = \\ k^{NiEDTA}_{H_2PDTA}(H_2PDTA)(NiEDTA) + \\ + k^{NiEDTA}_{HPDTA}(HDPTA)(NiEDTA) + \\ + k^{NiEDTA}_{PDTA}(PDTA(NiEDTA) \qquad \text{(Eq. 4)} \end{aligned}$$

No evidence is found of Ni(OH)EDTA reactivity; $\log k^{NiEDTA}_{Ni(OH)EDTA} = 0.55$ [7]. Calculations of the resolved rate constants were performed with an IBM 360/65 computer using a linear regression analysis program. Figure 2 shows a plot of the pH profile of the observed rate constant. The experimental data agree fairly well with the calculated pH profile suggesting equation 4 to be valid. We are unable to rationalize satisfactorily the increased rate at high pH shown by a few of the NMR points. The major source of error in the NMR rate constants is due to the uncertainty in the value of "m", which must be calculated for each run from the intercept of the rate plot. The resolved rate constant k^{NiEDTA}_{PDTA} as measured by NMR and polarimetry respectively, were $(12.2 \pm 0.9) \times 10^{-5}$ M^{-1} sec^{-1} and $(9.1 \pm 1.0) \times 10^{-5}$ M^{-1} sec^{-1} (reaction conditions described in Figure 2. The rate constant is about an order of magnitude smaller than that found for the symmetric EDTA exchange reaction with nickel [5]. The best estimates of $k^{NiEDTA}_{H_2PDTA}$ and k^{NiEDTA}_{HPDTA} are $(10 \pm 4) \times 10^{-6}$ and $(6 \pm 1) \times 10^{-6}$ M^{-1} sec^{-1}, respectively: Preliminary experiments reacting Ni(l-PDTA) with 1,2-diaminocyclohexanetetraacetate ion (CyDTA) have been so slow in rate that measurement is not feasible (little or no reaction in 30 days at 25 °C). The increase in steric hindrance of the entering aminocarboxylate is an important factor in determining the reaction rate of nickel aminocarboxylate exchange reactions.

The only other related reaction reported in the literature is that of CyDTA + Ni(EDTA) → Ni(CyDTA) + EDTA measured at 75 °C and pH < 7 in the presence of $Na_2B_4O_7$ as a buffer constituent [8]. Under these conditions, this reaction showed proton catalyzed dissociation as the predominant reaction pathway. Rate constants were obtained, however, for $HCyDTA^{3-}$ and H_2CyDTA^{2-} attacking Ni(EDTA) equal to 6.5×10^{-6} M^{-1} sec^{-1} and 2.3×10^{-5} M^{-1} sec^{-1}, respectively. No attempt is made to correlate these values to our measurements because of the major temperature difference and the presence of sodium ion which can complex a large fraction of the free CyDTA [9].

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