Coordination Chain Reactions. III. The Exchange of N,N,N′,N′-Tetrakis(2-aminoethyl)ethylenediaminezinc(II) and Ethylenediaminetetraacetatocuprate(II)

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Abstract: The exchange reaction of copper-EDTA and zinc-penten follows a chain mechanism and is catalyzed by low concentrations of EDTA or penten (N,N,N′,N′-tetrakis(2-aminoethyl)ethylenediamine). The exchange rate exhibits a maximum near pH 8.4 when equal concentrations of reactants are used. The pH profile for each chain-propagating step is determined and the two have opposite pH dependencies. The reaction rate of penten with copper-EDTA increases with pH while the reaction rate of EDTA with zinc-penten decreases with pH. The two rate constants are equal at pH 8.4 and account for the maximum in the exchange rate. Reversibility of a chain-propagating step and a switch in the identity of the rate-limiting step both can cause complicated kinetic behavior.

The ligand-exchange reaction (eq 1) of ethylenediaminetetraacetatocuprate(II) and N,N,N′,N′-

$$\mathrm{ZnPe^{2+} + CuY^{2-} \xrightleftharpoons{K_1} CuPe^{2+} + ZnY^{2-}} \qquad (1)$$

tetrakis(2-aminoethyl)ethylenediaminezinc(II) (abbreviated zinc-penten or $\mathrm{ZnPe^{2+}}$) is another example of a coordination chain-reaction system.[2,3] The slow rate of ligand exchange in reaction 1 is greatly accelerated by the addition of small amounts of free ligand, either EDTA or penten. The chain-propagating steps proposed for the reaction mechanism are given in eq 2 and 3 (with the protons omitted). Reaction 2 is significantly reversible below pH 8, and reaction 3 is slightly reversible above pH 10. Table I summarizes the effect of pH on the equilibrium constants of eq 1–3 as calculated from the stability constants[4,5] of the complexes and acidity constants of the ligands.

$$\mathrm{Pe + CuY^{2-} \xrightleftharpoons[k_{-2}]{k_2} CuPe^{2+} + Y^{4-}} \qquad (2)$$

$$\mathrm{Y^{4-} + ZnPe^{2+} \xrightleftharpoons[k_{-3}]{k_3} ZnY^{2-} + Pe} \qquad (3)$$

Table I. Conditional Equilibrium Constants of Reactions 1, 2, and 3

pH	Log K_1	Log K_2	Log K_3
6.0	3.90	−3.15	7.05
7.0	3.90	−1.46	5.36
8.0	3.90	0.59	3.31
9.0	3.90	2.59	1.31
10.0	3.90	3.55	0.35
11.0	3.90	3.64	0.26
12.0	3.90	3.64	0.26

Previous examples of coordination chain reactions used nickel complexes which are, in general, more sluggish in their reactions than the corresponding zinc complexes. The present system also introduces a branched hexadentate polyamine compared to the previous double ligand-exchange reactions with linear tetradentate and pentadentate polyamines.

Experimental Section

Penten was prepared from ethylenimine by the second method of Gauss, Moser, and Schwarzenbach.[6] Difficulty was encountered in the recrystallization of the amine pentahydrochloride so purification was achieved by preparative gas chromatography after a simple vacuum distillation to remove the polyamine from any residual sodium benzenesulfonate. The gas chromatograph used was a Wilkins Dual-Column instrument with a 6-ft, 0.25-in. o.d. diameter stainless steel column packed with 25% SE-30 silicone rubber gum (General Electric Co.) on 60–80 mesh silanized Chromosorb W (Johns-Mansville Co.). Penten has a retention time of 22 min at a column temperature of 200° and helium flow rate of 150 cc/min. The resultant penten was shown to be chromatographically pure by the observation of only a single peak upon reinjecting a sample into the gas chromatograph.

The pure penten was dissolved in water and standardized both by acid–base titration and by a mole-ratio plot with a standard copper solution. Excellent agreement was found between the two methods. Solutions of zinc-penten were prepared by stoichiometric addition of a standard $\mathrm{Zn(ClO_4)_2}$ solution to a measured amount of standard penten solution and also by addition of an excess of $\mathrm{Zn(ClO_4)_2}$ to a standard ligand solution and removal of the excess zinc by hydroxide precipitation at pH 10.5.

The exchange reaction in eq 1 was followed with a Cary Model 14 spectrophotometer thermostated at 25.0 ± 0.1°. The reaction conditions were such that the reaction was moderately rapid and mixing was done with a plexiglass plunger in a 1-cm rectangular cell. In this way, the first observations of the absorbance (A) could be easily measured in 7–10 sec after mixing. Ionic strength was controlled at 0.10 with potassium chloride. The formation of copper-penten was observed at 650 mμ when copper-EDTA was in excess and at 280 mμ when zinc-penten was in excess. First-order reaction rates were obtained by using one reactant in excess and by the addition of catalytic amounts of free ligand. Plots of $\ln (A_\infty - A)$ against time gave the values of the pseudo-first-order rate constant, k_0. As discussed in earlier papers,[2,7] the value of the rate constant for the reaction of total free ligand, $k_L^{ML'}$, was obtained by plots of $\mathrm{[EDTA]_{added}}$ against k_0 as shown in Figure 1. In each series of reactions, all conditions were identical except for the concentration of added free ligand. This was done because trace quantities of metal ions present can react with the catalytic quantities of free ligand added. The values of $k_L^{ML'}$ are obtained

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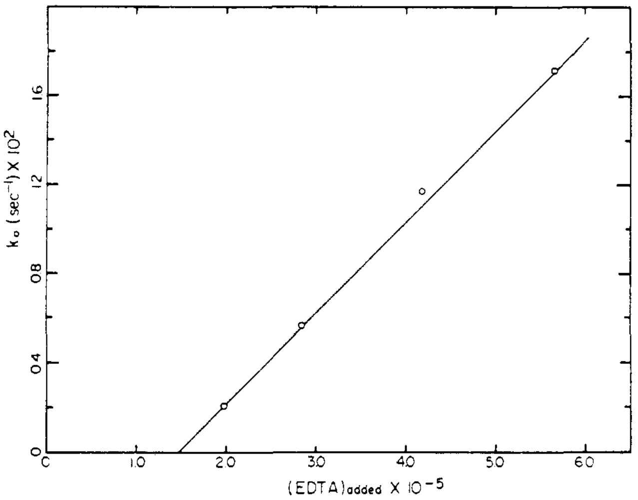

Figure 1. Dependence of the pseudo-first-order rate constant on concentration of added EDTA: $[CuY]_0 = 6.75 \times 10^{-3}$ M, $[ZnPe]_0 = 4.16 \times 10^{-4}$ M (pH 8.86, μ = 0.10, 25.0°).

from the slope of plots such as Figure 1. Values of $k_L{}^{ML'}$ and reaction conditions are shown in Table II.

Table II. Rate Constants and Conditions for ZnPe–CuY Chain Reactions (0.10 μ, 25.0°)

pH	$k_L{}^{ML'} \times 10^2$, M^{-1} sec^{-1}	$[CuY]_0$, M	$[ZnPe]_0$, M
8.93	3.2	4.51×10^{-3}	2.95×10^{-4}
8.10	12.1	4.51×10^{-3}	
8.83	3.5	7.31×10^{-3}	
8.14	12.9	2.94×10^{-3}	
10.02	0.45	7.31×10^{-3}	
7.98	3.4	8.44×10^{-5}	9.83×10^{-4}
7.28	0.75	8.44×10^{-5}	
7.79	2.9	8.44×10^{-5}	
8.00	3.76	8.44×10^{-5}	
8.86	4.27	6.75×10^{-3}	4.16×10^{-4}
8.49	6.93	6.75×10^{-3}	4.16×10^{-4}

A stopped-flow device[2] was used to study reaction 2 independent of the chain reaction, but the lack of appreciable changes in absorption spectra for the species in reaction 3 prevented its direct measurement. Half-lives of reaction 2 varied from 30 to 1000 msec, depending on the conditions used, and typical transmittance changes from the unreacted mixture to equilibrium were from about 90 to 85% transmittance with an instrumental noise level of 0.2% transmittance.

A value of the equilibrium constant of reaction 2 can be calculated from stopped-flow data by

$$K_2 = \left[\frac{\dfrac{A_e - A_0}{A_{CuPe} - A_0}}{\left(1 - \dfrac{A_e - A_0}{A_{CuPe} - A_0}\right)}\right]^2 \qquad (4)$$

The following terms are defined: A_e is the observed final absorbance, A_0 is the initial absorbance, and A_{CuPe} is the final absorbance if the reaction were to go completely to products. A value of log K_2 of −0.88 is calculated for reactions run at pH 7.35, in good agreement with the value expected from stability constant calculations (log K_2 = −0.70).

Results and Discussion

The exchange reaction in eq 1 with a small amount of free ligand added (either EDTA or penten) is first order in copper-EDTA and increases with pH below pH 8.

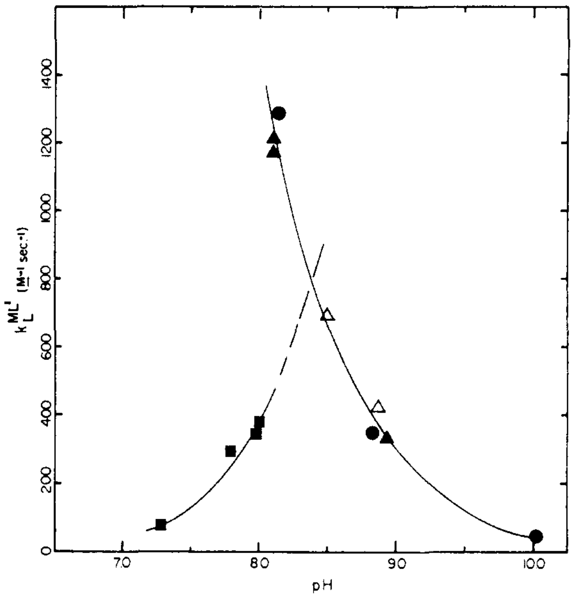

Figure 2. pH profile of $k_L{}^{ML'}$ (μ = 0.10, 25.0°): ■, 9.83×10^{-4} M $ZnPe^{2-}$, 0.844×10^{-4} M CuY^{2-}; ●, 2.95×10^{-4} M $ZnPe^{2+}$, 73.1×10^{-4} M CuY^{2-}; ▲, 2.95×10^{-4} M $ZnPe^{2+}$, 45.1×10^{-4} M CuY^{2-}; △, 4.16×10^{-4} M $ZnPe^{2+}$, 67.5×10^{-4} M CuY^{2-}.

However, the reaction is first order in zinc-penten and decreases with pH above pH 8.8. The reaction rate has a maximum between pH 8.0 and 8.8 where the reaction order depends to a great extent on the ratio of reactant concentrations. At all pH values, the reaction rate depends on the free-ligand concentration which is constant during individual reactions.

Figure 2 is a pH profile of the limiting reaction rate constant ($k_L{}^{ML'} = k_2$ or k_3 depending on the reactant concentrations and pH). A plot similar to Figure 1 was used to obtain each point in Figure 2. The points forming the curve on the left-hand side of Figure 2 were obtained with excess zinc-penten present, and the rate-limiting reaction was the chain-propagation step in eq 2. The right-hand curve was obtained with an excess of copper-EDTA where the chain-propagation step in eq 3 was rate limiting. The rate constant obtained at pH 8.7–8.9 was shown to be independent of copper-EDTA concentration by carrying out reactions at different concentration levels (Table II).

The pH profile for the rate constant, k_2, was established independently using the stopped-flow apparatus. The results of this study are summarized in Figure 3. Unprotonated penten reacts much faster with copper-EDTA then the protonated forms of the ligand. This behavior also has been observed for reactions of trien and tetren with copper-EDTA.[2] The stopped-flow data are in good agreement with the chain-reaction data at pH 7–8 and confirm the assignment of k_2 as the limiting rate constant for the left-hand side of Figure 2. The values of k_2 at pH 8.5 and above are consistent with the assignment of k_3 as the limiting rate constant at higher pH.

The sharp transition in the value of $k_L{}^{ML'}$ with pH (Figure 2) is due to the crossover of k_2 and k_3 as the rate-limiting constants. Previous coordination chain-reaction systems have not shown so sudden a switch in rate-determining steps as the pH changed.

Effect of Reversibility and of a Switch in the Rate-Determining Step. As discussed previously,[2] the rate

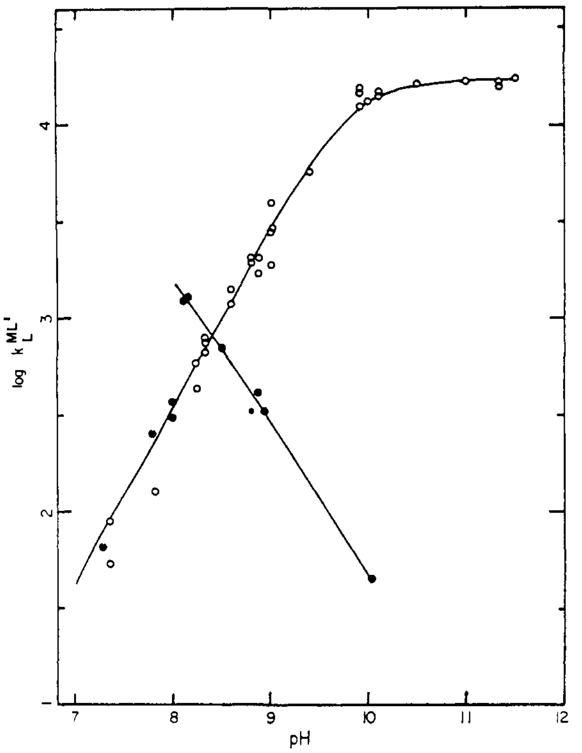

Figure 3. Stopped-flow data for k_2 and chain-reaction exchange constants (μ = 0.10, 25.0°): ○, k_2 determined by stopped-flow (the line through these points is a least-squares fit including the data from the chain reaction at low pH); ●, $k_L^{ML'}$ determined by chain reaction.

expression for a coordination chain reaction can become complicated despite the presence of added free ligand if the chain-propagating steps are reversible or if there is a switch in the rate-limiting step. Equation 5 gives the rate dependence based on the total free ligand present with the assumption that all of the exchange is carried by reactions 2 and 3. The relative

$$\frac{\text{rate}}{[\text{L}]_\text{T}} = \frac{k_2k_3[\text{CuY}^{2-}][\text{ZnPe}^{2+}] - k_{-2}k_{-3}[\text{ZnY}^{2-}][\text{CuPe}^{2+}]}{k_2[\text{CuY}^{2-}] + k_{-2}[\text{CuPe}^{2+}] + k_3[\text{ZnPe}^{2+}] + k_{-3}[\text{ZnY}^{2-}]} \tag{5}$$

contribution of the two terms in the numerator in eq 5 is simply the equilibrium constant, K_1, less the concentration quotient, $Q = [\text{ZnY}^{2-}][\text{CuPe}^{2+}]/[\text{CuY}^{2-}][\text{ZnPe}^{2+}]$. Because log K_1 equals 3.90 over the entire pH range from 6 to 12, the second numerator term is not important for less than 90–99% completion.

At low pH reaction 3 is not significantly reversible but reaction 2 is highly reversible and eq 6 expresses the concentration dependence of the exchange rate.

$$\frac{\text{rate}}{[\text{L}]_\text{T}} = \frac{k_2k_3[\text{CuY}^{2-}][\text{ZnPe}^{2+}]}{k_2[\text{CuY}^{2-}] + k_{-2}[\text{CuPe}^{2+}] + k_3[\text{ZnPe}^{2+}]} \tag{6}$$

However, Figure 4 shows that a good first-order rate plot is obtained for the first 2 half-lives of the exchange reaction at pH 7.28, where reaction 2 is very reversible. This is the case because zinc-penten was in excess, and at this pH $k_3 >> k_2$, so that eq 6 simplifies to eq 7. A second criteria for eq 7 to be valid is that

$$\frac{\text{rate}}{[\text{L}]_\text{T}} = k_2[\text{CuY}^{2-}] \tag{7}$$

$k_3[\text{ZnPe}^{2+}] >> k_{-2}[\text{CuPe}^{2+}]$, which also can be stated in the form

$$k_3 >> \left[\frac{1}{K_2}\frac{[\text{CuPe}^{2+}]}{[\text{ZnPe}^{2+}]}\right]k_2 \tag{8}$$

The condition of eq 8, when expressed in terms of the reactant concentrations used for the data in Figure 4, is that after 2 half-lives $k_3 >> 0.5k_2$. Figure 3 shows that this is certainly the case for this situation. If equal concentrations of reactants had been used at pH 7.28, the requirement from eq 8 would be $k_3 >> 20k_2$. Extrapolation of the k_3 value to pH 7.28 suggests that the latter requirement is not true and the reversibility of reaction 2 would slow the reaction rate. Nevertheless, reversibility of the rate-limiting step is less apt to give product suppression than is the case if the faster chain-propagating step is reversible.

At pH 8.0–8.8 neither reaction 2 nor reaction 3 is sufficiently reversible to complicate the kinetics, and eq 9 is valid for several half-lives. This is the pH

$$\frac{\text{rate}}{[\text{L}]_\text{T}} = \frac{k_2k_3[\text{CuY}^{2-}][\text{ZnPe}^{2+}]}{k_2[\text{CuY}^{2-}] + k_3[\text{ZnPe}^{2+}]} \tag{9}$$

range in which a switch occurs in the rate-limiting propagation step. As a result entirely different values for $k_L^{ML'}$ are obtained depending on which reactant is in excess. Thus Figure 2 shows two sets of values at pH 8.0–8.1. In this pH region, failure to use a large excess of one of the two reactants resulted in the type of deviation from first-order behavior expected from eq 9. The values for k_3 at pH 8.1 were obtained with a 10–25-fold excess of copper-EDTA so that initially the $k_2[\text{CuY}^{2-}]$ term is about five times the $k_3[\text{ZnPe}^{2+}]$ term, and deviations from first-order dependence in zinc-penten were slight. However, at slightly lower pH under the same reaction conditions, poor plots resulted with variable and fractional reaction orders.

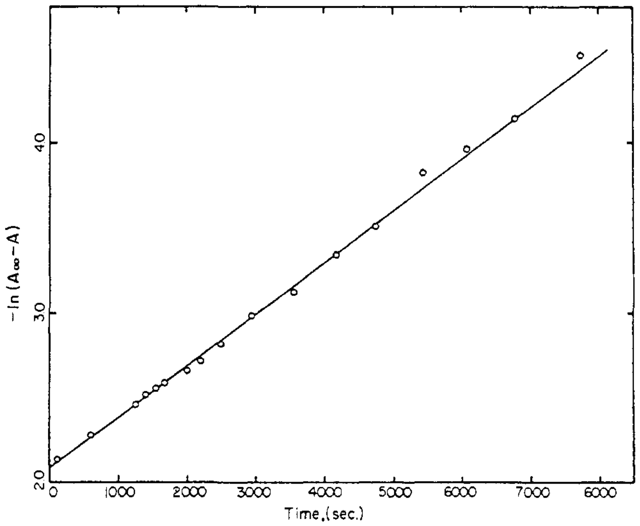

Figure 4. First-order plot of chain reaction under conditions where reaction 2 is reversible, but also is rate-limiting: $[\text{CuY}]_0$ = 8.44 × 10^{-5} *M*, $[\text{ZnPe}]_0$ = 9.83 × 10^{-4} *M*, $[\text{Y}]_\text{added}$ = 8.44 × 10^{-6} *M* (pH 7.28, μ = 0.10, 25.0°).

When the initial concentrations of the reactants were equal and the pH was 8.0 to 8.8, the plots were first order. However, $k_L^{ML'}$ was less than either of the rate constants k_2 or k_3. The maximum deviation at conditions of equal initial complex concentrations would be one-half the true value of k_2 or k_3 at exactly the pH at which $k_2 = k_3$.

Requirements for Coordination Chain Reactions. The three coordination chain-reactions systems studied have all used copper-EDTA as one reactant, and the other reactant has been nickel-trien, nickel-tetren, or zinc-penten, respectively. Chain character will result if the rate at which each ligand replaces the other from its complex is greater than the rate at which the solvent (or its conjugate acid or base) replaces the ligand from its complex. The greater the ratio of these rates, the greater are the chain lengths and the more readily are the chain reaction properties observed. One ligand can assist the removal of another if there is a favorable reaction intermediate with both ligands on the metal, but too stable a mixed complex must not be formed or else no ligand will be released to continue the chain reaction. Multidentate ligands which almost completely unwrap from the metal before the rate-limiting step in the solvent-assisted dissociation are particularly suitable for chain reactions. This appears to be the case for a number of octahedral complexes, but a complex such as tris(1,10-phenanthroline)iron(II) is not suitable because an early bond breaking is the rate-determining step. Many square-planar nickel complexes are unsuitable for the same reason.

Copper has been used with the three EDTA–polyamine systems because the copper-polyamines form stronger complexes than copper-EDTA, while the opposite is true for most other metal ions including nickel, zinc, cadmium, and cobalt. As a result the exchange reaction is thermodynamically favorable and easy to follow. Chain reactions can occur without a large driving force for the exchange, and one such case has been reported for the exchange of EDTA and propylenediaminetetraacetate between their lead and copper complexes which was followed by optical rotation.[8] However, care must be used in the interpretation of the resulting kinetics with such systems because the difficulties inherent in eq 5 are apt to occur. Thus, if both chain-propagating reactions are easily reversed and if both have similar rate constants, then all the terms in eq 5 may be important.

Conclusions

Reaction 1 is another example of a chain-reaction system which responds kinetically to traces of free multidentate ligands. Partial pH profiles of both chain-propagating steps are determined from the chain system itself and are confirmed by independent measurement. The chain reaction is about the same speed as the nickel-trien–copper-EDTA chain reaction under similar conditions, but in the zinc-penten case, changes in pH cause a much sharper switch in the rate-determining step. The propagation rate constants have opposite pH dependencies and cross at pH 8.4 which accounts for the reaction speeds in the vicinity of pH 8.4. Hydrogen ion increases the rate of EDTA replacement of penten from zinc and decreases the rate of penten displacement of EDTA from copper. At all pH values, penten is significantly slower than trien or tetren in its reaction with copper-EDTA because of the bulkiness of the ligand and the additional protonated forms of penten.[9]

Chain-reaction systems in which very similar ligands are exchanged between two metal ions can be expected to have complicated kinetics due to product inhibition of the reaction rate and the possibility of a switch in the rate-limiting step during the reaction.

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