December, 1975] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(12), 3581—3584 (1975) 3581

Multidentate Ligand Kinetics. I. The Ligand Substitution Reaction between Ethylenediaminetetraacetatocuprate(II) and Triethylenetetraminezinc(II)

Tetsuo KATSUYAMA and Toshihiko KUMAI

Department of Basic Technology, Faculty of Engineering, Yamagata University, Yonezawa, Yamagata 992

(Received January 24, 1975)

The kinetics and the mechanism of the ligand substitution reaction between ethylenediaminetetraacetatocuprate(II)(CuY^{2-}) and triethylenetetraminezinc(II)(ZnT^{2+}) were studied spectrophotometrically in the pH range 7.0—10.5 at $I=0.2(NaClO_4)$ and 25.0 °C. The exchange reaction was accelerated by traces of either EDTA or triethylenetetramine(Trien). The exchange reaction was shown to proceed by the chain reaction mechanism where the chain-propagating steps are the reaction of CuY^{2-} with Trien and the reaction of ZnT^{2+} with EDTA. Each chain-propagating step was investigated. The apparent rate constant of the reaction of CuY^{2-} with Trien increases with pH, while that of ZnT^{2+} with EDTA decreases with pH.

Ligand substitution reactions between two multidentate ligand complexes have been studied by Margerum *et al.*[1-4] The exchange reactions were found to be accelerated by the addition of small numbers of free ligands and to be inhibited by the addition of small numbers of metal ions. A coordination chain reaction mechanism was proposed for the exchange reactions, where the chain-propagating steps are the reactions of metal complexes with free ligands.

These catalytic exchange reactions are useful for analysis.[5-7] In analytical applications, rapid coordination chain reactions are of interest for several reasons. (1) In coordination chain reactions, a metal impurity reacts very rapidly with ligands and the resulting complexes may influence the chain reaction. In rapid coordination chain reactions, this influence may be eliminated if the main chain reaction takes place rapidly. (2) In rapid coordination chain reactions, kinetic measurements can be easily repeated using the stopped-flow technique. Therefore, rapid analysis may be achieved by handling the results statistically with an on-line computer.

It seemed worthwhile to find rapid coordination chain reaction systems. In the present study, the kinetics and mechanism of the ligand substitution reaction between ethylenediaminetetraacetatocuprate(II)(CuY^{2-}) and triethylenetetraminezinc(II)(ZnT^{2+}) were studied.

$$CuY^{2-} + ZnT^{2+} \rightleftharpoons CuT^{2+} + ZnY^{2-} \quad (1)$$

The reaction of this system was greatly accelerated by the addition of free ligands.

Experimental

Reagents. Reagent grade zinc(II) and copper(II) perchlorates, and guaranteed reagent grade sodium perchlorate were recrystallized from their aqueous solutions. Guaranteed reagent grade triethylenetetramine(Trien) was purified by distillation at reduced pressure. EDTA used was a Dotite reagent. Water used was distilled with an all quartz distillation apparatus after passing through a column of mixed-bed ion exchange resin. A standard copper nitrate solution was prepared from copper plate, and used to standardize the Trien and EDTA solutions.

Solutions of CuY^{2-} and ZnT^{2+} were prepared by the following procedure. The ligand was dissolved in water and standardized. Metal perchlorate was added stoichiometrically to the ligand solution and also a slight excess of the metal perchlorate was added to the solution. The excess metal was precipitated as hydroxide at about pH 9. The resulting precipitate was filtered off and the solution prepared was adjusted to about pH 7 for storage. The concentrations of the solutions prepared were standardized by the following procedure. CuY^{2-}: a large excess of Trien was added to the CuY^{2-} solution and the concentration of the CuT^{2+} formed was measured spectrophotometrically. ZnT^{2+} : a slight excess of the copper(II) ion was added to the ZnT^{2+} solution. The zinc(II) ion liberated and the excess of copper(II) ion were precipitated at pH 9, because the reaction of ZnT^{2+} with the copper(II) ion proceeds essentially to completion. Then the concentration of the CuT^{2+} formed was measured spectrophotometrically.

Other reagents were of guaranteed reagent grade.

Kinetic Measurements and Apparatus. The kinetics of the double ligand-exchange reaction between CuY^{2-} and ZnT^{2+} was studied in the presence of a large excess of CuY^{2-} and small amounts of EDTA over a pH range 7.0—10.5. In the kinetic measurements, a stopped-flow technique was employed with a Hitachi Model RSP2 Rapid Scanning Spectrophotometer which was equipped with two syringes used as reactant containers. One of the syringes was filled with a CuY^{2-} solution containing small amounts of EDTA, and the other, with a ZnT^{2+} solution containing a buffer and sodium perchlorate. After the two reactant solutions were mixed, the change in the transmittance at 550 nm was recorded on a storage-type oscilloscope as a function of time. Molar absorption coefficients of CuT^{2+} and CuY^{2-} at 550 nm are 138 and 5, respectively, which were measured with a Hitachi 139 spectrophotometer. ZnT^{2+} and ZnY^{2-} do not absorb light at 550 nm.

A mannitol—boric acid—sodium borate or sodium borate—sodium hydroxide buffer system was used to control the pH of the solutions. All pH values were measured with a Toa-Electronics Model HM-15A digital pH-meter. The temperature was controlled at 25.0 °C and the ionic strength was adjusted to 0.2 with sodium perchlorate. In this study, several calculations were performed with the aid of an electronic computer (TOSBAC 40).

Results

Equilibrium reaction (1) is highly favored to proceed to the right so that the ligand exchange reaction between CuY^{2-} and ZnT^{2+} goes to completion and the reverse reaction can be neglected in the kinetic study.

At high pH(9.5—10.5), the rate equation can be expressed as

$$-\frac{d[ZnT^{2+}]}{dt} = k_1'[ZnT^{2+}] \quad (2)$$

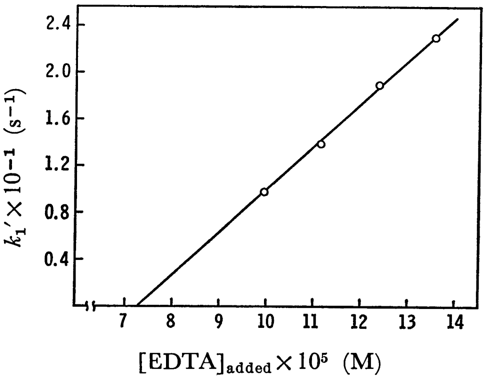

Fig. 1. Dependence of the conditional rate constant k_1' on concentration of added EDTA.
Conditions: $[CuY^{2-}] = 2.40 \times 10^{-2}$ mol/l, $[ZnT^{2+}] = 1.60 \times 10^{-3}$ mol/l, pH=10.12, I=0.2($NaClO_4$), 25.0 °C.

where k_1' is the conditional rate constant involving the added EDTA and hydrogen ion concentrations. The rate plots of $\log(A_\infty - A)$ *vs.* t were linear for over 80% of the reaction. The conditional rate constant k'_1 was determined from the slope of the straight line. In Fig. 1, the values of k_1' determined at pH 10.12 are plotted against the added EDTA concentration. It is evident from Fig. 1 that k_1' is linearly related to the added EDTA concentration [Ya] in the region above a threshold value b, and thus, the following relation is obtained:

$$k_1' = k_1([Ya]-b) \tag{3}$$

where k_1 is the slope of the straight line. The values of k_1 were obtained at various pH values.

On the other hand, for low pH (7.0—8.5), reaction (1) was of pseudo-zero-order with respect to ZnT^{2+}. Thus, the rate equation is given by

$$-\frac{d[ZnT^{2+}]}{dt} = k_0' \tag{4}$$

where k_0' is the conditional zero-order rate constant involving the CuY^{2-}, added EDTA and hydrogen ion concentrations. Integration of Eq. (4) yields

$$A = \Delta\varepsilon k_0' t + A_\infty - a\Delta\varepsilon \tag{5}$$

where A_∞ and A are the absorbance of the reaction system at $t=\infty$ and t, respectively, $\Delta\varepsilon$ is the difference in molar absorption coefficient between CuT^{2+} and CuY^{2-}, and a is the initial concentration of ZnT^{2+}. The plots of A *vs* t are linear for over 80% of the reaction. The conditional zero-order rate constant k_0' was calculated from the slope of the straight line. In Fig. 2, the values of k_0' determined at pH 7.55 are plotted against the added EDTA concentration. k_0' is linearly related to the added EDTA concentration, thus

$$k_0' = k_0([Ya]-b') \tag{6}$$

The values of the slope k_0 were obtained at various pH values.

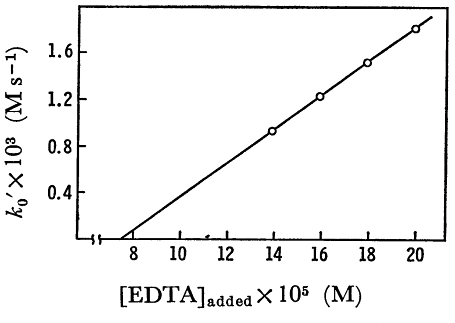

Fig. 2. Dependence of the conditional rate constant k_0' on concentration of added EDTA.
Conditions: $[CuY^{2-}] = 2.40 \times 10^{-2}$ mol/l, $[ZnT^{2+}] = 1.60 \times 10^{-3}$ mol/l, pH=7.55, I=0.2($NaClO_4$), 25.0 °C.

Discussion

Reaction Mechanism. The ligand-exchange reaction between CuY^{2-} and ZnT^{2+} can be shown to proceed by the chain reaction mechanism:

$$CuY^{2-} + T' \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CuT^{2+} + Y' \tag{7}$$

$$ZnT^{2+} + Y' \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} ZnY^{2-} + T' \tag{8}$$

where Y' and T' represent the sum of the uncomplexed species of EDTA and Trien, respectively. The equilibrium constants of reactions (1), (7) and (8) at an ionic strength I=0.2 were calculated from the stability constants of the related complexes and the protonation constants of the related ligands. The stability constants and the protonation constants at an ionic strength I=0.2 were estimated from the constants[8] at I=0.1 on the basis of the diagram of Ringbom.[9] The equilibrium constants calculated are plotted against pH in Fig. 3.

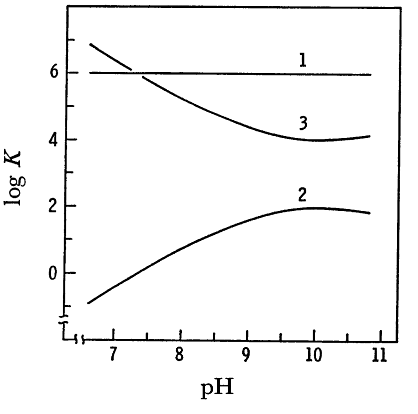

Fig. 3. Dependence of the conditional equilibrium constants of Eqs. (1), (7) and (8) on pH at 25 °C and I=0.2.
1: Eq. (1), 2: Eq. (7), 3: Eq. (8).

Steady-State Treatment. The rate expression derived from a steady-state treatment with the assumptions that all of the exchange is carried by reactions (7) and (8), and that the concentration of the free ligand remains constant throughout the exchange is

$$-\frac{d[ZnT^{2+}]}{dt} = \frac{(k_2k_3[CuY^{2-}][ZnT^{2+}]-k_{-2}k_{-3}[ZnY^{2-}][CuT^{2+}])[L]}{k_2[CuY^{2-}]+k_{-2}[CuT^{2+}]+k_3[ZnT^{2+}]+k_{-3}[ZnY^{2-}]} \tag{9}$$

where [L] is the total concentration of free ligands, EDTA and Trien. Because the value of the equilibrium constant of reaction (8) shows $k_3 \gg k_{-3}$, Eq. (9) can be simplified to

$$-\frac{d[ZnT^{2+}]}{dt} = \frac{(k_2k_3[CuY^{2-}][ZnT^{2+}])[L]}{k_2[CuY^{2-}]+k_{-2}[CuT^{2+}]+k_3[ZnT^{2+}]} \tag{10}$$

In the denominator of Eq. (10), term $k_2[CuY^{2-}]$ becomes predominant and the other terms may be neglected at pH 9.5—10.5, which will be shown later. Equation (10) then becomes

$$-\frac{d[ZnT^{2+}]}{dt} = k_3[L][ZnT^{2+}] \tag{11}$$

Since the metal impurity reacts very rapidly with added EDTA, the total concentration of free ligands in the solution is written as

$$[L] = [Ya] - [M] \tag{12}$$

where [Ya] and [M] are the concentrations of the added EDTA and metal impurity, respectively. Thus Eq. (11) becomes

$$-\frac{d[ZnT^{2+}]}{dt} = k_3([Ya]-[M])[ZnT^{2+}] \tag{13}$$

Equation (3) can be rewritten as

$$k_1' = k_1([Ya]-b) = k_1([Ya]-[M]) \tag{14}$$

where b equals [M]. Therefore, Eq. (13) agrees with the rate equation derived experimentally at high pH. Thus k_3 is equal to k_1.

On the other hand, in the denominator of Eq. (10), term $k_3[ZnT^{2+}]$ becomes predominant and the other terms may be neglected for pH 7.0—8.5, which will also be shown later. Equation (10) then becomes

$$-\frac{d[ZnT^{2+}]}{dt} = k_2[L][CuY^{2-}] \tag{15}$$

For a large excess of CuY^{2-}, $k_2[CuY^{2-}]$ can be constant during the reaction so that Eq. (15) becomes

$$-\frac{d[ZnT^{2+}]}{dt} = (\text{const.})[L] = (\text{const.})([Ya]-[M]) \tag{16}$$

Therefore, Eq. (16) agrees with the rate equation derived experimentally at low pH, because Eq. (6) can be rewritten as

$$k_0' = k_0([Ya]-[M]) \tag{17}$$

Thus k_2 can be calculated from the value of k_0. The values of k_2 and k_3 obtained are plotted against pH in Fig. 4. The approximations used in this discussion can be shown to be valid from Figs. 3 and 4, and the experimental conditions.

Several possible reactions excepting the chain-propagating steps may be eliminated from the exchange reaction mechanism by adding either EDTA or Trien to the reaction system, because the chain reaction pathway becomes predominant with the addition of the ligand.

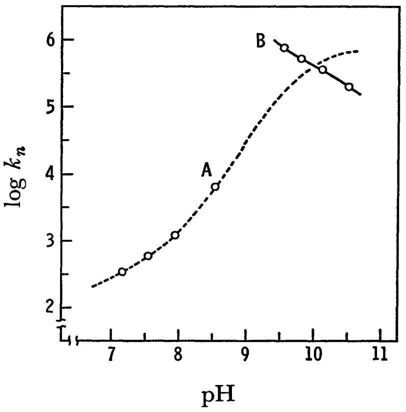

Fig. 4. Dependence of the apparent rate constants k_2 and k_3 on pH at 25.0 °C and I=0.2($NaClO_4$).
A: k_2, B: k_3. The dotted line(A) is the theoretical curve calculated with the aid of the individual rate constants.

Resolution of the Apparent Rate Constant k_2. From a steady-state consideration of reactions (7) and (8) with the assumption that the concentration of the free ligand remains constant, the following relation is derived

$$\frac{[Y']}{[T']} = \frac{k_2[CuY^{2-}]+k_{-3}[ZnY^{2-}]}{k_{-2}[CuT^{2+}]+k_3[ZnT^{2+}]} \approx \frac{k_2[CuY^{2-}]}{k_3[ZnT^{2+}]} \tag{18}$$

At low pH, the form $k_3\ [ZnT^{2+}] \gg k_2[CuY^{2-}]$ holds, as mentioned above, so that the total free ligand concentration in the solution becomes equal to the Trien concentration.

At low pH (7.0—8.5), the total uncomplexed Trien concentration is expressed as

$$[T'] = [T] + [HT^+] + [H_2T^{2+}] + [H_3T^{3+}] \tag{19}$$

Thus, the following relationship can be derived:

$$\begin{aligned} k_2[L][CuY^{2-}] &= k_2[T'][CuY^{2-}] \\ &= k_T[T][CuY^{2-}] + k_{HT}[HT^+][CuY^{2-}] \\ &\quad + k_{H_2T}[H_2T^{2+}][CuY^{2-}] + k_{H_3T}[H_3T^{3+}][CuY^{2-}] \end{aligned} \tag{20}$$

where k_T, k_{HT}, k_{H_2T} and k_{H_3T} are the resolved rate constants. With the protonation constants of Trien species, Eq. (20) is written as

$$\begin{aligned} &k_2(1+K_1[H^+]+K_1K_2[H^+]^2+K_1K_2K_3[H^+]^3) \\ &\quad = k_T + K_1[H^+]k_{HT} + K_1K_2[H^+]^2k_{H_2T} \\ &\qquad + K_1K_2K_3[H^+]^3k_{H_3T} \end{aligned} \tag{21}$$

where K_1, K_2 and K_3 are the successive protonation constants of HT^+, H_2T^{2+} and H_3T^{3+}, respectively. The apparent rate constant k_2 was resolved into the individual proton dependent terms, k_T, k_{HT}, k_{H_2T} and k_{H_3T}, satisfying Eq. (21) with the aid of a computer. The rate constants k_T, k_{HT}, k_{H_2T} and k_{H_3T} determined in this investigation are 9.1×10^5, 1.8×10^4, 3.6×10^2 and $4.4 \times 10\ M^{-1}s^{-1}$, respectively.

The resolved rate constants at I=0.1, which were estimated from those of this investigation (I=0.2) by evaluating the influence of the primary salt effect, agree approximately with the rate constants of the reaction of CuY^{2-} with Trien at I=0.1 which were determined by Margerum *et al.*[10] Using the resolved rate constants, the apparent rate constant k_2 can be calculated. The calculated values are shown in Fig. 4.

Characteristics of the Present System. The coordination chain reactions studied by Margerum *et al.* are slow. In analytical applications, their customary reaction time is about 10 min or longer. However, the reaction of the present system takes place rapidly. The reaction time is about 1 s at low pH and about 0.2 s at high pH.

The ligand substitution reaction of ZnT^{2+} with EDTA cannot be investigated by the usual spectrophotometric method as the spectral data of ZnT^{2+} and ZnY^{2-} are essentially identical. In this paper it was shown that the coordination chain reaction of the present system provides a useful method for the study of the ligand substitution reaction of ZnT^{2+} with EDTA.

References

1) D. C. Olson and D. W. Margerum, *J. Amer. Chem. Soc.*, **84**, 680 (1962).

2) D. C. Olson and D. W. Margerum, *ibid.*, **85**, 297 (1963).

3) D. W. Margerum and J. D. Carr, *ibid.*, **88**, 1639 (1966).

4) J. D. Carr and D. W. Margerum, *ibid.*, **88**, 1645 (1966).

5) D. W. Margerum and R. K. Steinhaus, *Anal. Chem.*, **37**, 222 (1965).

6) R. H. Stehl, D. W. Margerum, and J. J. Latterll, *ibid.*, **39**, 1346 (1967).

7) D. W. Margerum and R. H. Stehl, *ibid.*, **39**, 1351 (1967).

8) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-ion Complexes," The Chemical Society, London (1964).

9) A. Ringbom, "Complexation in Analytical Chemistry," Interscience Publishers Inc., New York, N.Y. (1963), p. 24.

10) J. D. Carr, R. A. Libby, and D. W. Margerum, *Inorg. Chem.*, **6**, 1083 (1967).