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The Kinetics of the Ligand Substitution Reaction of Copper(II)-nitrilotriacetate and -nitrilo(diacetic)propionate Complexes with *trans*-1,2-Cyclohexanediaminetetraacetate Ions*[1]

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Previous studies[1,2] have shown that the rate of the reaction of some nickel(II) complexes with *trans*-1,2-cyclohexanediaminetetraacetate (CyDTA) ions was independent of the concentrations of CyDTA and proceeded by means of the complete dissociation of the nickel(II) ion from the nickel(II) complex. Although CyDTA did not affect the rate of the dissociation of the nickel ion from the complex, the hydrogen ion promoted the dissociation reactions.[1,2] The same behavior was shown in the reaction of copper(II) complexes with CyDTA ions. In the present study, the rate constants of the dissociation reaction of copper(II)-nitrilotriacetate (NTA) and -nitrilo(diacetic)propionate (NDAP) complexes were determined and compared with those of the other metal complexes. The acid dissociation constant of the ligand and/or the formation constant of the complex is used in most methods when the rate constant is determined.

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*[1] Part IV of a series on the kinetics of the multidentate ligand-substitution reactions.

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1) M. Kimura, This Bulletin, **42**, 2841 (1969).

2) M. Kimura, *ibid.*, **42**, 2844 (1969).

However, this method of determining the dissociation rate constant using CyDTA as an indicator of the rate is abvantageous in that the rate constant can be determined without using any other constants.

Experimental

A solution of copper(II) nitrate was prepared by dissolving a known amount of pure copper metal in reagent-grade nitric acid. A chelating agent, NDAP, was synthesized by the same procedures as have been reported by Uehara *et al.*3) All the other chemicals and apparatus used were the same as those described in previous papers.1,4) The temperature was maintained at 25°C, and the ionic strength was adjusted to 0.2 with potassium nitrate.

Derivation of the Rate Equation

The overall substitution reaction of the copper-NTA or copper-NDAP complex with CyDTA can be expressed as follows:

$$CuX^- + \left\{\begin{array}{c} Cy^{4-} \\ \upharpoonleft\!\downharpoonright \\ \vdots \\ \upharpoonleft\!\downharpoonright \\ H_4Cy \end{array}\right\} \underset{k^-}{\overset{k^+}{\rightleftharpoons}} CuCy^{2-} + \left\{\begin{array}{c} X^{3-} \\ \upharpoonleft\!\downharpoonright \\ \vdots \\ \upharpoonleft\!\downharpoonright \\ H_3X \end{array}\right\} \qquad (1)$$

where X^{3-} denotes a tervalent NTA or NDAP anion, and Cy^{4-}, a quadrivalent CyDTA anion.

The rate of the forward reaction (1) was confirmed to be independent of the initial concentrations of CyDTA and also of NTA or NDAP. Therefore, the rate equation can be expressed as:

$$-\frac{d[CyDTA]}{dt} \equiv -\frac{d[CuX^-]}{dt}$$
$$= k^+[CuX^-] - k^-[CuCy^{2-}] \qquad (2)$$

The concentration that can be determined polarographically is [CyDTA] which is given by:

$$[CyDTA] = \sum_{j=0}^{4}[H_jCy^{(4-j)-}] \qquad (3)$$

By integrating Eq. (2), we obtain:

$$\ln([CuX^-] - [CuX^-]_e) =$$
$$-(k^+ + k^-)t + \ln([CuX^-]_i - [CuX^-]_e) \qquad (4)$$

where the subscripts i and e represent the initial and the equilibrium states respectively. At the equilibrium of the reaction, the following relation may be satisfied:

$$k^+/k^- = [CuCy^{2-}]_e/[CuX^-]_e$$
$$= (K_{CuCy}/K_{CuX}) \times ([Cy^{4-}]_i/[X^{3-}]_i) \fallingdotseq 10^8 \qquad (5)$$

Therefore, the relations of $k^- \ll k^+$ and $[CuX^-]_e \ll [CuX^-]_i$ are satisfied, and k^- and $[CuX^-]_e$ can be neglected under the present experimental conditions. Consequently, Eq. (4) was simplified to:

$$\ln[CuX^-] = -k^+t + \ln[CuX^-]_i \qquad (6)$$

Equation (6) shows that the plots of its left-hand side against t should give a straight line and that the value of k^+ can be obtained from the slope.

Results and Discussion

Figure 1 shows examples of a current-time curve and a plot of the left-hand side in Eq. (6) against the time, a plot which was obtained for the reaction of the copper-NTA complex with CyDTA. The plot gives a straight line, as may be expected from Eq. (6). The values of k^+ were not affected by the change in the initial concentrations of the copper-NTA complex, CyDTA, and NTA. The same behavior was also found in the reaction of the copper-NDAP complex with CyDTA. The plots of k^+ *versus* $[H^+]$ showed a straight line (see Fig. 2).

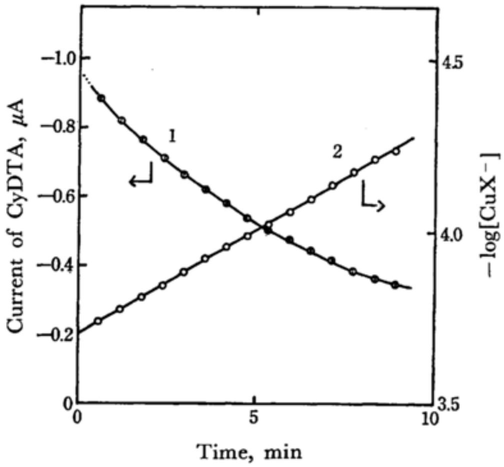

Fig. 1. A current-time curve (curve 1) and the left-hand side of Eq. (6) as a function of time (curve 2). The reaction is that of copper(II)-NTA complex with CyDTA. Measurement was made at +0.22V *vs.* SCE and was in acetate-buffer solution of pH 5.82 containing 0.04 M acetate ion at ionic strength 0.2 and at 25°C. Initial concentrations are: $[Cu\mathit{nta}^-]_i = 2.01\times10^{-4}$ M, $[NTA]_i = 2.7\times10^{-5}$ M and $[CyDTA]_i = 2.25\times10^{-4}$ M.

These results indicate that the overall reaction (1) proceeds through the following reaction paths:

$$CuX^- \underset{k_a^-}{\overset{k_{CuX}}{\rightleftharpoons}} Cu^{2+} + X^{3-} \qquad (7)$$

$$CuX^- + H^+ \underset{k_b^-}{\overset{k_{CuX}^{H}}{\rightleftharpoons}} Cu^{2+} + HX^{2-} \qquad (8)$$

$$Cu^{2+} + \left\{\begin{array}{c} Cy^{4-} \\ \upharpoonleft\!\downharpoonright \\ \vdots \\ \upharpoonleft\!\downharpoonright \\ H_4Cy \end{array}\right\} \overset{k_j^+}{\rightleftharpoons} CuCy^{2-} + jH^+ \qquad (9)$$

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3) A. Uehara, E. Kyuno and R. Tsuchiya, This Bulletin, **41**, 2385 (1968).

4) M. Kimura, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **89**, 1209 (1968).

where the relation:

$$\sum_{j=0}^{4} k_j{}^+[\mathrm{H}_j\mathrm{Cy}^{(4-j)-}] \gg k_\mathrm{a}{}^-[\mathrm{X}^{3-}] + k_\mathrm{b}{}^-[\mathrm{HX}^{2-}] \quad (10)$$

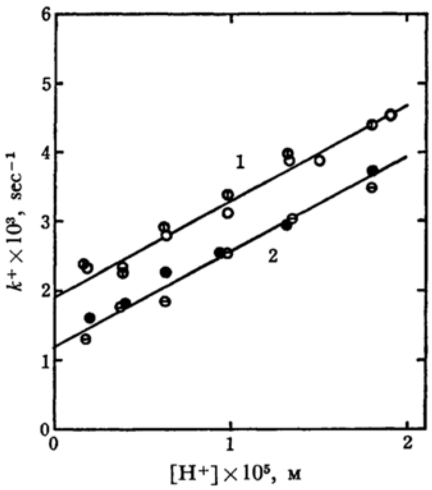

Fig. 2. k^+ as a function of the hydrogen ion concentration at ionic strength 0.2 and 25°C. Measurement was made in acetate-buffer solution containing 0.04 M acetate ion. The reactions are those of Cu(II)-NTA (curve 1) and Cu(II)-NDAP (curve 2) complexes with CyDTA. Initial concentrations for curve 1: $[\mathrm{Cu}nta^-]_i = 2.01 \times 10^{-4}$ M, $[\mathrm{NTA}]_i = 2.7 \times 10^{-5}$ M, $[\mathrm{CyDTA}]_i = 3.37 \times 10^{-4}$ M (⦶) and 2.25×10^{-4} M (○) Initial concentrations for curve 2: $[\mathrm{CyDTA}]_i = 2.25 \times 10^{-4}$ M, $[\mathrm{Cu}ndap^-]_i = 1.31 \times 10^{-4}$ M (⊖) and 2.62×10^{-4} M (●), $[\mathrm{NDAP}]_i = 1.1 \times 10^{-5}$ M (⊖) and 2.2×10^{-5} M (●).

is satisfied under the present experimental conditions. (However, the condition of Eq. (10) can not be satisfied near the final stage of the reaction because the concentration of CyDTA gradually decreases according to the progress of the forward reaction, while that of NTA (or NDAP) increases according to the reaction process.) From the reaction mechanism, the rate of the forward reaction (1) is represented by Eq. (11):

$$(\mathrm{Rate}) = k^+[\mathrm{CuX}^-] = (k_{\mathrm{CuX}} + k_{\mathrm{CuX}}^{\mathrm{H}}[\mathrm{H}^+])[\mathrm{CuX}^-] \quad (11)$$

The rate constants in Eq. (11) were determined from the plots of Fig. 2; they are given in Table 1.

TABLE 1. RATE CONSTANTS OF THE DISSOCIATION REACTIONS (7) AND (8), AT AN IONIC STRENGTH OF 0.2 AT 25°C

$k_{\mathrm{Cu(nta)}}$	1.9×10^{-3} sec^{-1}
$k_{\mathrm{Cu(ndap)}}$	1.2×10^{-3} sec^{-1}
$k_{\mathrm{Cu(nta)}}^{\mathrm{H}}$	1.4×10^2 l mol^{-1} sec^{-1}
$k_{\mathrm{Cu(ndap)}}^{\mathrm{H}}$	1.4×10^2 l mol^{-1} sec^{-1}

The value of $k_{\mathrm{Cu(nta)}}$ was about twice that of $k_{\mathrm{Cu(ndap)}}$. A similar tendency was also found in the nickel(II) complexes with NTA and NDAP, as have been reported previously.[1,2]

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