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The Kinetics of the Electrophilic Substitution Reaction of the *trans*-1,2-Cyclohexanediaminetetraacetatocadmate(II) Complex with Copper(II) Ion

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The kinetics and the mechanisms of the electrophilic substitution reaction of the metal-ethylenediaminetetraacetate(EDTA) complex have been studied for several different reaction systems.[1-9] These metal-ion exchange reactions are all shown to proceed through the reaction of the entering metal ion with the EDTA complex and through that of the dissociated EDTA anion with the entering metal ion. Recently, similar electrophilic substitution reactions have been studied with *trans*-1,2-cyclohexanediaminetetraacetic acid (CyDTA) in place of EDTA.[2,10-12] In this case, there was no direct reaction between the entering metal ion and the CyDTA complex. This behavior was confirmed in the present study. In most cases, a metal-CyDTA complex has a larger stability constant (from 1 to 3 larger in the logarithm scale) than the corresponding EDTA complex.[13] Therefore, the dissociation reaction of CyDTA complexes may be expected to be considerably slower than that of the corresponding EDTA complexes. This expectation was also examined in this study.

Experimental

The solutions of disodium CyDTA and copper(II) nitrate were the same as those described in previous papers.[14,15] The cadmium(II) nitrate solution was prepared by dissolving pure cadmium metal in nitric acid: it was standardized against a standard CyDTA solution by amperometric titration.

The apparatus and procedure were also the same in principle as those described in the previous papers.[14,15]

Results

The overall reaction in acetate media is represented by:

$$\left\{\begin{matrix}\mathrm{Cu^{2+}}\\ \upharpoonleft\downharpoonright\\ \mathrm{CuOAc^{+}}\\ \upharpoonleft\downharpoonright\\ \mathrm{Cu(OAc)_2}\end{matrix}\right\} + \mathrm{CdCy^{2-}} \overset{V_{i^+}}{\rightleftharpoons} \mathrm{CuCy^{2-}} + \left\{\begin{matrix}\mathrm{CdOAc^{+}}\\ \upharpoonleft\downharpoonright\\ \mathrm{Cd^{2+}}\end{matrix}\right\} \qquad (1)$$

Where Cy^{4-} denotes a tetravalent CyDTA anion. The forward reaction rate was obtained by the polarographic measurements of the copper(II)-ion concentration with the time. The copper-ion concentration that can be determined is an apparent concentration, *i.e.*, $[Cu^{2+}]_{app}=[Cu^{2+}]+[CuOAc^{+}]+[Cu(OAc)_2]$. Under the present experimental conditions, the forward reaction of Eq. (1) was so sluggish that the initial rate could be determined accurately. When the copper ion is present in a large excess over the cadmium ion, the initial rate was independent of the copper-ion concentrations, but it was proportional to the concentrations of the Cd(II)-CyDTA complex and the hydrogen ion (see Figs. 1, 2, and 3) On the other hand, when the cadmium ion is present in a large excess over the copper ion, the rate

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1) M. Kimura, This Bulletin, **42**, 404 (1969).

2) J. R. Kuempel and W. B. Schaap, *Inorg. Chem.*, **7**, 2435 (1968).

3) a) N. Tanaka, H. Osawa and M. Kamada, This Bulletin, **26**, 67 (1963); b) N. Tanaka and H. Ogino, *ibid.*, **36**, 175 (1962). c) N. Tanaka and M. Kamada, *ibid.*, **35**, 1596 (1962). d) K. Kato, *ibid.*, **33**, 600, (1960). e) N. Tanaka and K. Kato, *ibid.*, **32**, 1376 (1959). f) N. Tanaka, K. Kato and R. Tamamushi, *ibid.*, **31**, 283 (1958).

4) H. Ackermann and G. Schwarzenbach, *J. Phys. Chem.*, **35**, 485 (1952).

5) K. Bril, S. Bril and P. Krumholz, *ibid.*, **59**, 596 (1955); **60**, 251 (1956).

6) a) S. Jones and F. A. Long, *ibid.*, **56**, 25 (1952). b) C. M. Cook, Jr., and F. A. Long, *J. Amer. Chem. Soc.*, **80**, 33 (1958).

7) R. J. Day and C. N. Reilley, *Anal. Chem.*, **36**, 1073 (1964).

8) R. J. Kula and G. H. Reed, *ibid.*, **38**, 697 (1966).

9) a) T. J. Bydalek and D. W. Margerum, *J. Amer. Chem. Soc.*, **83**, 4326 (1961); *Inorg. Chem.*, **1**, 852 (1962); **2**, 678 (1963). b) D. W. Margerum, D. B. Rorabacher and J. F. G. Clarke, Jr., *ibid.* **2**, 667 (1963). c) D. B. Rorabacher and D. W. Margerum, *ibid.*, **3**, 382 (1964).

10) D. W. Margerum and T. J. Bydalek, *Inorg. Chem.*, **2**, 683 (1963).

11) D. L. Janes and D. W. Margerum, *ibid.*, **5**, 1135 (1966).

12) G. F. Smith and D. W. Margerum, *ibid.*, **8**, 135 (1969).

13) L. G. Sillen and A. E. Martell, "Stability Constants," Chemical Society, London (1964).

14) M. Kimura, *Nippon Kagaku Zasshi*, **89**, 1209 (1968).

15) M. Kimura, This Bulletin, **42**, 3588 (1969).

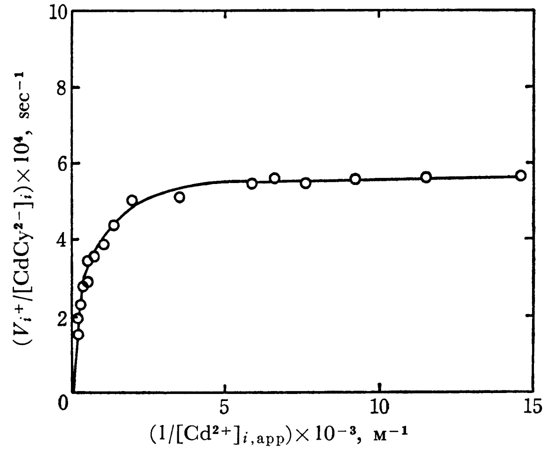

Fig. 1. $V_i^+/[\mathrm{CdCy^{2-}}]_i$ as a function of the reciprocal cadmium concentration at ionic strength 0.2 and 25°C.
Initial concentrations are 1.12 mM and 5.03×10^{-1} mM for $[\mathrm{CdCy^{2-}}]_i$ and $[\mathrm{Cu^{2+}}]_{i,\mathrm{app}}$ respectively, pH 4.90.

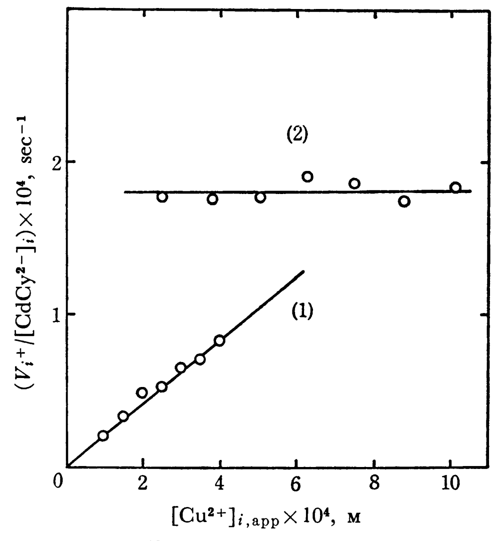

Fig. 2. $V_i^+/[\mathrm{CdCy^{2-}}]_i$ as a function of the concentration of copper ion at ionic strength 0.2 and 25°C.
Initial concentrations are $[\mathrm{CdCy^{2-}}]_i = 2.25$ mM, $[\mathrm{Cd^{2+}}]_{i,\mathrm{app}} = 6.3$ mM and pH 4.95 for curve 1, and $[\mathrm{CdCy^{2-}}]_i = 1.12$ mM, $[\mathrm{Cd^{2+}}]_{i,\mathrm{app}} = 3.3\times 10^{-2}$ mM and pH 5.42 for curve 2.

was proportional to the concentrations of the copper ion as well as those of the Cd(II)-CyDTA complex and the hydrogen ion, and the rate was inversely proportional to the concentrations of the cadmium ion (Figs. 1, 2, and 4). These results indicate that the reaction between the copper(II) ion and the cadmium(II)-CyDTA complex proceeds through the following reaction paths;

$$\mathrm{CdCy^{2-} + H^+ \underset{k^{HCy}_{Cd}}{\overset{k^{H}_{CdCy}}{\rightleftharpoons}} HCy^{3-} + Cd^{2+}} \qquad (2)$$

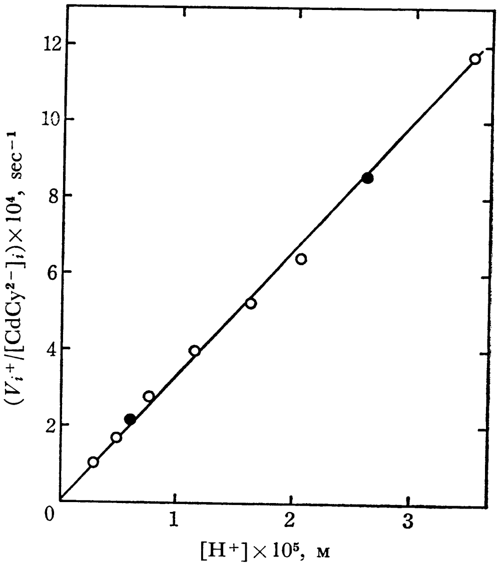

Fig. 3. $V_i^+/[\mathrm{CdCy^{2-}}]_i$ as a function of the hydrogen ion concentration at ionic strength 0.2 and 25°C.
Initial concentrations are $[\mathrm{CdCy^{2-}}]_i = 1.12$ mM and $[\mathrm{Cd^{2+}}]_{i,\mathrm{app}} = 3.3\times 10^{-2}$ mM for ○, $[\mathrm{CdCy^{2-}}]_i = 2.25$ mM and $[\mathrm{Cd^{2+}}]_{i,\mathrm{app}} = 6.6\times 10^{-2}$ mM for ●, and $[\mathrm{Cu^{2+}}]_{i,\mathrm{app}} = 5.03\times 10^{-1}$ mM for ○ and ●.

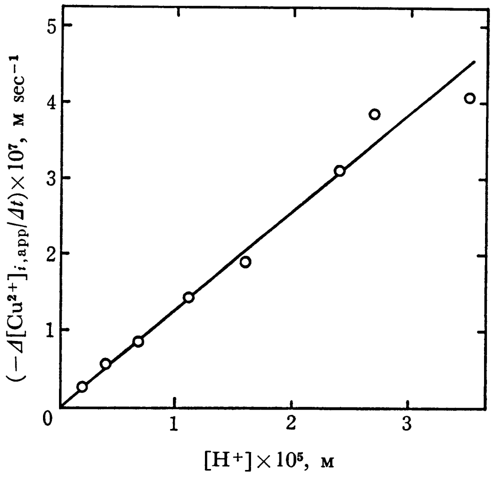

Fig. 4. Initial rate as a function of the hydrogen ion concentration at ionic strength 0.2 and 25°C.
Initial concentrations are 2.25 mM, 5.38 mM and 2.50×10^{-1} mM for $[\mathrm{CdCy^{2-}}]_i$, $[\mathrm{Cd^{2+}}]_{i,\mathrm{app}}$ and $[\mathrm{Cu^{2+}}]_{i,\mathrm{app}}$ respectively.

$$\mathrm{Cu^{2+} + HCy^{3-} \underset{k^{H}_{CuCy}}{\overset{k^{HCy}_{Cu}}{\rightleftharpoons}} CuCy^{2-} + H^+} \qquad (3)$$

Determination of the Rate Constant of the Dissociation Reaction of the Cadmium(II)-CyDTA Complex. When the copper ion is present in a large excess over the cadmium ion, the

Table 1. Rate constants of the reaction (at 25°C)

$$M^{2+} + HY^{3-} \underset{kb}{\overset{k_f}{\rightleftharpoons}} MY^{2-} + H^+$$

Reaction system	μ	Rate constant, l mol^{-1} sec^{-1} k_f	k_b	Method	Researcher
Cd-EDTA	0.1	6.4×10^9	3×10^{3}*	$E_{1/2}$	Aylward, Hayes[16a)]
Cd-EDTA	0.5	2.3×10^9	1×10^3	ϕ	Matsuda, Tamamushi[16b)]
Cd-EDTA	1.6	1×10^9	7.6×10^3	NMR	Sudmeier, Reilley[16c)]
Cu-EDTA	0.2	3.0×10^9	7.1*	Pol	Tanaka, Kato[3f)]
Cd-CyDTA	0.1	1.4×10^9	41.4	Sp	Smith, Magerum[12)]
Cd-CyDTA	0.2	1.1×10^{9}*	32.8	Pol	The present study
Cu-CyDTA	0.2	3.3×10^9	2.1*	Pol	The present study

* Calculated by the author using the relation of $k_f/k_b=K_{MY}K_{HY}$.

$E_{1/2}$ refers to the analysis of the half wave potential of polarograph, ϕ, the phase angle behavior, NMR, to the nuclear magnetic resonance, Pol, to the polarographic diffusion current measurement, and Sp, to the spectrophotometry.

rate-determining step is the dissociation reaction of the Cd(II)-CyDTA complex. Therefore, the rate is expressed as Eq. (4);

$$-\frac{\Delta[Cu^{2+}]_{i,app}}{\Delta t} = V_i{}^+ = k^{H}_{CdCy}[CdCy^{2-}]_i[H^+] \quad (4)$$

where the i subscript indicates the initial state. The initial rate was obtained as a function of the hydrogen-ion concentration at two different concentrations of both the cadmium-CyDTA complex and the cadmium ion. The results are given in Fig. 3. Figure 3 clearly indicates that the value of k^{H}_{CdCy} can be determined from the slope. The value of k^{H}_{CdCy} was 32.8 l mol^{-1}sec^{-1}.

Determination of the Rate Constant of the Complex-forming Reaction between the Hydrated Copper(II) Ion and the CyDTA Anion. When the cadmium ion is present in a large excess over the copper ion, the relation of k^{HCy}_{Cu} $[Cu^{2+}] \ll k^{HCy}_{Cd}$ $[Cd^{2+}]$ is satisfied. The following rate equation can then be deduced:

$$-\frac{\Delta[Cu^{2+}]_{i,app}}{\Delta t} = V_i{}^+ = k^{HCy}_{Cu}[Cu^{2+}]_i[HCy^{3-}]_i$$

$$= k_1\frac{[CdCy^{2-}]_i[Cu^{2+}]_{i,app}}{[Cd^{2+}]_{i,app}}[H^+] \quad (5)$$

$$k_1 = k^{HCy}_{Cu} \times$$

$$\frac{1+\beta_{CdOAc}[OAc^-]}{K_{CdCy}K_{HCy}(1+\beta_{CuOAc}[OAc^-]+\beta_{Cu(OAc)_2}[OAc^-]^2)}$$

$$= k^{HCy}_{Cu}\frac{1+16\times0.04}{10^{19.23}\times10^{-11.70}(1+52\times0.04+93\times0.04^2)}$$

$$= k^{HCy}_{Cu}\times1.37\times10^{-8} \quad (5')$$

The initial rate was obtained as a function of the hydrogen-ion concentration(Fig. 4) and also as a function of the concentrations of the copper ion (Curve 1 in Fig. 2). The rate constant, k^{HCy}_{Cu}, was determined to be 8.0×10^9 l mol^{-1}sec^{-1} from Fig. 2, and to be 8.7×10^9 l mol^{-1}sec^{-1} from Fig. 4.

Discussion

Several workers have studied the kinetics of the dissociation or formation reactions of copper-EDTA[3a,c,d,f)] and cadmium-EDTA[16)] complexes. A few of their representative data are given in Table 1, together with the present results on the CyDTA complexes. The rate constant of the complex-forming reaction does not show any large differences between EDTA and CyDTA, nor between cadmium and copper. However, the dissociation reactions of CyDTA complexes are much slower than those of the corresponding EDTA complexes, and the dissociation-rate constants of the cadmium-CyDTA and -EDTA complexes are, respectively, 16 and about 1000 times larger than those of the copper-CyDTA and EDTA complexes. These facts indicate that the rate of the dissociation of these complexes is dependent on the stability of the complex. In the present case, the ratios of the stability constants are;

$$K_{Cu(cydta)}/K_{Cu(edta)} = 10^{21.3}/10^{18.7} = 10^{1.6} \text{ and}$$

$$K_{Cd(cydta)}/K_{Cd(edta)} = 10^{19.2}/10^{16.4} = 10^{2.8}$$

There were two noticeable conclusions for comparing the kinetic behavior of the CyDTA complex with that of the EDTA complex; (1) although are direct reactions between the copper ion and EDTA complex, there were on appreciable direct reactions between the copper ion and the CyDTA complex, and (2) there was a close similarity between the hydrogen-ion reaction with the two complexes. This kinetic behavior is consistent with that of the other metal-CyDTA and -EDTA complexes.

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16) a) G. H. Aylward and J. W. Hayes, *Anal. Chem.*, **37**, (1965). b) K. Matsuda and R. Tamamushi, This Bulletin, **41**, 1563 (1968). c) J. L. Sudmeier and C. N. Reilley, *Inorg. Chem.*, **5**, 1047 (1966). d) J. Koryta and Z. Zabransky, *Collect. Czech. Chem. Commun.*, **25**, 3153 (1960). e) T. Fujisawa and N. Tanaka, *Nippon Kagaku Zasshi*, **87**, 965 (1966). f) N. Tanaka, R. Tamamushi and M. Kodama, *Z. Phys. Chem.* (Frankfurt am Main), **41**, 141 (1958).