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The Kinetics of the Ligand-substitution Reactions of Nitrilotriacetatoniccolate(II) Complexes with *trans*-1,2-Cyclohexanediaminetetraacetate Ions

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The kinetics of the ligand-substitution reactions of the nitrilotriacetatoniccolate(II) complexes with *trans*-1,2-cyclohexanediaminetetraacetate (CyDTA) ions were studied polarographically from pH 4.8 to 5.8 at an ionic strength of 0.2 and at 25°C. The reactions were found to proceed only through the dissociation reactions of the nitrilotriacetatoniccolate(II) complexes. The rate constants of the dissociation reactions were also determined. In contrast to the reactions of the same complex with ethylenediaminetetraacetate (EDTA) ions and *N*-2-hydroxyethylenediaminetriacetate (HEDTA) ions, there were no direct reactions of the nitrilotriacetatoniccolate(II) complexes with CyDTA ions. The reaction was of the first order in respect to the concentration of the nickel-complex and independent of the CyDTA concentration; the reaction of the complex with CyDTA ions was found to have the different mechanisms from the similar reaction with EDTA and HEDTA, and to be due to the steric effect of the cyclohexane ring in the CyDTA molecule.

In a previous paper[1] the kinetics of the ligand-substitution reactions of nickel(II)-nitrilotriacetate (NTA) complexes with EDTA ions and HEDTA ions were dealt with. Both reactions were found to proceed through four reaction paths, involving two paths of the dissociation reactions of Ni(II)-NTA complexes. Recently, it has been reported that the reactions of copper(II) ion with Ni(II)-CyDTA complexes,[2] and those of cadmium(II) ion with Ca(II)-CyDTA complexes,[3] behave different kinetically from the similar reactions with EDTA complexes.[3-5] These phenomena could be explained by the fact that the cyclohexane ring in CyDTA prevents the free rotation about the ethylenic bond between the two nitrogen atoms; with this steric restriction it is impossible to bond a different metal ion to each iminodiacetate segment of CyDTA, although such reaction intermediates are possible with EDTA.[2,3] It seems to be important and also interesting to examine whether a similar kinetic behavior holds in the case of the ligand-substitution reaction, particularly in the case of the reaction using CyDTA as the entering ligand. Thus, the ligand-substitution reactions of Ni(II)-NTA complexes with CyDTA ions have been investigated in the present study. The reaction mechanisms have been compared with those of the similar reactions with EDTA and HEDTA, and also with the metal-substitution reactions described above.

Experimental

The solutions of dipotassium nitrilotriacetate and dipotassium *trans*-1,2-cyclohexanediaminetetraacetate were prepared from commercial nitrilotriacetic acid (DOTITE NTA) and *trans*-1,2-cyclohexanediaminetetraacetic acid (DOTITE CyDTA) respectively, and were standardized against a standard solution of nickel(II) nitrate by amperometric titration. The standard solution of nickel(II) nitrate was prepared by dissolving an appropriate amount of pure nickel metal in reagent-grade nitric acid. The concentration of the nickel(II) solution was determined by the conventional gravimetric method, using dimethylglyoxime.[6] Commercial guaranteed reagents were used for acetate buffer solution and supporting electrolytes without further purification.

The rate of the reaction of nickel(II)-NTA complex with CyDTA was determined by measuring the decrease of the polarographic anodic diffusion-limiting currents of CyDTA ions with time.

Current-time curves were obtained with a Yanagimoto-PA-102 pen-recording polarograph. The dropping-mercury electrode had an m value of 1.9 mg/sec and a drop time, t_d, of 4.3 sec in an air-free solution contain-

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ing 0.2 M potassium nitrate at 25°C and at −0.5 V *vs.* SCE.

Measurements were made at 25°C in an acetate buffer solution containing 0.04 M acetate ion. The ionic strength of the solution was adjusted to 0.2 with potassium nitrate. Gelatin (0.005% in concentration) was added as a maximum suppressor. The pH of the solution was measured after the polarographic measurements with a Hitachi-Horiba Model F-5 pH meter equipped with a glass electrode.

Results and Discussion

The overall ligand-substitution reactions between nickel(II)-NTA complexes and CyDTA ions can apparently be expressed by:

$$\mathrm{NiX^-} + \left\{\begin{array}{c} \mathrm{Z^{4-}} \\ \rightleftharpoons \\ | \\ \rightleftharpoons \\ \mathrm{H_4Z} \end{array}\right\} \xrightleftharpoons{V_i^+} \mathrm{NiZ^{2-}} + \left\{\begin{array}{c} \mathrm{X^{3-}} \\ \rightleftharpoons \\ | \\ \rightleftharpoons \\ \mathrm{H_3X} \end{array}\right\} \qquad (1)$$

Where X^{3-} and Z^{4-} denote a tervalent NTA anion and a tetravalent CyDTA anion respectively.

The concentrations that can be determined polarographically, [CyDTA] are given by:

$$[\mathrm{CyDTA}] = \sum_{j=0}^{4} [\mathrm{H}_j\mathrm{Z}^{(4-j)-}]$$

Under the present experimental conditions, the rate of the reaction given by Eq. (1) was so slow that the initial rate of the forward reaction, $-\Delta[\mathrm{CyDTA}]_i/\Delta t$, could be determined accurately. The subscript i indicates the initial state.

Table 1 shows the characteristics of the reaction of Ni(II)-NTA complexes with CyDTA ions, which were obtained from the preliminary measurements of the initial rate under varied conditions.

Judging from these characteristics, the reaction mechanism of the ligand-substitution reaction between Ni(II)-NTA complex and CyDTA ions may be considered to be as follows:

$$\mathrm{NiX^-} \underset{k_a^-}{\overset{k_{\mathrm{NiX}}}{\rightleftharpoons}} \mathrm{Ni^{2+}} + \mathrm{X^{3-}} \qquad (2)$$

$$\mathrm{NiX^-} + \mathrm{H^+} \underset{k_b^-}{\overset{k_{\mathrm{NiX}}^{\mathrm{H}}}{\rightleftharpoons}} \mathrm{Ni^{2+}} + \mathrm{HX^{2-}} \qquad (3)$$

$$\mathrm{Ni^{2+}} + \left\{\begin{array}{c} \mathrm{Z^{4-}} \\ \rightleftharpoons \\ | \\ \rightleftharpoons \\ \mathrm{H}_j\mathrm{Z}^{(4-j)-} \end{array}\right\} \xrightleftharpoons{k_j^+} \mathrm{NiZ^{2-}} + j\mathrm{H^+} \qquad (4)$$

Consequently, it was found that the relations of:

$$\sum_{j=0}^{4} k_j^+[\mathrm{H}_j\mathrm{Z}^{(4-j)-}] \gg k_a^-[\mathrm{X^{3-}}] + k_b^-[\mathrm{HX^{2-}}]$$

are satisfactorily fulfilled under the present experimental conditions from the series No. 3 in Table 1, and that there are no paths of the direct reaction of CyDTA ions with the complex from the series No. 4 in Table 1. Therefore, the overall reaction rate for the reaction the (1) is expressed by:

$$-\Delta[\mathrm{CyDTA}]_i/\Delta t \equiv V_i^+ = [\mathrm{NiX^-}]_i\{k_{\mathrm{NiX}} + k_{\mathrm{NiX}}^{\mathrm{H}}[\mathrm{H^+}]\} \qquad (5)$$

Determination of the Rate Constant. The initial rate of the reaction (1), $-\Delta[\mathrm{CyDTA}]_i/\Delta t$, was determined under the conditions given by series No. 1 in Table 1. The values of $V_i^+/[\mathrm{NiX^-}]_i$ were plotted against [H$^+$] according to Eq. (5). These plots gave straight lines, as shown in Fig. 1, from which the values of the rate constants in Eq. (5) were determined. The rate constants obtained are given in Table 2, together with the values previously reported.[1)]

In Table 2 it can be seen that the values obtained in the present study are in good agreement with those obtained from the other reaction systems. The

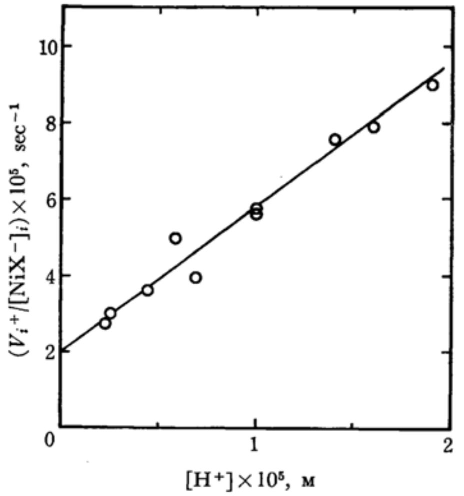

Fig. 1. $V_i^+/[\mathrm{NiX^-}]_i$ as a function of the hydrogen ion concentration in acetate buffer-potassium nitrate solutions of ionic strength 0.2 at 25°C. Initial concentrations are $[\mathrm{NiX^-}]_i = 2.02\times10^{-3}$ M and $[\mathrm{CyDTA}]_i = 4.49\times10^{-4}$ M. Concentration of uncomplexed NTA is $[\mathrm{NTA}]_f = 2.6\times10^{-4}$ M.

Table 1. Characteristics of the reaction of Ni(II)-NTA complex with CyDTA ions

Series No.	[H$^+$]	$[\mathrm{NiX^-}]_i$	$[\mathrm{NTA}]_f$*	$[\mathrm{CyDTA}]_i$	Initial rate (V_i^+)
1	varied	const.	—	—	first-order for [H$^+$]
2	const.	varied	—	—	proportional to $[\mathrm{NiX^-}]_i$
3	const.	const.	varied	—	independent of $[\mathrm{NTA}]_f$
4	const.	const.	—	varied	independent of $[\mathrm{CyDTA}]_i$

* $[\mathrm{NTA}]_f$ indicates the concentration of uncomplexed NTA.

TABLE 2. RATE CONSTANTS OF THE DISSOCIATION REACTION AT THE IONIC STRENGTH OF 0.2 AT 25°C

Reaction system	k_{NiX} (sec^{-1})	$k^{\mathrm{H}}_{\mathrm{NiX}}$ ($\mathrm{M}^{-1}\,\mathrm{sec}^{-1}$)	Investigator
NiX-EDTA	3.0×10^{-5}	3.7	M. Kimura1)
NiX-HEDTA	3.4×10^{-5}	3.7	M. Kimura1)
NiX-CyDTA	2.0×10^{-5}	3.8	This study

reactions of Ni(II)-NTA complex with EDTA and HEDTA were of the first-order in the concentrations of EDTA and HEDTA.1) However, the reaction of the same complex with CyDTA was independent of the concentration of CyDTA. Experimental examples of this behavior are shown in Fig. 2. Margerum and Bydalek2) reported that the metal-substitution reaction of copper(II) ion with Ni(II)-CyDTA complex does not include copper ion attack of Ni(II)-CyDTA complex; the absence of any copper dependence may be attributed to the inability of the copper(II) ion to form binuclear intermediates such as [Ni-CyDTA-Cu] because of hindered rotation and steric blocking due to the cyclohexane ring. Recently, Kuempel and Schaap3) reported similar behavior in the reaction of the cadmium(II) ion with Ca(II)-CyDTA complex. The results obtained in the present study on the ligand-substitution reaction, using CyDTA as an entering ligand molecule, may be consistent with those of the two previous papers on metal-substitution reactions involving CyDTA.

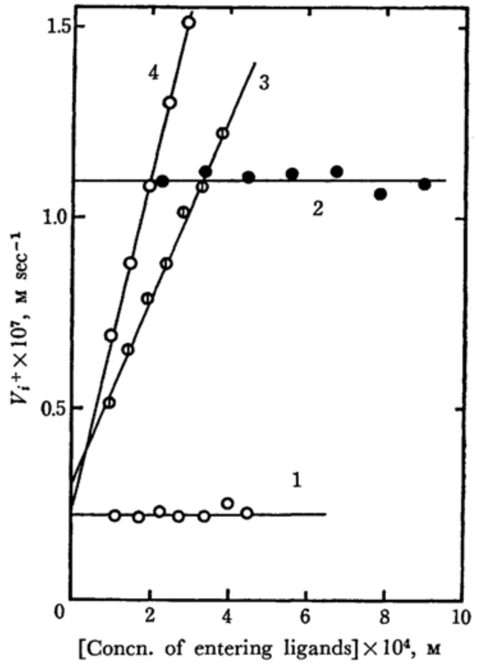

Fig. 2. V_i^+ as a function of the concentrations of the entering ligands. The conditions are the same as for Fig. 1. The entering ligands are CyDTA (1 and 2), EDTA (3) and HEDTA (4). The initial concentrations of complexes, $[\mathrm{NiX}^-]_i$ are 0.81 mM (1), 2.02 mM (2) and 0.40 mM (3 and 4). The pH values of the solutions are 5.70 (1), 5.10 (2), 5.00 (3) and 5.26 (4).

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