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Kinetics of Multidentate Ligand Substitution Reactions. XIV. Substitution Reactions of Ethylenediaminetetraacetic Acid (EDTA) and *N*-(2-Hydroxyethyl)ethylenediamine-*N*,*N'*,*N'*-triacetic Acid (EDTA-OH) with Nickel(II)-Ethylenediaminemonoacetate (EDMA) and -Diethylenetriamine (Dien) Complexes

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The kinetics of the substitution reactions of EDTA and EDTA-OH with nickel(II)-EDMA and -Dien complexes were studied using the polarographic technique. The substitution reactions of EDTA and EDTA-OH with the nickel(II)-EDMA complex were found to have a common reaction mechanism. They were first-order with respect to EDTA or EDTA-OH, and also first-order with respect to the nickel(II)-EDMA complex with a 1: 1 composition; their reaction mechanism could be formulated as:

$$\mathrm{NiX_2^0} \rightleftharpoons \mathrm{NiX^+} + \mathrm{X^-} \quad \text{in a rapid equilibrium}$$

$$\mathrm{NiX^+} + \left\{\begin{array}{l} \mathrm{HY}^{1-m} \overset{k_{\mathrm{HY}}}{\rightleftharpoons} \mathrm{NiY}^{2-m} + \mathrm{HX}^0 \\ \mathrm{Y}^{m-} \overset{k_{\mathrm{Y}}}{\rightleftharpoons} \mathrm{NiY}^{2-m} + \mathrm{X}^- \end{array}\right. \qquad \text{r.d.s.}$$

The substitution reactions of EDTA and EDTA-OH with the nickel(II)-Dien complex were also studied under experimental conditions where the reaction could be treated as a pseudo-first-order reaction. The reactions were first-order with respect to the concentration of EDTA or EDTA-OH. However, their reaction rate were independent of the concentrations of the nickel(II)-Dien complex and of uncomplexed Dien. This fact was ascribed to the formation of a stable outer-sphere complex between the nickel(II)-Dien complex with a 1: 2 ratio and the EDTA or EDTA-OH anion, through which the substitution reaction proceeds.

Previous papers in this series[1-3] have dealt with substitution reactions involving nickel(II)-iminodiacetate (IDA), aspartate (Asp), -ethylenediaminemonoacetate (EDMA), and -nitrilotriacetate (NTA) complexes. Those reactions have been shown to proceed invariably through a nickel(II) complex of a 1: 1 composition, a complex which is in a rapid equilibrium with a 1: 2 ratio complex. The substitution reactions of the nickel(II)-EDMA complex with EDTA and EDTA-OH were also found to proceed with the 1: 1 ratio nickel(II)-EDMA complex. However, in sharp contrast, the substitution reactions of the nickel(II)-diethylenetriamine (Dien) complex with EDTA and EDTA-OH are zero-order in concentrations of complexed and uncomplexed Dien. In this paper, the substitution reactions of nickel(II)-EDMA and Dien complexes with EDTA and EDTA-OH will be dealt with by employing the polarographic method. The reaction mechanism and the structure of the reaction intermediate also will be discussed in detail.

Experimental

Reagents. The ways of preparing EDMA dihydrochloride and of its purification were described previously.[4] The Dien used in this study was purified twice by distilling it under reduced pressure. The EDTA and EDTA-OH were recrystallized from their aqueous solutions by adding pure HCl and ethanol. The preparation of standard nickel(II) nitrate solution was also described previously.[5] The other reagents were of an analytical-reagent grade and were used without further purification.

Apparatus and Experimental Procedures. The apparatus and the experimental procedures were the same as those described previously.[3] In this study, all the measurements were conducted in solutions of an ionic strength of 0.30 ($NaClO_4$ for the EDMA system, KNO_3 for the Dien system). In the kinetic study of the substitution reaction of the nickel(II)-EDMA complex, no buffer reagent was used, because the free EDMA has enough buffer capacity to maintain the pH values of the solutions constant. In the substitution reactions of the nickel(II)-Dien complex, however, a phosphate buffer mixture was used over the entire pH range convered. All the sample solutions contained large excesses of complexed and uncomplexed Dien over EDTA or EDTA-OH. Therefore, all reactions could be treated as pseudo-first-order reactions.

Results and Discussion

Substitution Reactions of the Nickel(II)-EDMA Complex with EDTA or EDTA-OH. As in the case of the substitution reaction of the nickel(II)-EDMA complex with diethylenetriaminepentaacetic acid (DTPA),[2] provided that the other experimental conditions are kept constant, the apparent pseudo-first-order rate constants, k_{ap}^{+}'s, as determined from the slope of the linear log (i_0/i_t) *vs.* t plot, were i) inversely proportional to the concentration of uncomplexed EDMA, ii) exactly proportional to the total concentration of the nickel(II) ion, and iii) independent of the initial concentration of EDTA or EDTA-OH. Furthermore, the k_{ap}^{+} value

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[1] M. Kodama and T. Ueda, This Bulletin, **43**, 419 (1970).

[2] M. Kodama, Y. Fujii, and T. Ueda, *ibid.*, **43**, 2085 (1970),

[3] M. Kodama, *ibid.*, **42**, 2532 (1969).

[4] Y. Fujii, E. Kyuno, and R. Tsuchiya, *ibid.*, **43**, 786 (1970).

[5] M. Kodama, S. Karasawa, and T. Watanabe, *ibid.*, **44**, 1815 (1971).

multiplied by $K_2\cdot[\mathrm{X}]_f\cdot(\alpha_\mathrm{H})_\mathrm{X}/[\mathrm{Ni(II)}]_t\cdot(\alpha_\mathrm{H})_\mathrm{Y}$ was found to be a linear function of the hydrogen-ion concentration and to be given by Eq. (1) (Fig. 1):

$$k^+_{ap}\times\frac{K_2\cdot[\mathrm{X}]_f\cdot(\alpha_\mathrm{H})_\mathrm{Y}}{(\alpha_\mathrm{H})_\mathrm{X}\cdot[\mathrm{Ni(II)}]_t}=k_\alpha+k_\beta[\mathrm{H}^+] \qquad (1)$$

where K_2 is the second successive formation constant of the nickel(II)-EDMA complex; $[\mathrm{X}]_f$, the concentration of uncomplexed EDMA; $(\alpha_\mathrm{H})_\mathrm{Y}$, the (α_H) value of EDTA or EDTA-OH, and $(\alpha_\mathrm{H})_\mathrm{X}$, the (α_H) value of EDMA. As was discussed in connection with the substitution reaction of the nickel(II)-EDMA complex with DTPA,[2)] these facts clearly indicate that the substitution reactions of the nickel(II)-EDMA complex with EDTA and EDTA-OH can be depicted as:

$$\mathrm{NiX}_2^0 \rightleftharpoons \mathrm{NiX}^+ + \mathrm{X}^- \quad \text{in a rapid equilibrium}$$

$$\mathrm{NiX}^+ + \begin{cases}\mathrm{HY}^{1-m} \overset{k_\mathrm{HY}}{\rightleftharpoons} \mathrm{NiY}^{2-m} + \mathrm{HX}^0 \\ \mathrm{Y}^{m-} \overset{k_\mathrm{Y}}{\rightleftharpoons} \mathrm{NiY}^{2-m} + \mathrm{X}^-\end{cases} \qquad \text{r.d.s. I}$$

where Y^{m-} and X^- are completely-deprotonated EDTA or EDTA-OH and EDMA anions respectively. On the basis of the above reaction mechanism, k^+_{ap} can be written as:

$$k^+_{ap}=\frac{[\mathrm{Ni(II)}]_t}{(1+K_2'\cdot[\mathrm{X}]_f)\cdot(\alpha_\mathrm{H})_\mathrm{Y}}\times\left(k_\mathrm{Y}+k_\mathrm{HY}\cdot\frac{[\mathrm{H}^+]}{K_n}\right) \qquad (2)$$

where $[\mathrm{Ni(II)}]_t$ and K_n denote the total concentration of the nickel(II) ion and the fourth dissociation constant of EDTA or the third dissociation constant of EDTA-OH respectively. The fact that, in the substitution reaction of EDTA-OH with the nickel(II)-EDMA complex, the $k^+_{ap}\cdot K'_2\cdot[\mathrm{X}]_f\cdot(\alpha_\mathrm{H})_\mathrm{Y}/[\mathrm{Ni(II)}]_t$ value is almost constant under the present experimental conditions implies that the reaction proceeds only through its tervalent anion. From the slopes and intercepts of straight lines in Fig. 1, the k_HY and k_Y values were determined; they are listed in Table 1. The chloride ion was found to have no effect on the reaction.

TABLE 1. RATE CONSTANTS (μ=0.30,25°C)

System	k_Y, M^{-1} sec^{-1}	k_HY, M^{-1} sec^{-1}
EDTA—Ni(II)-EDMA	1.5×10^3	$3.9_0\times10^2$
EDTA-OH—Ni(II)-EDMA	2.8×10^2	—
EDTA—Ni(II)-Dien	—	$5.2_5\times10^{-2}$
EDTA-OH—Ni(II)-Dien	—	$1.1_8\times10^{-1}$

Substitution Reactions of the Nickel(II)-Dien Complex with EDTA and EDTA-OH. The substitution reaction of the nickel(II)-Dien complex with EDTA was studied in the pH range from 7.10 to 9.00. At pH's lower than 8.00, a phosphate buffer mixture was used to keep the solution pH constant. However, it had no effect on the rate of the substitution reaction. As in the case of the substitution reaction of the EDMA complex, the k^+_{ap} value was independent of the initial concentration of EDTA or EDTA-OH. However, in striking contrast to the findings observed in the substitution reaction of the nickel(II)-EDMA complex, the k^+_{ap} value was independent of the concentrations of uncomplexed Dien and of the nickle(II) ions. Considering that, under the present experimental conditions, all the nickel(II) ions exist in the form of $\mathrm{NiX_2}^{2+}$,[2)] the above findings clearly suggest that the EDTA and EDTA-OH anions form a stable outer-sphere complex with NiX_2^{2+}, only through which the reactions proceed. Furthermore, the k^+_{ap} value multiplied by $(\alpha_\mathrm{H})_\mathrm{Y}$ was found to be a linear function of the hydrogen-ion concentration, corresponding to the following relation:

$$k^+_{ap}\cdot(\alpha_\mathrm{H})_\mathrm{Y}=\text{constant}\times[\mathrm{H}^+] \qquad (3)$$

Some typical results were reproduced in Fig. 2. From these experimental facts, we can conclude that the EDTA and EDTA-OH reactions with the nickel(II)-Dien complex under the present experimental conditions have the following reaction mechanism, IIa:

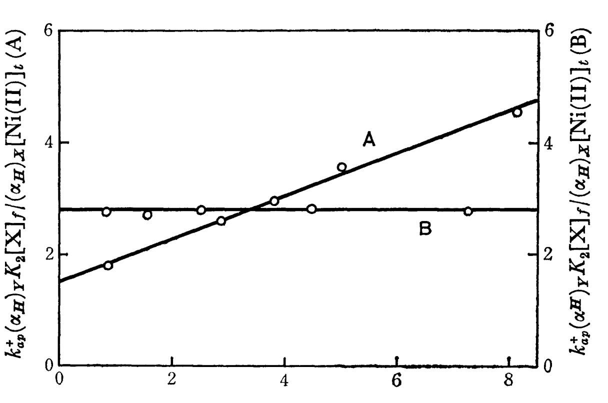

Fig. 1. The plot of $k^+_{ap}K_2[\mathrm{X}]_f(\alpha_H)_Y/[\mathrm{Ni(II)}]_t(\alpha_H)_X$ against the concentration of hydrogen ion.
Total concentration of nickel(II)-ion=10.0 mM
Initial concentration of EDTA or EDTA-OH=0.52 mM
μ=0.30, 25°C
A: EDTA system, $[\mathrm{X}]_f$=20.0 mM
B: EDTA-OH system, $[\mathrm{X}]_f$=15.0 mM

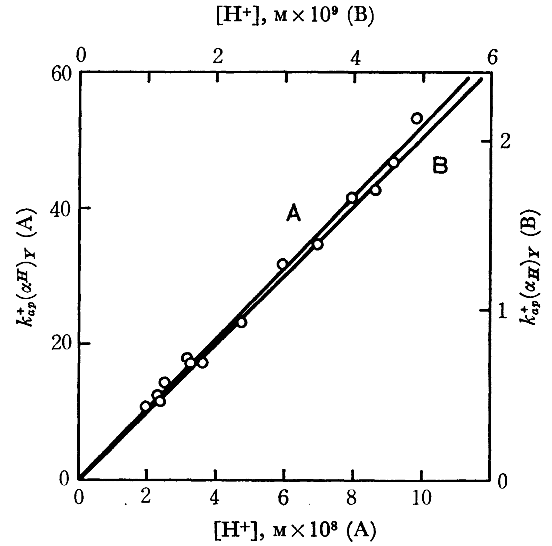

Fig. 2. The plot of k^+_{ap} $(\alpha_H)_Y$ against the concentration of hydrogen ion.
Total concentration of nickel(II)-ion=6.0 mM
Initial concentration of EDTA or EDTA-OH=0.52 mM
The concentration of uncomplexed Dien=18.0 mM
μ=0.30, 25°C
A: EDTA system B: EDTA-OH system

$$NiX_2^{2+} + HY^{1-m} \overset{K_{as}}{\rightleftarrows} NiX_2^{2+} \cdots HY^{1-m} \quad \text{rapid}$$

$$NiX_2^{2+} \cdots HY^{1-m} \overset{k_{HY}}{\rightleftarrows} NiY^{2-m} + HX^{+} + X^{0} \quad \text{r.d.s. IIa}$$

For the above reaction mechanism, if the formation of the outer-sphere complex, $NiX_2^{2+}\cdots HY^{1-m}$, is complete, k_{ap}^{+} can be written as:

$$k_{ap}^{+} = \frac{1}{(\alpha_H)_Y} \times \frac{k_{HY}\cdot[H^+]}{K_n} \qquad (4)$$

Therefore, from the slope of the linear relations in Fig. 2, the k_{HY} values for the EDTA and EDTA-OH reactions were determined. These values are also listed in Table 1.

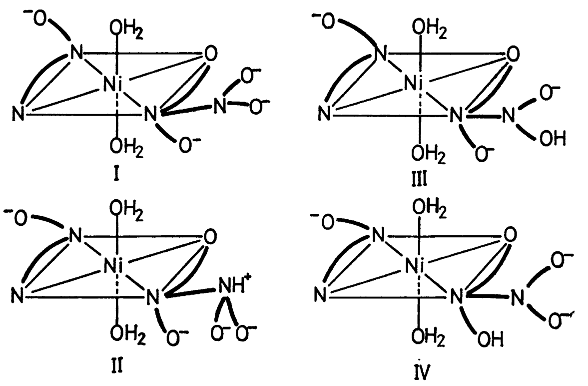

Fig. 3. Reaction intermediates.

As in the case of the substitution reaction of the nickel(II)-EDMA complex with DTPA, if the reaction of the nickel(II)-EDMA complex with EDTA proceeds through the two reaction intermediates (I and II) in Fig. 3, and if the dissociation of the EDMA anion from them is the rate-determining step, on the basis of these reaction intermediates the k_Y and k_{HY} values can be calculated from the $k_c = k_{Ni}^{-en} K_{Ni-en} K_{Ni-gly}/K_{NiX}$ relation.⁶⁾ Here, k_{Ni}^{-en} is the rate constant of the dissociation of the nickel(II)-ethylenediamine complex; K_{Ni-en}, the stability constant of the 1 : 1 nickel(II)-ethylenediamine complex; K_{Ni-gly}, the stability constant of the 1: 1 nickel(II)-glycinate complex, and K_{NiX}, the stability constant of the 1: 1 nickel(II)-EDMA complex. The calculated k_Y and k_{HY} values were 1.0×10^3 and 6.4×10^2 respectively. Of course, the electrostatic contribution to the stability of the reaction intermediate and the statistical factor were also taken into account. The nickel(II)-*N*-ethylglycinate complex was used as a glycinate model. The agreement of the observed k_Y and k_{HY} values with the calculated ones can be regarded as satisfactory. The rate constants calculated on the basis of every reaction intermediate other than I and II showed no good agreement with the observed values. Similarly, one of the following two reaction intermediates (III and IV in Fig. 3) would be possible for the substitution reaction of EDTA-OH with the nickel(II)-EDMA complex. The k_{HY} values calculated on the basis of III and IV were 1.6×10^2 and $8.1 \times 10\text{M}^{-1}\text{sec}^{-1}$ respectively. The former value agreed well with the observed value; this supports the reaction intermediate III.

In the substitution reactions of the nickel(II)-Dien complex, we previously assumed the formation of an outer-sphere complex between NiX_2^{2+} and HY^{1-m} in order to explain the reaction profile. However, it is very hard to believe that two Dien molecules dissociate simultaneously from the nickel(II) ion in the outer-sphere complex. For this reason, the experimental fact that the reaction rate is practically independent of the nickel(II)-Dien complex concentration indicates that the rate-determining step is the dissociation of the first Dien molecule from the nickel(II) ion, which is then followed by the rapid formation of a mixed 1 : 1 : 1 nickel(II), Dien, Y^{m-} complex and the rapid dissociation of the second Dien molecule from it. If the outer-sphere complex is depicted as V, the k_{HY} value can be given by $K_{Ni-L}\cdot K_{st} \times k_{rds}/K_2$. Here, K_2 denotes the second successive formation constant of the nickel(II)-Dien complex; K_{Ni-L}, the stability of the leaving Dien segment, and k_{rds}, the rate constant of the dissociation of the first Dien molecule from the reaction intermediate, V in Fig. 4. By approximating the k_{rds} value to the dissociation rate constant of a 1: 2 ratio nickel(II)-ethylenediamine complex ($\log k = 0.72$⁷⁾), and K_{Ni-L}, to the second successive formation constant of the nickel(II)-*N*-(2-hydroxyethyl)ethylenediamine complex,⁸⁾ the k_{HY} value was calculated to be 8.4×10^{-2} from the above relation. The k_{HY} value obtained experimentally agreed well with this value. To complete the substitution reaction, the above rate-determining step should be followed by the rapid dissociation of the second Dien molecule from the reaction intermediate. By analogy with the substitution reaction of the nickel(II)-Dien complex with DTPA, the latter step would proceed through the following mixed-ligand reaction intermediate (VI), where the dissociation of Dien from it is slow. Here, it must be noted that if

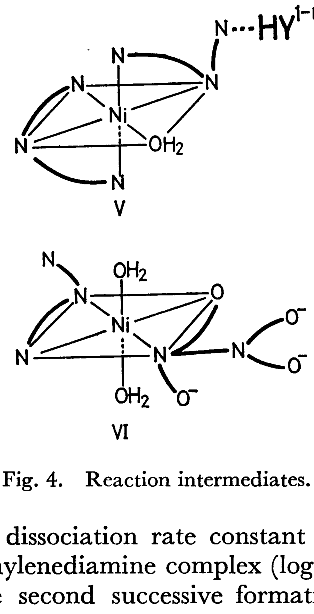

Fig. 4. Reaction intermediates.

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6) D. B. Rorabacher and D. W. Margerum, *Inorg. Chem.*, **3**, 382 (1964).

7) R. Gould, ed., "Mechanisms of Inorganic Reactions," American Chemical Society, Washington D. C. (1965), p. 70.

8) L. G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes," 2nd ed., The Chemical Society, London (1964).

the formation of the reaction intermediate VI is rapid enough, the rate constant calculated on the basis of the reaction intermediate VI should be much larger than the k_{HY} value obtained experimentally. By the common way of calculating the rate constant, the k_{HY} values for the EDTA and EDTA-OH systems were calculated to be 390. This rate constant, large compared with the observed k_{HY} value, shows that the IIa reaction mechanism can reasonably be rewritten as:

$$\mathrm{NiX_2^{2+}} + \mathrm{HY^{1-m}} \overset{K_{as}}{\rightleftarrows} \mathrm{NiX_2^{2+}} \cdots \mathrm{HY^{1-m}} \quad \text{in a rapid equilibrium}$$

$$\mathrm{NiX_2^{2+}} \cdots \mathrm{HY^{1-m}} \overset{k_{HY}}{\rightleftarrows} \mathrm{NiXY^{2-m}} + \mathrm{HX^+} \quad \text{r.d.s. IIa}$$

$$\mathrm{NiXY^{2-m}} \rightleftarrows \mathrm{NiY^{2-m}} + \mathrm{X^0} \quad \text{rapid}$$

The formation of a mixed-ligand complex of the nickel(II) ion involving both Dien and the EDTA or EDTA-OH anion as a reaction product could be disproved spectrophotometrically. In order to ascertain the formation of an outer-sphere complex between $\mathrm{NiX_2}^{2+}$ and the EDTA or EDTA-OH anion, a conductometric investigation was also carried out. However, it could provide no experimental evidence justifying the formation of an outer-sphere complex. Since the K_{as} value predicted from the Fuoss equation[9] is not large enough for the completion of the outer-sphere complex formation, it may be assumed that the internal hydrogen-bond formation between the HY^{1-m} anion and the free nitrogen atom of coordinated Dien plays an important role in the stabilization of the outer-sphere complex.

The substitution reaction of the cobalt(II)-Dien complex with EDTA was also studied. However, it proceeds so rapidly that we could not determine its rate or reaction mechanism by the present polarographic technique.

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9) R. M. Fuoss, *J. Amer. Chem. Soc.*, **80**, 5059 (1958).