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Kinetics of Multidentate Ligand Substitution Reactions. II. Substitution Reactions of BT with Nitrilotriacetato Nickelate(II) Chelate and with Ethylenediaminetetraacetato Nickelate(II) Chelate

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This paper reports a spectrophotometric study of the solution equilibria and the kinetics of the substitution reaction of Eriochrom Black T (BT) with nickel(II)-NTA and with nickel(II)-EDTA chelates. In solutions of pH 8.50—9.50 containing a large excess of uncomplexed NTA over BT and nickel(II)-NTA chelate, BT forms only 1-to-1 normal chelate, NiD^-, with the nickel(II) ion, the stability constant of which is $10^{20.8}(\mu=0.30)$. Kinetically, the ligand-exchange reaction of BT with the nickel(II)-NTA chelate was found to proceed through the following two simultaneous reaction paths and to be much faster than that with the nickel(II)-EDTA chelate,

$$\text{i)}\quad \begin{array}{l} NiX^- + HD^{2-} \rightleftharpoons NiD^- + HX^{2-} \\ \text{rapid}\upharpoonleft\downharpoonright \\ NiX_2^{4-} \end{array} \qquad \text{ii)}\quad \begin{array}{l} HD^{2-} \overset{\text{rapid}}{\rightleftharpoons} D^{3-} + H^+ \\ NiX^- + D^{3-} \rightleftharpoons NiD^- + X^{3-} \\ \text{rapid}\upharpoonleft\downharpoonright \\ NiX_2^{4-} \qquad \text{rate-determining step} \end{array}$$

where NiX^-, NiX_2^{4-}, HD^{2-}, and D^{3-} represent Ni(II)-NTA chelate of 1-to-1 composition, Ni(II)-NTA chelate of 1-to-2 composition, doubly deprotonated BT anion and completely deprotonated BT anion, respectively. The substitution reaction of BT with nickel(II)-EDTA chelate was found to proceed mainly through the following reaction path,

$$HD^{2-} \overset{\text{rapid}}{\rightleftharpoons} D^{3-} + H^+ \qquad \underset{\text{rate-determining step}}{NiY^{2-} + D^{3-} \rightleftharpoons NiD^- + Y^{4-}}$$

and the contribution of the following reaction to the whole reaction is negligible at pH 9.00—10.50.

$$NiY^{2-} + HD^{2-} \rightleftharpoons NiD^- + HY^{3-}$$

In a previous paper,[1] the kinetics of the substitution reaction of Eriochrom Black T (BT, H_3D) and ethylenediaminetetraacetato cobaltate(II) were studied spectrophotometrically. The substitution

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[1] M. Kodama, This Bulletin, **40**, 2575 (1967).

reaction was found to proceed through doubly dissociated and completely dissociated BT ions, but contribution of the reaction path where the dissociation of Co(II)-EDTA chelate is rate-determining is negligible.

In this paper, we report the kinetics of the substitution reactions of BT with nitrilotriacetato nickelate(II) chelate (Ni(II)-NTA) and with ethylenediaminetetraacetato nickelate (II) chelate (Ni(II)-EDTA).

Experimental

Reagents. NTA and EDTA were recrystallized as free acids, and their solutions were standardized by the methods described previously.[1,2] Nickel(II) perchlorate solution was prepared by the following procedure. A known amount of metallic nickel of 99.99% purity was dissolved in dilute HNO_3 solution (1+1), and the nickel(II) was precipitated as hydroxide. The nickel(II) hydroxide was washed thoroughly with redistilled water and dissolved in diluted perchloric acid solution (0.25 M). The concentration of nickel(II) perchlorate solution was standardized against a standard EDTA solution using Murexide as indicator.[3] The purification of BT and the test of its purity are also described in an earlier paper.[2]

Apparatus and Procedure. The apparatus and the experimental procedures were the same as described previously.[1] In this study no buffer reagent was used because uncomplexed EDTA and NTA are considered to have enough buffer capacity to maintain pH values constnat.

Results and Discussion

The Substitution Reaction of BT with Nickel(II)-NTA Chelate. First, the composition and the stability constant of nickel(II)-BT chelate were determined by the same method as in the equilibrium study of the BT-cobalt(II)-EDTA system.[1] As shown in Fig. 1, the concentration ratio between uncomplexed BT and nickel(II)-BT chelate can be determined successfully by measuring the absorbance at 640 mμ. Under the experimental conditions where free NTA is present in a large excess over BT and nickel(II)-NTA chelate, by the analogy to the equilibrium between BT and zinc(II)-NTA chelate,[2] the following relation can be derived when only 1-to-1 chelate, NiD^-, is formed between BT and the nickel(II) ion.

$$\log \frac{A_D - A}{A - A_{NiD}} \cdot \frac{1}{m - \dfrac{A_D - A}{A_D - A_{NiD}}} \cdot [BT]_0 = \log \frac{K_{NiD}}{K_{NiX}} \frac{(\alpha_H)_x}{(\alpha_H)_{BT}} + \log \frac{1}{[X]_f \cdot \left\{1 + \dfrac{K_{NiX_2} \cdot [X]_f}{(\alpha_H)_x}\right\}} \qquad (1)$$

where symbols, A_D, A, $(\alpha_H)_{BT}$ and $[X]_f$, have the same meanings as were used in the previous paper[2] and other notation definitions used are as follows. A_{NiD}: Absorbance of the solution where all the BT ions are considered to form complex with nickel(II) ion, m: The ratio of the total concentration of nickel(II) to that of BT, $[BT]_0$: The total concentration of BT, K_{NiX}: Stability constant of Ni(II)-NTA chelate of 1-to-1 composition, K_{NiX_2}: Equilibrium constant defined as $K_{NiX_2} = [NiX_2^{4-}]/[NiX^-] \cdot [X^{3-}]$, K_{NiD}: Stability constant of Ni(II)-BT chelate, $(\alpha_H)_x$: (α_H) value of NTA.

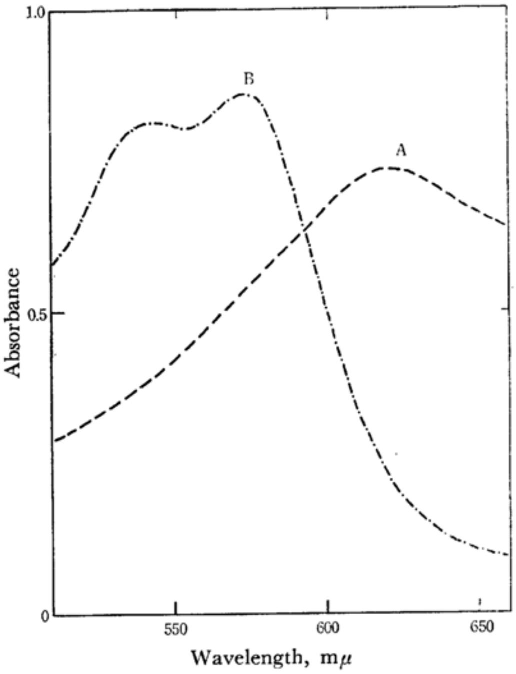

Fig. 1. Absorption curves.
$\mu = 0.30$, pH = 9.45
The concentration of uncomplexed NTA = 27.0 mM
The concentration of BT = 2.26×10^{-5} M
A. No nickel(II) - NTA chelate
B. 9.0 mM nickel(II) - NTA chelate

The ratio of the total concentration of nickel(II) to that of BT m, was made 1.50 and all measurements were conducted in solutions at constant pH 9.54. A straight line with a slope of unity was obtained by plotting

$$\log \frac{A_D - A}{A - A_{NiD}} \cdot \frac{1}{m - \dfrac{A_D - A}{A_D - A_{NiD}}} \cdot [BT]_0 \quad vs.$$

$$\log \frac{1}{[X]_f \cdot \left\{1 + \dfrac{K_{NiX_2} \cdot [X]_f}{(\alpha_H)_x}\right\}}$$

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[2] M. Kodama and H. Ebine, *ibid.*, **40**, 1857 (1967).
[3] H. Flaschka and H. Abdie, *Chemist-Analyst*, **44**, 30 (1955).

showing a confirmatory evidence that under the present experimental conditions only normal chelate $\mathrm{NiD^-}$ is formed (Fig. 2). From the intercept, K_{NiX} value⁴⁾ and pK values⁵⁾ in Table 1, the K_{NiD} value was determined to be $10^{20.8}$ (μ= 0.30, 25°C). This value can satisfactorily account for the well-known interference of nickel(II) ions in the EDTA titration of Mg(II) using BT as indicator.

As described previously,²⁾ the numerical values used in the above calculation were estimated from the related stability and the dissociation constants.⁴⁾ The concentration of free NTA $[\mathrm{X}]_f$ was calculated by using the following relation.

$$[\mathrm{X}]_f=\frac{-\left\{1-\dfrac{K_{\mathrm{NiX_2}}}{(\alpha_{\mathrm{H}})_x}([\mathrm{X}]_t-2[\mathrm{Ni(II)}]_t)\right\}+\sqrt{1+\dfrac{2\cdot K_{\mathrm{NiX_2}}\cdot[\mathrm{X}]_t}{(\alpha_{\mathrm{H}})_x}+\dfrac{K^2{}_{\mathrm{NiX_2}}}{(\alpha_{\mathrm{H}})_x{}^2}([\mathrm{X}]_t-2\cdot[\mathrm{Ni(II)}]_t)^2}}{\dfrac{2\cdot K_{\mathrm{NiX_2}}}{(\alpha_{\mathrm{H}})_x}} \tag{2}$$

where $[\mathrm{X}]_t$ and $[\mathrm{Ni(II)}]_t$ refer to the total concentrations of NTA and nickel(II), respectively.

The kinetics of the substitution reaction of BT with Ni(II)-NTA chelates was studied at 16°C in the presence of a large excess of NTA and its nickel(II) chelate at a pH range 8.50—9.50. Therefore, the reaction can be treated as a pseudo first-order reaction, and simplified to,

$$\left\{\begin{array}{c}\mathrm{HD^{2-}}\\ \upharpoonleft\downharpoonright\\ \mathrm{D^{3-}}\end{array}\right. \underset{k^-}{\overset{k^+}{\rightleftharpoons}} \mathrm{NiD^-} \tag{3}$$

The reaction gave invariably the linear relation between $\log(A_{\mathrm{D}}/(A-A_{\mathrm{NiD}}))$ and time, t, with the intercept identical with $\log(\varepsilon_{\mathrm{BT}}/(\varepsilon_{\mathrm{BT}}-\varepsilon_{\mathrm{NiD}}))$ (Fig. 3). Where $\varepsilon_{\mathrm{BT}}$ and $\varepsilon_{\mathrm{NiD}}$ represent the apparent extinction coefficient of uncomplexed BT and the true extinction coefficient of nickel(II)-BT chelate, respectively. The apparent extinction coefficient of uncomplexed BT, $\varepsilon_{\mathrm{BT}}$, is constant

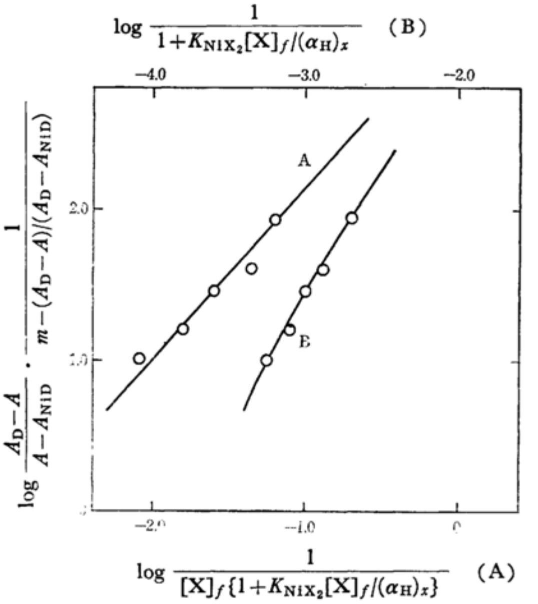

Fig. 2. The plot of $\log[\mathrm{X}]_f(1+K_{\mathrm{NiX_2}}[\mathrm{X}]_f/(\alpha_{\mathrm{H}})_x)$ against $\log\dfrac{A_{\mathrm{D}}-A}{A-A_{\mathrm{NiD}}}\cdot\dfrac{1}{m-\dfrac{A_{\mathrm{D}}-A}{A_{\mathrm{D}}-A_{\mathrm{NiD}}}}$.

μ=0.30, pH=9.54, λ=640 mμ
Initial concentration of BT=2.89×10^{-5} M
The concentration of uncomplexed NTA, $[\mathrm{X}]_f$, ranged from 10 mM to 50 mM.

Table 1. Equilibrium constants (μ=0.30)*

i) Stability constants of Ni(II)-NTA chelates
K_{NiX}⁴⁾$=10^{11.09}$ $K_{\mathrm{NiX_2}}$⁷⁾$=10^{4.47}$
ii) Dissociation constants of NTA⁵⁾
pK_1=1.86 pK_2=2.38 pK_3=9.54
iii) Dissociation constants of BT⁹⁾
pK_1=6.80 pK_2=11.31

* These values were calculated from the related dissociation constants and the stability constants in the solution of ionic strength 0.10 at 20°C and the activity constants of the ions calculated by means of Davis equation in the same way as was described previously.²⁾

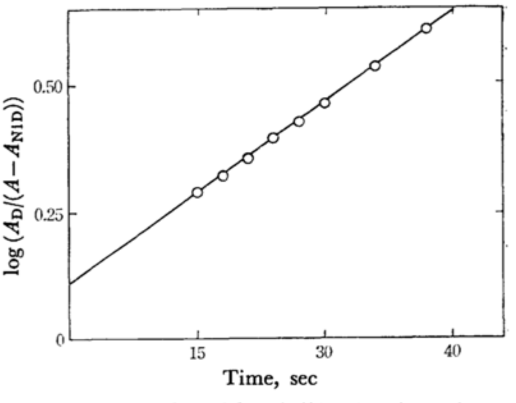

Fig. 3. The plot of $\log A_{\mathrm{D}}/(\mathrm{A}-\mathrm{A}_{\mathrm{NiD}})$ against t.
μ=0.30, pH=9.40, λ=630 mμ
Initial concentration of BT=2.00×10^{-5} M
The concentration of uncomplexed NTA=12.0 mM
The concentration of Ni(II)-NTA chelate=9.10 mM

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4) G. Schwarzenbach, G. Anderegg, W. Schneider and H. Senn, *Helv. Chim. Acta,* **38,** 1147 (1955).

5) G. Schwarzenbach and R. Gut, *ibid.,* **39,** 1589 (1956).

when the pH value of the solution is kept constant, because it can be thermodynamically equated as $(\varepsilon_{H_2D}[H^+]^2/k_1\cdot k_2+\varepsilon_{HD}\cdot[H^+]/k_2+\varepsilon_D)/(\alpha_H)_{BT}$. Therefore, in this study, ε_{BT} value observed at the pH, where the kinetic measurement was conducted, was used in the analysis of experimental data. Here, ε_{H_2D}, ε_{HD} and ε_D mean true molar extinction coefficients of singly deprotonated, doubly deprotonated and completely deprotonated BT anion respectively, and k's are dissociation constants of BT.[9] Strictly k_1 should refer to the dissociation of sulfonic acid, but Schwarzenbach's notation was followed here, k_1 and k_2 referring to the dissociation of the phenolic hydrogen atoms. Considering that the stability constants of Ni(II)-BT chelate is much greater than that of nickel(II)-NTA chelate, under the present experimental conditions where the concentration of free NTA (the sum of concentrations of free singly deprotonated, doubly deprotonated and completely deprotonated NTA anions and of free NTA) is comparable with that of nickel(II)-NTA chelate, the concentration of free BT (the sum of concentrations of free singly deprotonated, doubly deprotonated and completely deprotonated BT anion and of free BT) at equilibrium, $[BT]_e$, is negligibly small as compared with its initial concentration, $[BT]_0$, and the free BT concentration at t, [BT], at an early stage of the reaction. Therefore, the slope of the linear relation between $\log(A_D/(A-A_{NiD}))$ and t should correspond to the apparent rate constant, k^+, of the reaction (3) as was discussed in the substitution reaction of BT with cobalt(II)-EDTA chelate.[1]

The following facts were also found in the preliminary experiments where free NTA ranged from 10 mM to 40 mM and nickel(II)-NTA chelate, from 2.0 mM to 9.0 mM.

i) The slope of the linear relation between $\log(A_D/(A-A_{NiD}))$ and t was independent of the initial concentration of BT, $[BT]_0$, in solutions of a given pH, a given concentration of free NTA and a given total concentration of nickel(II)-NTA chelate (Table 2).

TABLE 2. DEPENDENCE OF THE SLOPE ON THE INITIAL CONCENTRATION OF BT

pH=9.25, μ=0.30
Concentration of uncomplexed NTA=27.0 mM
Total concentration of Ni(II)-NTA chelate=6.50 mM

Concentration of BT, 10^{-5} M	Slope, sec^{-1}
0.90	3.33×10^{-3}
1.50	3.47×10^{-3}
2.00	3.50×10^{-3}
3.00	3.40×10^{-3}

ii) In solutions of a given pH and given initial concentrations of BT and of uncomplexed NTA, the slope of the above linear relation was proportional to the total concentration of Ni(II)-NTA chelate, $[NiX]_t$ (Table 3).

TABLE 3. DEPENDENCE OF THE SLOPE ON THE TOTAL CONCENTRATION OF Ni(II)-NTA CHELATES

pH=9.40, μ=0.30
Initial concentration of BT=2.00×10^{-5} M
Concentration of uncomplexed NTA=12.0 mM

Concentration of Ni(II)-NTA chelate, mM	Concentration ratio	Slope, sec^{-1}	Slope ratio
2.60	1.00	3.33×10^{-3}	1.00
3.90	1.50	5.20×10^{-3}	1.56
6.50	2.50	8.66×10^{-3}	2.60
9.10	3.50	1.18×10^{-2}	3.53

iii) In solutions of a given pH, a given initial concentration of BT and a given total concentration of Ni(II)-NTA chelate, the slope of the linear relation was inversely proportional to $1+K_{NiX_2}\cdot[X]_f/(\alpha_H)_x$ value (Table 4).

TABLE 4. DEPENDENCE OF THE SLOPE ON THE CONCENTRATION OF UNCOMPLEXED NTA

pH=9.25, μ=0.30
Initial concentration of BT=2.00×10^{-5} M
Total concentration of Ni(II)-NTA chelate=6.50 mM

Concentration of uncomplexed NTA, mM	$1+\frac{K_{NiX_2}\cdot[X]_f}{(\alpha_H)_x}$ (A)	Slope sec^{-1}	$A\times$slope
12.0	121	8.00×10^{-3}	9.70×10^{-1}
17.0	171	5.73×10^{-3}	9.80×10^{-1}
27.0	271	3.50×10^{-3}	9.50×10^{-1}

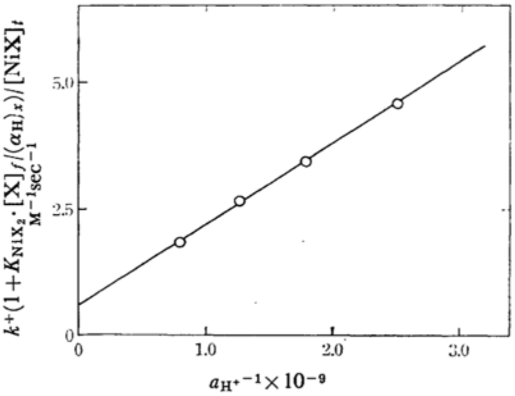
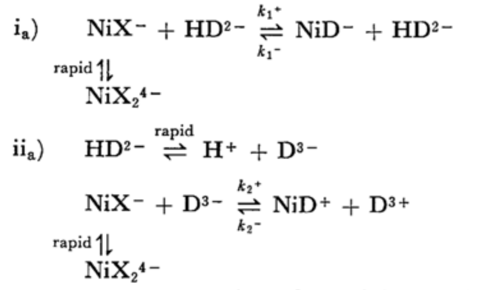


Fig. 4. Relation between $k^+(1+K_{NiX_2}\cdot[X]_f/(\alpha_H)_x)/[NiX]_t$ and the concentration of hydrogen ion.
μ=0.30
Initial concentration of BT=2.00×10^{-5} M
The concentration of uncomplexed NTA=12.0 mM
The concentration of Ni(II)-NTA chelate=6.50 mM

iv) In solutions of a given initial concentration of BT and given concentrations of free NTA and Ni(II)-NTA chelates, the slope of the linear relation was a linear function of the reciprocal of the hydrogen ion concentration and given by the Eq. (4) (Fig. 4).

$$\text{slope} = k_a + k_b/[\mathrm{H}^+] \qquad (4)$$

The nickel(II) ion can form chelates of 1-to-1 as well as 1-to-2 composition and the concentration of the former is given by $[\mathrm{NiX}]_t/(1+K_{\mathrm{NiX}_2}\cdot[\mathrm{X}]_f/(\alpha_{\mathrm{H}})_x)$. Thus, the above experimental results clearly suggest that the substitution reaction of BT and nickel(II)-NTA chelates has the following reaction mechanism.



$$\begin{array}{ll} \mathrm{i_a)} & \mathrm{NiX^-} + \mathrm{HD^{2-}} \underset{k_1^-}{\overset{k_1^+}{\rightleftharpoons}} \mathrm{NiD^-} + \mathrm{HD^{2-}} \\ & \text{rapid}\upharpoonleft\downharpoonright \\ & \mathrm{NiX_2{}^{4-}} \\ \mathrm{ii_a)} & \mathrm{HD^{2-}} \overset{\text{rapid}}{\rightleftharpoons} \mathrm{H^+} + \mathrm{D^{3-}} \\ & \mathrm{NiX^-} + \mathrm{D^{3-}} \underset{k_2^-}{\overset{k_2^+}{\rightleftharpoons}} \mathrm{NiD^+} + \mathrm{D^{3+}} \\ & \text{rapid}\upharpoonleft\downharpoonright \\ & \mathrm{NiX_2{}^{4-}} \end{array}$$

(rate-determining step)

The following relation can be derived, as was proposed for the substitution reaction of BT and Co(II)-EDTA chelate.1)

$$\text{slope} = (k_1{}^+ + k_2{}^+\cdot k_2{}^{9)}/[\mathrm{H}^+])\,\frac{[\mathrm{NiX}]_t}{1+\dfrac{K_{\mathrm{NiX}_2}\cdot[\mathrm{X}]_f}{(\alpha_{\mathrm{H}})_x}} \qquad (5)$$

From the linear relation between the slope $\times(1+K_{\mathrm{NiX}_2}\cdot[\mathrm{X}]_f/(\alpha_{\mathrm{H}})_x)/[\mathrm{NiX}]_t$ and $1/[\mathrm{H}^+]$ (Fig. 4), $k_1{}^+$ and $k_2{}^+$ were determined to be 5.8×10^1 $\mathrm{M}^{-1}\,\mathrm{sec}^{-1}$ and 3.27×10^4 $\mathrm{M}^{-1}\,\mathrm{sec}^{-1}$, respectively.

Similar results were also obtained in the experiments at 24.5°C and 30°C and given in Table 5 along with the results at 16°C. Linear relation was found between $\log k^+$ and $1/T$ for those two elementary reactions, which made it possible to calculate the heat and the entropy of activation. The results for $k_2{}^+$ are shown in Table 5. Values for the elementary reaction ($\mathrm{i_a}$) are considered less accurate as compared with the other data and not given here.

TABLE 5. RATE CONSTANTS, $k_2{}^+$, FOR BT REACTION WITH Ni(II)-NTA AT VARIOUS TEMPERATURES, AND HEAT OF ACTIVATION AND ENTROPY OF ACTIVATION FOR REACTION (iia)

Temperature °C	Rate constant $\mathrm{M}^{-1}\,\mathrm{sec}^{-1}$	$\Delta H^\neq$ kcal/mol	$\Delta S^\neq$ e. u.
16	3.27×10^4		
24.5	1.15×10^5	11.5	37.6
30	2.51×10^5		

During the course of the exchange reaction, BT is considered to hold its planar configuration. Therefore, less conformational freedom would be lost in the substitution reaction. On the basis of this fact, as far as the conformational freedom is concerned, the great gain in the conformational freedom in the leaving NTA or EDTA ion may contribute to the positive entropy of activation. This expectation was satisfied by the results listed in Table 5.

The Substitution Reaction of BT with Nickel(II)-EDTA Chelate. The substitution reaction of BT with Ni(II)-EDTA chelate was also studied in the presence of a large excess of free EDTA and its nickel(II) chelate ions over BT in the pH range 9.00—10.50 at 15°C. The reaction gave the linear relation between $\log(A_{\mathrm{D}}/(A-A_{\mathrm{NiD}}))$ and time, t, whose intercept was identical with $\log(\varepsilon_{\mathrm{BT}}/(\varepsilon_{\mathrm{BT}}-\varepsilon_{\mathrm{NiD}}))$ (Fig. 5). An analogous relation among $[\mathrm{BT}]_0$, $[\mathrm{BT}]$ and $[\mathrm{BT}]_e$ also holds for the present system, and this fact clearly indicates that the slope of the linear relation can exactly correspond to the apparent rate constant, k^+, of the pseudo first-order reaction (3).

In addition to the above fact, the following experimental facts were also found under the present experimental conditions (free EDTA ranged from

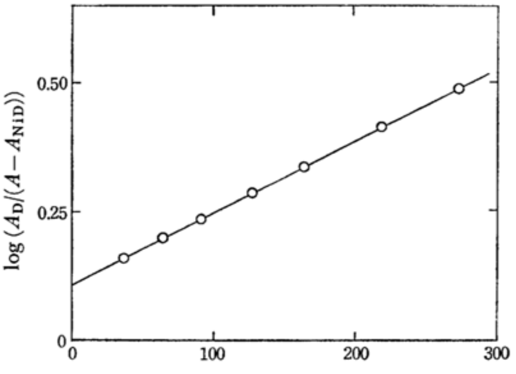


Fig. 5. The plot of $\log(A_{\mathrm{D}}/(A-A_{\mathrm{NiD}}))$ against t.
$\mu=0.30$, pH$=10.25$, $\lambda=630\,\mathrm{m}\mu$
Initial concentration of BT$=2.25\times10^{-5}$ M
The concentration of uncomplexed EDTA$=10.0$ mM
The concentration of Ni(II)-EDTA$=16.51$ mM

TABLE 6. DEPENDENCE OF THE SLOPE ON THE CONCENTRATION OF UNCOMPLEXED EDTA
pH$=10.0$, $\mu=0.30$
Initial concentration of BT$=2.25\times10^{-5}$ M
Concentration of Ni(II)-EDTA$=8.25_5$ mM

Concentration of uncomplexed EDTA, mM	Slope, sec^{-1}
10	3.20×10^{-4}
15	3.22×10^{-4}
25	3.18×10^{-4}

10 to 40 mM and Ni(II)-EDTA, from 8.0 mM to 25.0 mM).

i) The slope of the plot of $\log(A_D/(A-A_{\mathrm{NiD}}))$ against t was independent of the concentration of uncomplexed EDTA in solutions of a given pH and the given concentrations of BT, $[\mathrm{BT}]_0$, and nickel(II)-EDTA chelate (Table 6).

ii) The slope of the plot of $\log(A_D/(A-A_{\mathrm{NiD}}))$ against t was independent of the initial concentration of BT in solutions of a given pH and given concentrations of free EDTA and its nickel(II) chelate (Table 7).

TABLE 7. DEPENDENCE OF THE SLOPE ON THE INITIAL CONCENTRATION OF BT

pH=10.0, μ=0.30
Concentration of uncomplexed EDTA=10.0 mM
Concentration of Ni(II)-EDTA=8.25_5 mM

Concentration of BT, 10^{-5} M	Slope, sec^{-1}
1.61	3.18×10^{-4}
2.25	3.20×10^{-4}
3.21	3.15×10^{-4}

iii) The slope of the above linear relation was proportional to the concentration of nickel(II)-EDTA chelate, [NiY], in solutions of a given pH and the given concentrations of BT, $[\mathrm{BT}]_0$ and of free EDTA (Table 8).

TABLE 8. DEPENDENCE OF THE SLOPE ON THE CONCENTRATION OF Ni(II)-EDTA CHELATE

pH=10.25, μ=0.30
Concentration of uncomplexed EDTA=10.0 mM
Initial concentration of BT=2.25×10^{-5} M

Concentration of Ni(II)-EDTA, mM	Concentration ratio	Slope, sec^{-1}	Slope ratio
8.25_5	1.00	5.62×10^{-4}	1.00
16.51	2.00	1.12×10^{-3}	2.00
24.77	3.00	1.70×10^{-3}	3.03

iv) The slope for the linear relation was found to be a linear function of the reciprocal of the hydrogen ion concentration and given by Eq. (6) (Fig. 6).

$$\text{slope} = k_{\mathrm{i}} + k_{\mathrm{ii}}/[\mathrm{H^+}] \tag{6}$$

where k_{i} is almost zero.

Since Ni(II)-EDTA chelate behaves in an identical manner with Co(II)-EDTA chelate, it can be concluded that the substitution reaction of BT with Ni(II)-EDTA chelate proceeds mainly through the reaction path (ii$_b$), and the percentage of the contribution of the reaction path (i$_b$) is practically zero.

i$_b$) $\mathrm{HD^{2-} + NiY^{2-}} \underset{k_1^-}{\overset{k_1^+}{\rightleftharpoons}} \mathrm{NiD^- + HY^{3-}}$

ii$_b$) $\mathrm{HD^{2-}} \overset{\text{rapid}}{\rightleftharpoons} \mathrm{H^+ + D^{3-}}$

$\mathrm{D^{3-} + NiY^{2-}} \underset{k_2^-}{\overset{k_2^+}{\rightleftharpoons}} \mathrm{NiD^- + Y^{4-}}$
(rate-determining step)

where $\mathrm{NiY^{2-}}$, $\mathrm{HY^{3-}}$ and $\mathrm{Y^{4-}}$ mean Ni(II)-EDTA chelate, triply deprotonated EDTA anion and completely deprotonated EDTA anion, respectively.

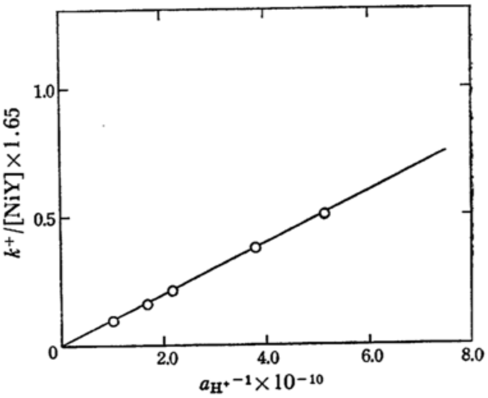


Fig. 6. Relation between $k^+/[\mathrm{NiY}]$ and the concentration of hydrogen ion.
μ=0.30
Initial concentration of BT=2.25×10^{-5} M
The concentration of uncomplexed EDTA= 10.0 mM
The concentration of Ni(II)-EDTA chelate= 8.25_5 mM

On these assumptions, the following relation can be obtained.

$$k^+ = \frac{k_2^+ \cdot k_2^{9)}}{[\mathrm{H^+}]} \cdot [\mathrm{NiY^{2-}}] \tag{7}$$

From the linear relationship between $k^+/[\mathrm{NiY}]$ and $1/[\mathrm{H^+}]$ (Fig. 6), k_2^+ value was determined to be 1.25 M^{-1} sec^{-1}.

The above reaction mechanism proposed for the substitution reactions of BT clearly involves the formation of mixed ligand intermediate complexes between BT and nickel(II) chelate of NTA or EDTA. By forming coordinate bonds with a nickel(II) ion prior to the complete dissociation to give $\mathrm{X^{3-}}$ or $\mathrm{Y^{4-}}$ from the nickel(II) ion, BT is considered to block the reformation of the nickel(II)-NTA or nickel(II)-EDTA bonds and to help the dissociation of NTA or EDTA anion. Thus, rate constants of the substitution reactions of metal(II)-NTA and EDTA chelates with BT are expected to be much greater than those of the dissociation of metal(II)-NTA and -EDTA chelates. A comparison of the rate constant of the dissociation reaction of cobalt(II)-EDTA chelate reported by Tanaka *et al.*[6] with that of the substitution reaction of BT

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[6] N. Tanaka, H. Osawa and M. Kamada, This Bulletin, **36**, 68 (1963).

with cobalt(II)-EDTA chelate[1] clearly confirms this explanation. Since the protonation of chelate is responsible to the rapid dissociation of metal chelate, the finding that $k_2{}^+$ value for the reaction of BT with nickel(II)-EDTA chelate is much greater than the rate constant for the dissociation of protonated nickel(II)-EDTA chelate, $NiHY^-$ [10],[*1] is also an evidence for the above expectation. As in the case of the exchange reaction of EDTA with nickel(II)-polyamine,[8] the protonation of the incoming ligand (Strictly, in the substitution reaction of BT, incompletely dissociation of BT, HD^{2-}) tends to slow the reaction ($k_2{}^+$ is much greater than $k_1{}^+$).

Generally, for the reaction mechanism involving the formation of mixed ligand intermdiate complexes, the reaction rate is expected to be sensitive to the steric effect. The kinetic studies of the substitution reaction of BT with cobalt(II) and nickel(II) chelates of other chelons (EDTA-OH, GEDTA, CyDTA and DTPA) are now in progress. The importance of the steric effect on the rate of the substitution reaction of BT and the assignment of the reaction mechanism will be discussed in some detail in the subsequent paper.

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7) G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, **31**, 331 (1948).

8) D. B. Rorabacher and D. W. Margerum, *Inorg. Chem.*, **3**, 382 (1963).

9) G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, **31**, 678 (1948).

10) N. Tanaka and Y. Sakuma, This Bulletin, **32**, 578 (1959).

[*1] The rate constant was calculated from the reverse rate constant and appropriate stability constant to be $2.8\times10^{-6}\ \text{M}^{-1}\,\text{sec}^{-1}$.