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The Kinetics of Substitution Reactions Involving Metal Complexes. XI. The Reactions between Nickel(II) Ions and Copper(II)- and Cobalt(II)-Nitrilotriacetate Complexes

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The kinetics of the substitution reaction of nickel(II) and copper(II)-nitrilotriacetate complexes and that of nickel(II) and cobalt(II)-nitrilotriacetate complexes in acetate buffer solutions have been studied by a similar method in principle to that reported previously. The reactions were treated as to proceed through both hydrated metal ions and monoacetato complexes. The rate constants of eight reaction paths, of which four involve hydrated nickel(II) ions and the others, monoacetatonickel(II) complexes, were determined at ionic strength 0.2 at 0°C. The backward reactions were found to proceed also through eight reaction paths in which the dissociation of Ni(II)-nitrilotriacetate complexes is rate-determining. The values of rate constants obtained for the forward and the backward reactions indicate that all the reactions proceeding through monoacetatonickel(II) complexes are faster than the corresponding reactions through hydrated nickel(II) ions.

A number of previous studies on the substitution reactions involving metal-ethylenediaminetetraacetate (EDTA) complexes indicated that the reaction rate decreased with increasing concentrations of acetate ions.[1-8] However, Tanaka and Sakuma[9] found, in their studies on the complex-forming reaction between nickel(II) and EDTA, that the reactions proceeding through acetatonickel(II) complexes are faster than the corresponding reactions through hydrated nickel(II) ions. Recently, Bydalek,[10] who studied the effect of acetate ions on the substitution reaction between nickel(II) and copper(II)-EDTA complexes, obtained a similar result to that reported by Tanaka and Sakuma.[9] It seemed to be interesting that the effect of acetate ions on the reactions involving nickel(II) ions is opposite to that on the reactions involving some other metals.

In the present study, substitution reactions between nickel(II) and copper(II)- and cobalt(II)-nitrilotriacetate (NAT) complexes have been investigated in acetate buffer solutions at ionic strength 0.2 at 0°C, and the rate constants of the paths in which the reactions proceed through hydrated nickel(II) ions and monoacetatonickel(II) complexes have been determined and compared with those of the corresponding reactions of other metal ions.

Experimental

The preparation and the standardization of the solutions of nickel(II) nitrate,[11] cobalt(II) nitrate,[12] copper(II) nitrate[13] and nitrilotriacetate[11] were made by the same procedures as described in the previous papers cited. All other chemicals used were of the analytical reagent grade.

The rates of the forward and the backward reactions between nickel(II) and copper(II)-NTA complexes were determined by the measurement of the increase and the decrease with time, respectively, of the polarographic diffusion current of copper(II) ions in acetate buffer solutions. In the case of the forward and the backward reaction between nickel(II) and cobalt(II)-NTA complexes, the diffusion current of nickel(II) ions was measured with time in acetate buffer solutions.

Current-time curves were obtained with a Yanagimoto Graphrecorder with an applying potentiometer equipped. The dropping mercury electrode had an m value of 1.23 mg/sec and a drop time t_d of 5.3 sec in an air-free solution containing 0.1 M potassium nitrate and 0.1 M acetate buffer at 25°C at -0.5 V *vs.* SCE.

Measurements were made at 0°C in acetate buffer

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1) H. Ackermann and G. Schwarzenbach, *Helv. Chim. Acta*, **35**, 485 (1952).
2) K. Kato, This Bulletin, **33**, 600 (1960).
3) N. Tanaka and K. Kato, *ibid.*, **32**, 1376 (1959).
4) N. Tanaka, H. Osawa and M. Kamada, *ibid.*, **36**, 67 (1963).
5) N. Tanaka and M. Kamada, *ibid.*, **53**, 1596 (1962).
6) N. Tanaka and K. Kato, *ibid.*, **33**, 1236 (1960).
7) N. Tanaka, H. Osawa and M. Kamada, *ibid.*, **36**, 530 (1963).
8) N. Tanaka and H. Ogino, *ibid.*, **36**, 175 (1963).
9) N. Tanaka and Y. Sakuma, *ibid.*, **32**, 578 (1959).
10) T. J. Bydalek, *Inorg. Chem.*, **4**, 232 (1965).
11) N. Tanaka and K. Kato, This Bulletin, **32**, 516 (1959).
12) N. Tanaka and H. Ogino, *ibid.*, **38**, 439 (1965).
13) N. Tanaka, K. Kato and R. Tamamushi, *ibid.*, **31**, 283 (1958).

TABLE 1. CHARACTERISTICS OF THE SUBSTITUTION REACTION BETWEEN Ni(II) AND M(II)-NTA COMPLEXES

Forward reaction

Series No.	$[H^+]$	$[Ni^{2+}]_{0,app}$	$[MX^-]_0$	$[M^{2+}]_{0,app}$	$[OAc^-]$	Apparent initial rate ($v^+_{0,app}$)
1	varied	const.	const.	const.	const.	linear to $[H^+]$
2	const.	varied	const.	const.	const.	proportional to $[Ni^{2+}]_{0,app}$
3	const.	const.	varied	const.	const.	proportional to $[MX^-]_0$
4	const.	const.	const.	varied	const.	linear to $1/[M^{2+}]_{0,app}$
5	const.	const.	const.	const.	varied	increase with $[OAc^-]$

Backward reaction

Series No.	$[H^+]$	$[M^{2+}]_{0,app}$	$[NiX^-]_0$	$[Ni^{2+}]_{0,app}$	$[OAc^-]$	Apparent initial rate ($v^-_{0,app}$)
6	varied	const.	const.	—	const.	linear to $[H^+]$
7	const.	varied	const.	—	const.	linear to $[M^{2+}]_{0,app}$
8	const.	const.	varied	—	const.	proportional to $[NiX^-]_0$
9	const.	const.	const.	varied	const.	independent of $[Ni^{2+}]_{0,app}$
10	const.	const.	const.	—	varied	increase with $[OAc^-]$

solutions of ionic strength 0.2, being adjusted with potassium nitrate. Gelatin was added as a maximum suppressor by 0.01% in concentration in the case of the measurement of the copper wave, while polyoxyethylenelauryl ether (LEO) was added by 2×10^{-6} M in concentration in the case of the measurement of the nickel wave. The pH of the solution was measured after the polarographic measurement with a Hitachi-Horiba Model M-4 pH meter with a glass electrode.

Results

In a solution containing acetate ions up to 0.2 M in concentration, copper(II) forms mono- and diacetato complexes,[14] whereas nickel(II)[11] and cobalt(II)[15] form only monoacetato complexes. If copper(II) and cobalt(II) are represented with M(II), the overall substitution reaction between nickel(II) and copper(II)-NTA complexes and that between nickel(II) and cobalt(II)-NTA complexes are expressed by

$$\left\{\begin{matrix} Ni^{2+} \\ \upharpoonleft\downharpoonright \\ NiOAc^{+} \end{matrix}\right\} + MX^- \rightleftharpoons$$

$$NiX^- + \left\{\begin{matrix} M^{2+} \\ \upharpoonleft\downharpoonright \\ M(OAc)_n^{(2-n)+} \end{matrix}\right\} \qquad (1)$$

where X^{3-} means a tervalent NTA anion.

The concentrations of simple copper(II) and simple nickel(II) ions that can be determined polarographically are apparent concentrations, *i. e.*, $[Cu^{2+}]_{app}$ and $[Ni^{2+}]_{app}$ respectively, which are given by

$$[Cu^{2+}]_{app} = \sum_{n=0}^{2} [Cu(OAc)_n^{(2-n)+}] \qquad (2)$$

and

$$[Ni^{2+}]_{app} = \sum_{n=0}^{1} [Ni(OAc)_n^{(2-n)+}] \qquad (2')$$

Under the present experimental conditions, the rate of the substitution reaction between Ni(II) and M(II)-NTA complexes was so slow that the apparent initial rates of the reactions, $\Delta[Cu^{2+}]_{0,app}/\Delta t$ and $-\Delta[Ni^{2+}]_{0,app}/\Delta t$ for the forward reactions and $-\Delta[Cu^{2+}]_{0,app}/\Delta t$ and $\Delta[Ni^{2+}]_{0,app}/\Delta t$ for the backward reactions, were able to be determined accurately, where the subscript 0 means the initial state.

In Table 1 are given the characteristics of the substitution reactions between Ni(II) and M(II)-NTA complexes which were obtained from the preliminary measurements of the apparent initial rates of the forward and the backward reactions under varied conditions.

From these characteristics the reaction mechanism of the substitution reaction between Ni(II) and M(II)-NTA complexes was considered as follows:

$$\text{(i)} \quad Ni^{2+} + MX^- \underset{k_{Ih}^-}{\overset{k_{Ih}^+}{\rightleftharpoons}} M^{2+} + NiX^- \qquad (3)$$

$$NiOAc^+ + MX^- \underset{k_{Ic}^-}{\overset{k_{Ic}^+}{\rightleftharpoons}}$$

$$MOAc^+ + NiX^- \qquad (3')$$

$$\text{(ii)} \quad MX^- + H^+ \rightleftharpoons MHX \qquad (4)$$

$$Ni^{2+} + MHX \underset{k_{IIh}^-}{\overset{k_{IIh}^+}{\rightleftharpoons}} M^{2+} + NiHX \qquad (5)$$

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[14] N. Tanaka and K. Kato, *ibid.*, **33**, 417 (1960).

[15] N. Tanaka, M. Kamada, H. Osawa and G. Sato, *ibid.*, **33**, 1412 (1960).

$$\mathrm{NiOAc^+ + MHX \underset{k^-_{IIc}}{\overset{k^+_{IIc}}{\rightleftharpoons}} MOAc^+ + NiHX} \tag{5'}$$

$$\mathrm{NiX^- + H^+ \rightleftharpoons NiHX} \tag{6}$$

$$\text{(iii)}\quad \mathrm{MX^- \rightleftharpoons \left\{\begin{matrix} M^{2+} \\ \upharpoonleft\downharpoonright \\ M(OAc)_n{}^{(2-n)+} \end{matrix}\right\} + X^{3-}} \tag{7}$$

$$\mathrm{Ni^{2+} + X^{3-} \underset{k^-_{IIIh}}{\overset{k^+_{IIIh}}{\rightleftharpoons}} NiX^-} \tag{8}$$

$$\mathrm{NiOAc^+ + X^{3-} \underset{k^-_{IIIc}}{\overset{k^+_{IIIc}}{\rightleftharpoons}} NiX^- + OAc^-} \tag{8'}$$

$$\text{(iv)}\quad \mathrm{MHX \rightleftharpoons \left\{\begin{matrix} M^{2+} \\ \upharpoonleft\downharpoonright \\ M(OAc)_n{}^{(2-n)+} \end{matrix}\right\} + HX^{2-}} \tag{9}$$

$$\mathrm{Ni^{2+} + HX^{2-} \underset{k^-_{IVh}}{\overset{k^+_{IVh}}{\rightleftharpoons}} NiHX} \tag{10}$$

$$\mathrm{NiOAc^+ + HX^{2-} \underset{k^-_{IVc}}{\overset{k^+_{IVc}}{\rightleftharpoons}} NiHX + OAc^-} \tag{10'}$$

In the present treatment, it was assumed that the equilibria between hydrated ions and acetato complexes were maintained while the substitution reactions took place. Then, Eqs. (11) and (12) were obtained for the rates of the forward and the backward reactions, respectively.

$$v^+{}_{0,\mathrm{app}} = \frac{[\mathrm{MX^-}]_0[\mathrm{Ni^{2+}}]_{0,\mathrm{app}}}{1 + \beta_{\mathrm{NiOAc}}[\mathrm{OAc^-}]}\Bigg\{k^+_{Ih} + k^+_{1c}[\mathrm{OAc^-}] + k^+_{2h}[\mathrm{H^+}] + k^+_{2c}[\mathrm{OAc^-}][\mathrm{H^+}] + (k^+_{3h} + k^+_{3c}[\mathrm{OAc^-}] + k^+_{4h}[\mathrm{H^+}] + k^+_{4c}[\mathrm{OAc^-}][\mathrm{H^+}])\frac{\sum_0^n \beta_{\mathrm{M(OAc)}_n}[\mathrm{OAc^-}]^n}{[\mathrm{M^{2+}}]_{0,\mathrm{app}}}\Bigg\} \tag{11}$$

where

$$k^+_{1c} = k^+_{Ic}\beta_{\mathrm{NiOAc}}, \quad k^+_{2h} = k^+_{IIh}K^{\mathrm{H}}_{\mathrm{MHX}},$$
$$k^+_{2c} = k^+_{IIc}\beta_{\mathrm{NiOAc}}K^{\mathrm{H}}_{\mathrm{MHX}}, \quad k^+_{3h} = k^+_{IIIh}/K_{\mathrm{MX}},$$
$$k^+_{3c} = k^+_{IIIc}\beta_{\mathrm{NiOAc}}/K_{\mathrm{MX}}, \quad k^+_{4h} = k^+_{IVh}/(K_{\mathrm{MX}}K_{\mathrm{HX}}),$$
$$k^+_{4c} = k^+_{IVc}\beta_{\mathrm{NiOAc}}/(K_{\mathrm{MX}}K_{\mathrm{HX}}) \tag{11'}$$

$$v^-{}_{0,\mathrm{app}} = [\mathrm{NiX^-}]_0\Bigg\{(k^-_{Ih} + k^-_{1c}[\mathrm{OAc^-}] + k^-_{2h}[\mathrm{H^+}] + k^-_{2c}[\mathrm{H^+}][\mathrm{OAc^-}])\frac{[\mathrm{M^{2+}}]_{0,\mathrm{app}}}{\sum_0^n \beta_{\mathrm{M(OAc)}_n}[\mathrm{OAc^-}]^n} + k^-_{IIIh} + k^-_{IIIc}[\mathrm{OAc^-}] + k^-_{4h}[\mathrm{H^+}] + k^-_{4c}[\mathrm{OAc^-}][\mathrm{H^+}]\Bigg\} \tag{12}$$

where

$$k^-_{1c} = k^-_{Ic}\beta_{\mathrm{MOAc}}, \quad k^-_{2h} = k^-_{IIh}K^{\mathrm{H}}_{\mathrm{NiHX}},$$
$$k^-_{2c} = k^-_{IIc}K^{\mathrm{H}}_{\mathrm{NiHX}}\beta_{\mathrm{MOAc}}, \quad k^-_{4h} = k^-_{IVh}K^{\mathrm{H}}_{\mathrm{NiHX}},$$
$$k^-_{4c} = k^-_{IVc}K^{\mathrm{H}}_{\mathrm{NiHX}} \tag{12'}$$

In these equations, the initial concentrations, $[\mathrm{Ni^{2+}}]_{0,\mathrm{app}}$, $[\mathrm{M^{2+}}]_{0,\mathrm{app}}$, $[\mathrm{NiX^-}]_0$, and $[\mathrm{MX^-}]_0$ are substituted for $[\mathrm{Ni^{2+}}]_{\mathrm{app}}$, $[\mathrm{M^{2+}}]_{\mathrm{app}}$, $[\mathrm{NiX^-}]$ and $[\mathrm{MX^-}]$, respectively. The changes of their concentrations during the period of the measurement of the initial rates of the reactions were considered to be negligibly small under the experimental conditions.

Equation (11) indicates that, if the values of $v^+{}_{0,\mathrm{app}}/([\mathrm{Ni^{2+}}]_{0,\mathrm{app}}[\mathrm{MX^-}]_0)$ are plotted against $1/[\mathrm{M^{2+}}]_{0,\mathrm{app}}$ under the conditions at which all quantities but $[\mathrm{M^{2+}}]_{0,\mathrm{app}}$ are kept constant, a straight line should be obtained with an intercept at $1/[\mathrm{M^{2+}}]_{0,\mathrm{app}}=0$ given by

$$\frac{1}{1 + \beta_{\mathrm{NiOAc}}[\mathrm{OAc^-}]}(k^+_{Ih} + k^+_{1c}[\mathrm{OAc^-}] + k^+_{2h}[\mathrm{H^+}] + k^+_{2c}[\mathrm{OAc^-}][\mathrm{H^+}]) \tag{13}$$

and a slope given by

$$\frac{\sum_0^n \beta_{\mathrm{M(OAc)}_n}[\mathrm{OAc^-}]^n}{1 + \beta_{\mathrm{NiOAc}}[\mathrm{OAc^-}]}(k^+_{3h} + k^+_{3c}[\mathrm{OAc^-}] + k^+_{4h}[\mathrm{H^+}] + k^+_{4c}[\mathrm{OAc^-}][\mathrm{H^+}]) \tag{14}$$

Therefore, if the values of the intercept and the slope obtained at varied concentrations of hydrogen ions and acetate ions are plotted against the hydrogen ion and the acetate ion concentrations, the values of the rate constants in Eq. (11) can be determined.

The same is applied for the backward reactions. According to Eq. (12) the plots of $v^-{}_{0,\mathrm{app}}/[\mathrm{NiX^-}]_{0,\mathrm{app}}$ against $[\mathrm{M^{2+}}]_{0,\mathrm{app}}$ give a straight line with an intercept at $[\mathrm{M^{2+}}]_{0,\mathrm{app}}=0$ and a slope expressed by

$$k^-_{IIIh} + k^-_{IIIc}[\mathrm{OAc^-}] + k^-_{4h}[\mathrm{H^+}] + k^-_{4c}[\mathrm{OAc^-}][\mathrm{H^+}] \tag{15}$$

and

$$\frac{1}{\sum_0^n \beta_{\mathrm{M(OAc)}_n}[\mathrm{OAc^-}]^n}(k^-_{Ih} + k^-_{1c}[\mathrm{OAc^-}] + k^-_{2h}[\mathrm{H^+}] + k^-_{2c}[\mathrm{OAc^-}][\mathrm{H^+}]) \tag{16}$$

respectively. The rate constants in Eq. (12) can be determined from the values of intercepts and slopes obtained at varied concentrations of hydrogen ions and acetate ions.

Determination of the Rate Constants of the Forward Reactions. The apparent initial rates of the forward reaction of the substitution reaction with Cu(II)-NTA complexes, $\Delta[Cu^{2+}]_{0,app}/\Delta t$, were determined under the conditions given by series No. 4 in Table 1 but two different concentrations of acetate ions. The values of $v^+{}_{0,app}/([CuX^-]_0[Ni^{2+}]_{0,app})$ were plotted against $1/[Cu^{2+}]_{0,app}$ according to Eq. (11), in which $\Delta[Cu^{2+}]_{0,app}/\Delta t$ was substituted for $v^+{}_{0,app}$ and Cu for M. (See Fig. 1). The intercepts at $1/[Cu^{2+}]_{0,app}=0$ and the slopes of the plots correspond to Eqs. (13) and (14), respectively, which were plotted against the hydrogen ion concentration according to Eqs. (13) and (14), respectively. These plots gave straight lines as are shown in Figs. 2 and 3, from which the values of the rate

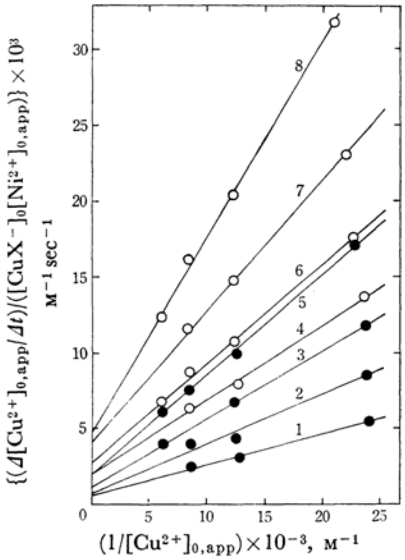

Fig. 1. $(\Delta[Cu^{2+}]_{0,app}/\Delta t)/([CuX^-]_0[Ni^{2+}]_{0,app})$ as a function of the reciprocal of $[Cu^{2+}]_{0,app}$ in acetate buffer - potassium nitrate solutions of ionic strength 0.2 at 0°C. Initial concentrations are $[CuX^-]_0=2.0\times10^{-4}$ M and $[Ni^{2+}]_{0,app}=9.90\times10^{-3}$ M. The pH values of the solutions are (1) pH 5.43, (2 and 6) pH 5.24, (3 and 7) pH 5.04, (4) pH 5.51 and (5 and 8) pH 4.82. Concentrations of acetate ions are 0.05 M for ● and 0.10 M for ○.

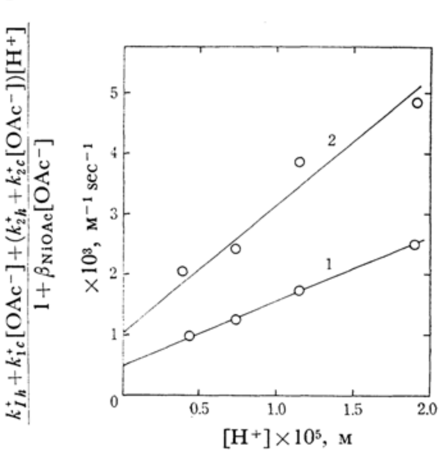

Fig. 2. Eq. (13) as a function of the hydrogen ion concentration. The conditions are the same as for Fig. 1. Concentrations of acetate ions are 0.05 M for curve 1 and 0.10 M for curve 2.

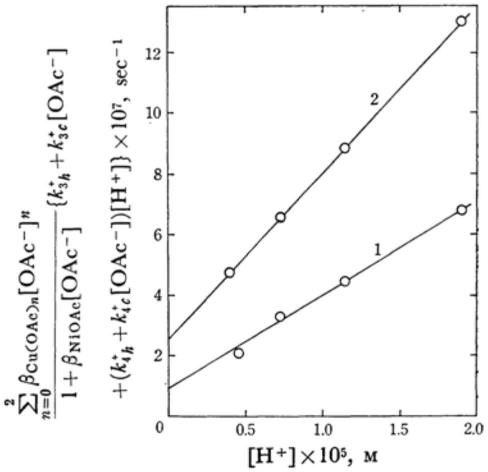

Fig. 3. Eq. (14) as a function of the hydrogen ion concentration. The conditions are the same as for Fig. 1. Concentrations of acetate ions are 0.05 M for curve 1 and 0.10 M for curve 2.

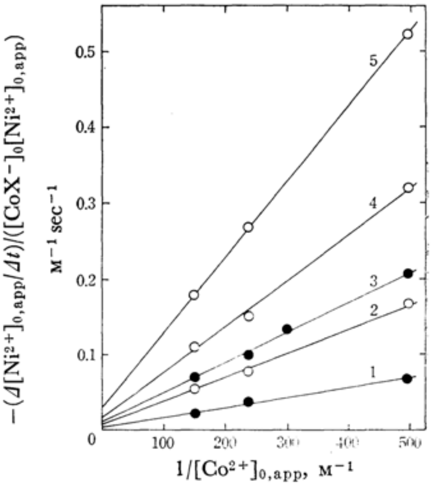

Fig. 4. $-(\Delta[Ni^{2+}]_{0,app}/\Delta t)/([CoX^-]_0[Ni^{2+}]_{0,app})$ as a functions of the reciprocal of $[Co^{2+}]_{0,app}$ in acetate buffer - potassium nitrate solutions of ionic strength 0.2 at 0°C. Initial concentrations are $[CoX^-]_0=4.35\times10^{-3}$ M and $[Ni^{2+}]_{0,app}=1.98\times10^{-4}$ M. The pH values of the solutions are (1 and 2) pH 5.17, (4) pH 4.80 and (3 and 5) pH 4.52. Concentrations of acetate ions are 0.05 M for ● and 0.20 M for ○.

TABLE 2. RATE CONSTANTS IN EQ. (11) OBTAINED EOR THE SUBSTITUTION REACTIONS AT IONIC STRENGTH 0.2 AT 0°C

Reaction system	Rate constant*							
	k_{Ih}^{+}	k_{1c}^{+}	k_{2h}^{+}	k_{2c}^{+}	k_{3h}^{+}	k_{3c}^{+}	k_{4h}^{+}	k_{4c}^{+}
Ni^{2+} - CuX^-	$\sim 2\times10^{-4}$	$\sim 1\times10^{-2}$	6×10	2×10^{3}	1.6×10^{-8}	4.8×10^{-7}	1×10^{-2}	$4._7\times10^{-2}$
Ni^{2+} - CoX^-	$\sim 1\times10^{-3}$	$\sim 1\times10^{-2}$	$8._3\times10$	$4._6\times10^{3}$	1.5×10^{-5}	6.9×10^{-4}	5.0	78.4

* Units of rate constants: sec^{-1} for k_{3h}^{+}; $l\,mol^{-1}\,sec^{-1}$ for k_{Ih}^{+}, k_{3c}^{+} and k_{4h}^{+}; $l^2\,mol^{-2}\,sec^{-1}$ for k_{1c}^{+}, k_{2h}^{+} and k_{4c}^{+}; $l^3\,mol^{-3}\,sec^{-1}$ for k_{2c}^{+}.

TABLE 3. RATE CONSTANTS FOR FORWARD REACTIONS OF REACTIONS (3), (3′), (5), (5′), (8), (8′), (10) AND (10′) OBTAINED AT IONIC STRENGTH 0.2 AT 0°C

Reaction system	Rate constant, $l\,mol^{-1}\,sec^{-1}$							
	k_{Ih}^{+}	k_{Ic}^{+}	k_{IIh}^{+}	k_{IIc}^{+}	k_{IIIh}^{+}	k_{IIIc}^{+}	k_{IVh}^{+}	k_{IVc}^{+}
Ni^{2+} - CuX^-	$\sim 2\times10^{-4}$	$\sim 4\times10^{-3}$	2×10^{-2}	2×10^{-1}	$5._6\times10^{4}$	$7._1\times10^{5}$	4	8
Ni^{2+} - CoX^-	$\sim 1\times10^{-3}$	$\sim 5\times10^{-3}$	$2._8\times10^{-2}$	$6._4\times10^{-1}$	$8._7\times10^{4}$	$1._7\times10^{6}$	4	24

constants in Eq. (11) were determined (Table 2). The rate constants for the reactions (3), (3′), (5), (5′), (8), (8′), (10) and (10′) were calculated with the aid of the relations given in Eqs (11′), which are given in Table 3.

The same treatment was applied for the substitution reactions between Ni(II) and Co(II)-NTA complexes. The values of the apparent initial rate $v^{+}_{0,app}$ divided by $[CoX^-]_0[Ni^{2+}]_{0,app}$ which was measured as $-\Delta[Ni^{2+}]_{0,app}/\Delta t$, were plotted against $1/[Co^{2+}]_{0,app}$ (Fig. 4). The straight lines in Fig. 4 indicate clearly that Eq. (11) holds also in the case of the substitution reaction between Ni(II) and Co(II)-NTA complexes. From the intercepts and the slopes the rate constants in Eq. (11) and those for the rate-determining steps for various paths were claculated by the same procedure as in the case of the reactions of Ni(II) and Cu(II)-NTA complexes. The values of the rate constant obtained are also given in Tables 2 and 3.

The formation constants, $\beta_{M(OAc)n}$ and K_{MX}, and the equilibrium constants, K_{MHX}^{H} and K_{HX}, which were used in this calculation are given in Table 4. All the values but K_{HX} were determined by the polarographic method at ionic strength 0.2 at 0°C. The thermodynamic constant K_{HX} which was determined by Hughes and Martell[16] at 0°C was used after correction for ionic strength with the aid of the extended Debye-Hückel equation.

TABLE 4. FORMATION AND EQUILIBRIUM CONSTANTS AT IONIC STRENGTH 0.2 AT 0°C*

$\log K_{CoX}$	9.8	β_{NiOAc}	2.4
$\log K_{NiX}$	11.1_8	β_{CoOAc}	2.7
$\log K_{CuX}$	12.5_4	β_{CuOAc}	33
$\log K_{CoHX}^{H}$	$3._5$	$\beta_{Cu(OAc)_2}$	50
$\log K_{NiHX}^{H}$	3.4_8	pK_{HX}[16]	9.9_4
$\log K_{CuHX}^{H}$	$3._5$		

* Details will be published elswhere.

Determination of the Rate Constants of the Backward Reactions. The apparent intial rates of the backward reaction $(v^{-}_{0,app})$ were

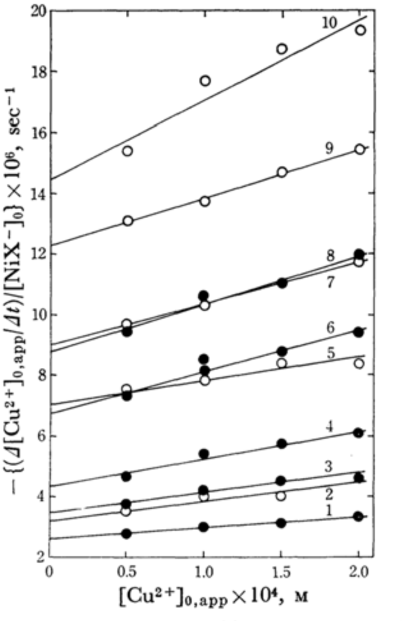

Fig. 5. $-(\Delta[Cu^{2+}]_{0,app}/\Delta t)/[NiX^-]_0$ as a function of $[Cu^{2+}]_{0,app}$ in acetate buffer - potassium nitrate solutions of ionic strength 0.2 at 0°C. Initial concentrations are $[Ni^{2+}]_{0,app}=1.47\times10^{-3}$ M and $[NiX^-]_0=3.48\times10^{-3}$ M. The pH values of the solutions are (1) pH 5.65, (2) pH 5.70, (3) pH 5.40, (4) pH 5.24, (5) pH 5.28, (6 and 9) pH 4.98, (7) pH 5.13 and (8 and 10) pH 4.88. Concentrations of acetate ions are 0.05 M for ● and 0.10 M for ○.

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16) V. L. Hughes and A. E. Martell, *J. Am. Chem. Soc.*, **78**, 1319 (1956).

measured for the substitution reactions of Ni(II)-NTA complexes with Cu(II) and those with Co(II). The plots of $v^{-}_{0,\mathrm{app}}/[\mathrm{NiX}^-]_0$ *versus* $[\mathrm{Cu}^{2+}]_{0,\mathrm{app}}$ for the substitution reaction between Ni(II) and Cu(II)-NTA complexes and those of $v^{-}_{0,\mathrm{app}}/[\mathrm{NiX}^-]_0$ *versus* $[\mathrm{Co}^{2+}]_{0,\mathrm{app}}$ for the substitution reaction between Ni(II) and Co(II)-NTA are given in Figs. 5 and 6. The straight lines of those plots indicate that the reaction mechanisms expressed with Eqs. (3) to (10′) operate also in the backward reactions. The intercepts at $[\mathrm{Cu}^{2+}]_{0,\mathrm{app}}$ or $[\mathrm{Co}^{2+}]_{0,\mathrm{app}}=0$ and the slopes of those plots are treated according to Eqs. (15) and (16), respectively. Examples are given in Figs. 7 and 8 for the substitution reactions involving Cu^{2+} ions.

The rate constants in Eq. (12) were obtained from the plots, and the rate constants of the backward reactions of reactions (3), (3′), (5), (5′), (8), (8′), (10) and (10′) were calculated with the aid of the relations in Eqs. (12′) and are given in Tables 5 and 6. Various constants given in Table 4 were used also in this calculation.

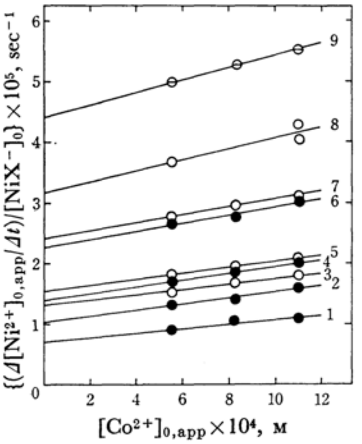

Fig. 6. $(\Delta[\mathrm{Ni}^{2+}]_{0,\mathrm{app}}/\Delta t)/[\mathrm{NiX}^-]_0$ as a function of $[\mathrm{Co}^{2+}]_{0,\mathrm{app}}$ in acetate buffer - potassium nitrate solutions of ionic strength 0.2 at 0°C. Initial concentrations are $[\mathrm{Ni}^{2+}]_{0,\mathrm{app}}=3.1\times10^{-5}$ M and $[\mathrm{NiX}^-]_0=9.7_0\times10^{-4}$ M. The pH values of the solutions are (1 and 3) pH 4.87, (2 and 5) pH 4.75, (4 and 7) pH 4.51 and (6, 8 and 9) pH 4.37. Concentrations of acetate ions are 0.05 M for ●, 0.10 M for ○ and 0.15 M for ⊖.

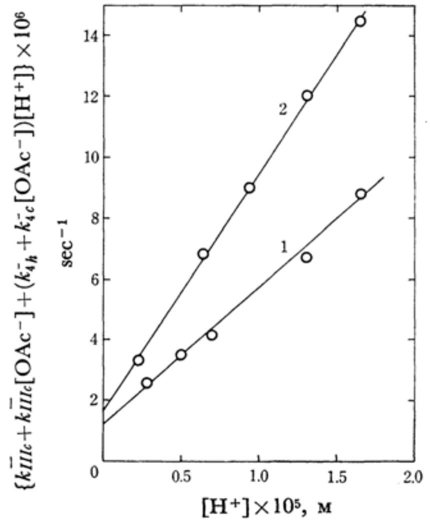

Fig. 7. Eq. (15) as function of the hydrogen ion concentration. The conditions are the same as for Fig. 5. Concentrations of acetate ions are 0.05 M for curve 1 and 0.10 M for curve 2.

TABLE 5. RATE CONSTANTS IN EQ. (12) OBTAINED FOR THE SUBSTITUTION REACTIONS AT IONIC STRENGTH 0.2 AT 0°C

Reaction system	Rate constant*							
	k^{-}_{Ih}	k^{-}_{1c}	k^{-}_{2h}	k^{-}_{2c}	k^{-}_{IIIh}	k^{-}_{IIIc}	k^{-}_{4h}	k^{-}_{4c}
Cu^{2+} - NiX^-	$\sim2\times10^{-3}$	$\sim1\times10^{-2}$	$\sim2\times10^{3}$	$\sim5\times10^{4}$	$8._0\times10^{-7}$	$8._8\times10^{-6}$	2.5×10^{-1}	6.0
Co^{2+} - NiX^-	$\sim8\times10^{-4}$	$\sim2\times10^{-3}$	$\sim6\times10$	$\sim8\times10^{2}$	1×10^{-6}	1×10^{-5}	2.1×10^{-2}	4.0

* Units of rate constants: sec^{-1} for k^{-}_{IIIh}; l mol^{-1} sec^{-1} for k^{-}_{Ih}, k^{-}_{IIIc} and k^{-}_{4h}; l^2 mol^{-2} sec^{-1} for k^{-}_{1c}, k^{-}_{2h} and k^{-}_{4c}; l^3 mol^{-3} sec^{-1} for k^{-}_{2c}.

TABLE 6. RATE CONSTANTS FOR BACKWARD REACTIONS OF REACTIONS (3), (3′), (5), (5′), (8), (8′), (10) AND (10′) AT IONIC STRENGTH 0.2 AT 0°C

Reaction system	Rate constant*							
	k^{-}_{Ih}	k^{-}_{Ic}	k^{-}_{IIh}	k^{-}_{IIc}	k^{-}_{IIIh}	k^{-}_{IIIc}	k^{-}_{IVh}	k^{-}_{IVc}
Cu^{2+} - NiX^-	$\sim2\times10^{-3}$	$\sim4\times10^{-4}$	~1	$\sim5\times10^{-1}$	$8._0\times10^{-7}$	$8._8\times10^{-6}$	$8._4\times10^{-5}$	2.0×10^{-3}
Co^{2+} - NiX^-	$\sim8\times10^{-4}$	$\sim7\times10^{-4}$	$\sim2\times10^{-2}$	$\sim1\times10^{-1}$	1×10^{-6}	1×10^{-5}	7.0×10^{-5}	1.3×10^{-3}

* Units of rate constants: sec^{-1} for k^{-}_{IIIh} and k^{-}_{IVh}; l mol^{-1} sec^{-1} for k^{-}_{Ih}, k^{-}_{Ic}, k^{-}_{IIh}, k^{-}_{IIc}, k^{-}_{IIIc} and k^{-}_{IVc}.

TABLE 7. RATE CONSTANTS OF SUBSTITUTION AND COMPLEX-FORMING REACTIONS INVOLVING NTA-COMPLEXES

Reaction	Temp. °C	μ	Rate constant		Researcher
			k_f $l\ \mathrm{mol^{-1}\ sec^{-1}}$	k_b $l\ \mathrm{mol^{-1}\ sec^{-1}}$	
$Ni^{2+}+CuX^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} NiX^-+Cu^{2+}$	25	1.25	—	1.39×10^{-3}	Bydalek and Blomster[17]
	0	0.2	$\sim2\times10^{-4}$	$\sim2\times10^{-3}$	The present authors[a]
				k_b, $\mathrm{sec^{-1}}$	
$Ni^{2+}+X^{3-} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} NiX^-$	25	1.25	4.8×10^5	3.5×10^{-6}	Bydalek and Blomster
	0	0.2	$5._6\times10^4$	$8._0\times10^{-7}$	The present authors[a]
	0	0.2	$8._7\times10^4$	1×10^{-6}	The present authors[b]
$Ni^{2+}+HX^{2-} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} NiHX$	25	1.25	7.51	1.5×10^{-4}[c]	Bydalek and Blomster[17]
	0	0.2	4	$8._4\times10^{-5}$	The present authors[a]
	0	0.2	4	7.0×10^{-5}	The present authors[b]

a) Obtained from the reaction systems Ni^{2+} - CuX^- and Cu^{2+} - NiX^-.

b) Obtained from the reaction systems Ni^{2+} - CoX^- and Co^{2+} - NiX^-.

c) Calculated by the present authors using the value of 4.34×10^{-1} $l\ \mathrm{mol^{-1}\ sec^{-1}}$ for the reaction, $NiX^- + H^+ \rightarrow Ni^{2+} + HX^{2-}$, which was reported by Bydalek and Blomster.[17]

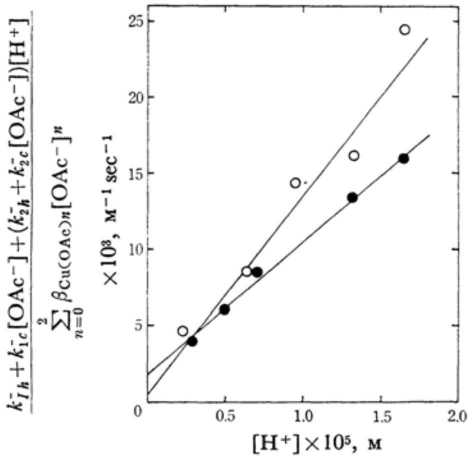

Fig. 8. Eq. (16) as a function of the hydrogen ion concentration. The conditions are the same as for Fig. 5. Concentrations of acetate ions are 0.05 M for ● and 0.10 M for ○.

Discussion

The rate constants, $\overset{+}{k}_{IIIh}$, $\overset{+}{k}_{IIIc}$, $\overset{+}{k}_{IVh}$, $\overset{+}{k}_{IVc}$, $\bar{k}_{IIIh}$, $\bar{k}_{IIIc}$, $\bar{k}_{IVh}$ and $\bar{k}_{IVc}$ for the reactions,

$$Ni^{2+} + X^{3-} \rightleftharpoons NiX^-$$

$$NiOAc^+ + X^{3-} \rightleftharpoons NiX^- + OAc^-$$

$$Ni^{2+} + HX^{2-} \rightleftharpoons NiHX$$

$$NiOAc^+ + HX^{2-} \rightleftharpoons NiHX + OAc^-$$

have been determined in the studies of two different substitution reactions between nickel(II) and copper(II)-NTA complexes, and between nickel(II) and cobalt(II)-NTA complexes.

These determinations were made with four independent systems, Ni^{2+} - CuX^-, Ni^{2+} - CoX^-, Cu^{2+}-NiX^-, and Co^{2+} - NiX^-. The values of the rate constant obtained with the systems Ni^{2+} - CoX^- and Co^{2+}-NiX^- are in agreement with those obtained with the systems Ni^{2+} - CuX^- and Cu^{2+} - NiX^-. (See Tables 3 and 6). The ratios $\overset{+}{k}_{IIIh}/\bar{k}_{IIIh}$ and $\overset{+}{k}_{IVh}/\bar{k}_{IVh}$ for the reaction between Ni^{2+} and X^{3-} and that between Ni^{2+} and HX^{2-} are $10^{10.9}$ and $10^{4.7}$, respectively. These values are compared to the formation constants for NiX^- and NiHX, which are $10^{11.18}$ and $10^{4.72}$, respectively. The ratios of the rate constants are in satisfactory agreement with the corresponding formation constants.

Recently, Bydalek and Blomster[17] reported on the kinetics of the substitution reaction between hydrated nickel(II) and copper(II)-NTA complexes. The measurements were carried out by the spectrophotometric method at ionic strength 1.25 at 25°C. Their results are given in Table 7 together with the results obtained by the present authors. Considering the difference of the experimental conditions, it may be said that the values obtained by Bydalek and Blomster are in essential agreement with the corresponding values obtained in this study.

The rate constants in Table 3 indicate that all reactions proceeding through Ni^{2+} (hydrated) ions are slower than the corresponding reactions through $NiOAc^+$ ions. Similar phenomena have been known in the complex-forming reactions of Ni(II)-EDTA complexes,[9] and the substitution reactions between nickel(II) and copper(II)-EDTA complexes.[10] Bydalek[10] reported that $NiOAc^+$ ions might have a larger water-exchange rate than aquonickel(II) ions and therefore $NiOAc^+$ ions may react faster than hydrated Ni^{2+} ions with copper(II)-EDTA complexes.

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[17] T. J. Bydalek and M. L. Blomster, *Inorg. Chem.*, **3**, 667 (1964).