BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 2375—2378 (1968)

The Kinetics of Substitution Reactions Involving Metal Complexes. XII. The Reactions between Copper(II) Ions and Zinc(II)-nitrilotriacetate Complexes

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(Received November 13, 1967)

The kinetic study of the substitution reaction of copper(II) ions and zinc(II)-nitrilotriacetate complexes in acetate buffer solutions has been carried out with the same procedure as reported previously. The reaction was treated as to proceed through both hydrated metal ions and monoacetato complexes. The rate constants for eight elementary reaction paths, of which four involve the hydrated copper(II) ions and the others the monoacetatocopper(II) complexes, were determined at ionic strength 0.23 at 0°C. The values obtained indicate that all the reactions proceeding through hydrated copper(II) ions are faster than the corresponding reactions proceeding through monoacetatocopper(II) complexes.

Our previous study¹⁾ showed that monoacetatonickel(II) ions react with nitrilotriacetate (NTA) anions faster than hydrated nickel(II) ions do. Since this was considered to be due to the characteristics of nickel(II) but not NTA ions, the confirmation was undertaken in the present study.

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1) N. Tanaka and M. Kimura, This Bulletin, **40**, 2100 (1967).

The substitution reactions between copper(II) ions and zinc(II)-nitrilotriacetate complexes have been investigated, and the rate constants for eight reactions including the reactions between copper(II) ions and nitrilotriacetate anions have been determined.

Experimental

A solution of zinc(II) nitrate was prepared by dissolving a known amount of pure zinc metal in reagent-grade nitric acid. The preparation and standardization of all other chemicals used were the same as described in the previous paper.1)

The rate of the reaction between copper(II) ions and zinc(II)-NTA complexes was determined by the measurement of the polarographic limiting diffusion current of copper(II) ions in acetate buffer solutions at 0°C and ionic strength 0.23. The ionic strength was adjusted with potassium nitrate. Gelatin was added as a maximum suppressor by 0.01% in concentration. The pH of the solution was measured after the polarographic measurement with a Hitachi-Horiba Model M-4 pH meter.

Result

In the acetate buffer solution containing acetate ions up to 0.2 M in concentration, the overall substitution reaction of copper(II) ions and zinc(II)-NTA complexes is written as

$$\left\{\begin{matrix} Cu^{2+} \\ \upharpoonleft\downharpoonright \\ CuOAc^{+} \\ \upharpoonleft\downharpoonright \\ Cu(OAc)_2 \end{matrix}\right\} + ZnX^{-} \overset{k_{app}^{+}}{\rightleftharpoons} CuX^{-} + \left\{\begin{matrix} Zn^{2+} \\ \upharpoonleft\downharpoonright \\ ZnOAc^{+} \end{matrix}\right\} \qquad (1)$$

where X^{3-} means a tervalent NTA anion. Under the condition that both Zn(II) ions and Zn(II)-NTA complexes are present in a large excess over copper(II) ions, the substitution reaction (1) can be treated as a pseudo-first order reaction. The apparent rate constants of the forward reaction (1), k_{app}^{+}, were obtained by similar treatments as given in the previous papers.2-4) The values of k_{app}^{+} were obtained as a function of the hydrogen ion concentration at two different concentrations of zinc(II) ions and at three different concentrations of acetate ions. Their plots against the hydrogen ion concentration are given in Fig. 1. Figure 1 clearly indicates that a linear relation exists between k_{app}^{+} and $[H^{+}]$, and that the values of k_{app}^{+} at $[H^{+}]=0$, which were obtained by extrapolation, are dependent on the concentrations of zinc(II) ions and acetate ions.

On the basis of the dependencies of the observed apparent rate constants on the concentrations of zinc(II) ions, Zn(II)-NTA complexes, hydrogen ions and acetate ions, which are identical to those of the substitution reaction of copper(II) ions and zinc(II)-EDTA complexes,4) the following mechanisms were set down for reaction (1).

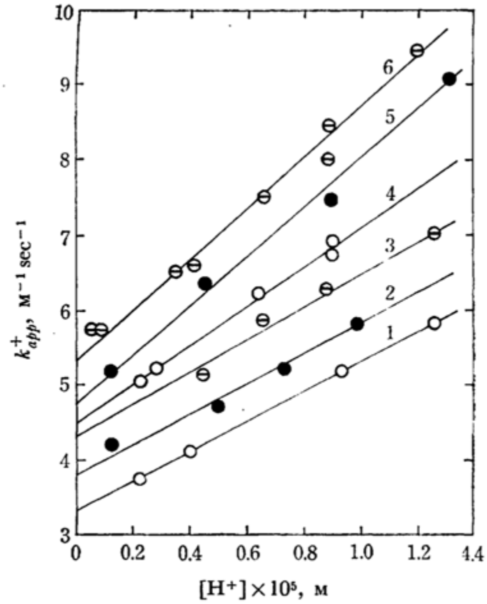

Fig. 1. k_{app}^{+} as a function of the hydrogen ion concentration in acetate buffer - potassium nitrate solutions of ionic strength 0.23 at 0°C. Initial concentrations are $[Cu^{2+}]_{0,app}=2.00\times10^{-4}$ M; $[ZnX^{-}]_0=4.35\times10^{-3}$ M; $[Zn^{2+}]_{0,app}=11.68\times10^{-3}$ M (plots 1, 2 and 3) and $[Zn^{2+}]_{0,app}=6.34\times10^{-3}$ M (plots 4, 5 and 6). Concentrations of free acetate are 0.048 M for ⊖, 0.097 M for ●, and 0.196 M for ○.

(i) $$Cu^{2+} + ZnX^{-} \overset{k_{Ih}^{+}}{\rightleftharpoons} CuX^{-} + Zn^{2+} \qquad (2)$$

$$CuOAc^{+} + ZnX^{-} \overset{k_{Ic}^{+}}{\rightleftharpoons} CuX^{-} + ZnOAc^{+} \qquad (2')$$

(ii) $$ZnX^{-} + H^{+} \rightleftharpoons ZnHX \qquad (3)$$

$$Cu^{2+} + ZnHX \overset{k_{IIh}^{+}}{\rightleftharpoons} CuHX + Zn^{2+} \qquad (4)$$

$$CuOAc^{+} + ZnHX \overset{k_{IIc}^{+}}{\rightleftharpoons} CuHX + ZnOAc^{+} \qquad (4')$$

$$CuHX \rightleftharpoons CuX^{-} + H^{+} \qquad (5)$$

(iii) $$ZnX^{-} \rightleftharpoons \left\{\begin{matrix} Zn^{2+} \\ \upharpoonleft\downharpoonright \\ ZnOAc^{+} \end{matrix}\right\} + X^{3-} \qquad (6)$$

$$Cu^{2+} + X^{3-} \overset{k_{IIIh}^{+}}{\rightleftharpoons} CuX^{-} \qquad (7)$$

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2) N. Tanaka, K. Kato and R. Tamamushi, This Bulletin, **31**, 283 (1958).
3) N. Tanaka and K. Kato, *ibid.*, **32**, 1376 (1959).
4) K. Kato, *ibid.*, **33**, 200 (1960).

$$\mathrm{CuOAc^+ + X^{3-} \overset{k^+_{IIIc}}{\rightleftharpoons} CuX^- + OAc^-} \tag{7'}$$

$$\text{(iv)}\quad \mathrm{ZnX^- + H^+ \rightleftharpoons \left\{\begin{matrix} Zn^{2+} \\ \upharpoonleft\downharpoonright \\ ZnOAc^+ \end{matrix}\right\} + HX^{2-}} \tag{8}$$

$$\mathrm{Cu^{2+} + HX^{2-} \overset{k^+_{IVh}}{\rightleftharpoons} CuHX} \tag{9}$$

$$\mathrm{CuOAc^+ + HX^{2-} \overset{k^+_{IVc}}{\rightleftharpoons} CuHX + OAc^-} \tag{9'}$$

From the same treatment in principle as in the previous papers,[2-5] Eq. (10) is obtained for the rate equation for reaction (1).

$$k^+_{app} = \frac{1}{\sum\limits_{n=0}^{2} \beta_{\mathrm{Cu(OAc)}_n}[\mathrm{OAc^-}]^n} \Bigg[k^+_{\mathrm{1h}} + k^+_{\mathrm{1c}}[\mathrm{OAc^-}] + (k^+_{\mathrm{2h}} + k^+_{\mathrm{2c}}[\mathrm{OAc^-}])[\mathrm{H^+}] + \{k^+_{\mathrm{3h}} + k^+_{\mathrm{3c}}[\mathrm{OAc^-}] + (k^+_{\mathrm{4h}} + k^+_{\mathrm{4c}}[\mathrm{OAc^-}])[\mathrm{H^+}]\} \times \frac{1+\beta_{\mathrm{ZnOAc}}[\mathrm{OAc^-}]}{[\mathrm{Zn^{2+}}]_{0,\mathrm{app}}} \Bigg] \tag{10}$$

where,

$$\left.\begin{aligned} &k^+_{\mathrm{1c}} = k^+_{\mathrm{Ic}}\beta_{\mathrm{CuOAc}},\ k^+_{\mathrm{2h}} = k^+_{\mathrm{IIh}}K^{\mathrm{H}}_{\mathrm{ZnHX}}, \\ &k^+_{\mathrm{2c}} = k^+_{\mathrm{IIc}}\beta_{\mathrm{CuOAc}}K^{\mathrm{H}}_{\mathrm{ZnHX}},\ k^+_{\mathrm{3h}} = k^+_{\mathrm{IIIh}}/K_{\mathrm{ZnX}}, \\ &k^+_{\mathrm{3c}} = k^+_{\mathrm{IIIc}}\beta_{\mathrm{CuOAc}}/K_{\mathrm{ZnX}},\ k^+_{\mathrm{4h}} = k^+_{\mathrm{IVh}}/(K_{\mathrm{ZnX}}K_{\mathrm{HX}}), \\ &k^+_{\mathrm{4c}} = k^+_{\mathrm{IVc}}\beta_{\mathrm{CuOAc}}/(K_{\mathrm{ZnX}}K_{\mathrm{HX}}) \end{aligned}\right\} \tag{10'}$$

In Eq. (10), the initial concentration $[\mathrm{Zn^{2+}}]_{0,\mathrm{app}}$ is substituted for $[\mathrm{Zn^{2+}}]_{\mathrm{app}}$.

TABLE 1. RATE CONSTANTS IN EQ. (10) OBTAINED AT IONIC STRENGTH 0.23 AT 0°C

	Rate constant	
k^+_{1h}	$5._4$	$l\ \mathrm{mol^{-1}\ sec^{-1}}$
k^+_{1c}	7.6×10	$l^2\ \mathrm{mol^{-2}\ sec^{-1}}$
k^+_{2h}	$\sim1\times10^5$	$l^2\ \mathrm{mol^{-2}\ sec^{-1}}$
k^+_{2c}	$\sim1\times10^6$	$l^3\ \mathrm{mol^{-3}\ sec^{-1}}$
k^+_{3h}	1.60×10^{-2}	$\mathrm{sec^{-1}}$
k^+_{3c}	3.0×10^{-1}	$l\ \mathrm{mol^{-1}\ sec^{-1}}$
k^+_{4h}	4×10^3	$l\ \mathrm{mol^{-1}\ sec^{-1}}$
k^+_{4c}	2×10^4	$l^2\ \mathrm{mol^{-2}\ sec^{-1}}$

TABLE 2. RATE CONSTANTS FOR REACTIONS (2), (2'), (4), (4'), (7), (7'), (9) AND (9') AT IONIC STRENGTH 0.23 AT 0°C

	Rate constant, $l\ \mathrm{mol^{-1}\ sec^{-1}}$
k^+_{Ih}	$5._4$
k^+_{Ic}	$2._3$
k^+_{IIh}	~30
k^+_{IIc}	~10
k^+_{IIIh}	2.0×10^8
k^+_{IIIc}	1.1×10^8
k^+_{IVh}	5×10^3
k^+_{IVc}	1×10^3

The rate constants in Eq. (10) were obtained from the analysis of those plots in Fig. 1, and are given in Table 1.

The rate constants for reactions (2), (2'), (4), (4'), (7), (7'), (9) and (9') were calculated from the relations given in Eqs. (10') and are given in Table 2. The values of K_{ZnX} and $K^{\mathrm{H}}_{\mathrm{ZnHX}}$ which were used in the calculation are $10^{10.06}$ and $10^{3.5}$, respectively. They are the values which were determined by the polarographic method at ionic strength 0.2 at 0°C.[6] The values of K_{HX}, β_{CuOAc} and $\beta_{\mathrm{Cu(OAc)_2}}$ are the same as those used in the previous paper.[1]

Discussion

The values in Table 2 indicate that all the reactions proceeding through hydrated copper(II) ions are faster than the corresponding reactions through monoacetatocopper(II) ions. This contrasts with the results obtained in the case of the substitution reactions involving nickel(II) ions and confirms our previous consideration.

With the rate constants obtained in this study, the ratios of the rate constants for the reactions,

$$\mathrm{M^{2+} + X^{3-} \underset{k^-_{IIIh}}{\overset{k^+_{IIIh}}{\rightleftharpoons}} MX^-} \tag{11}$$

$$\mathrm{M^{2+} + HX^{2-} \underset{k^-_{IVh}}{\overset{k^+_{IVh}}{\rightleftharpoons}} MX^- + H^+} \tag{12}$$

may be discussed. For reactions (11) and (12), the following relation holds.

$$k^+_{\mathrm{IIIh}}/k^+_{\mathrm{IVh}} = (k^-_{\mathrm{IIIh}}/k^-_{\mathrm{IVh}})/K_{\mathrm{HX}} \tag{13}$$

If it is assumed that the treatment given by Bydalek

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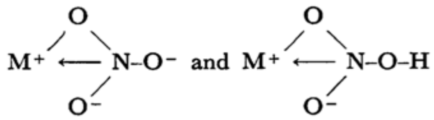
[5] N. Tanaka and H. Ogino, This Bulletin, **36**, 175 (1963).

[6] Y. Saito, Ph. D. Thesis, Tohoku University (1967).

TABLE 3. THE RATIOS OF THE RATE CONSTANTS FOR REACTIONS (11) AND (12)

Metal	Temp., °C	μ	$k^+_{\mathrm{IIIh}}/k^+_{\mathrm{IVh}}$	$k^-_{\mathrm{IIIh}}/k^-_{\mathrm{IVh}}$	Investigators
Ni^{2+}	25	1.25	6.4×10^4	8×10^{-6}	Bydalek and Blomster[8]
Ni^{2+}	0	0.2	2×10^4	5×10^{-6}	Tanaka and Kimura[1]
Ni^{2+}	0	0.2	1.4×10^4	3×10^{-6}	Tanaka and Kimura[1]
Cd^{2+}	25	0.2		1×10^{-5}	Tanaka *et al.*[9]
Cu^{2+}	0	0.23	4×10^4		This stuydy

and Margerum[7] and Bydalek and Blomster[8] can be applied to these reactions, and that the same reaction intermediates given by the latter authors for the Ni(II)-NTA reactions,



are formed in reactions (11) and (12), respectively, the ratio $k^-_{\mathrm{IIIh}}/k^-_{\mathrm{IVh}}$ is considered to be equal to the value of the acid dissociation constant for acetic acid, $10^{-4.7}$. Then, the ratio $k^+_{\mathrm{IIIh}}/k^+_{\mathrm{IVh}}$ was calculated to be

$$k^+_{\mathrm{IIIh}}/k^+_{\mathrm{IVh}} = (k^-_{\mathrm{IIIh}}/k^-_{\mathrm{IVh}})/K_{\mathrm{HX}} = 10^{5.3}$$

Since this relation holds for any metal ion, the ratio must be the same irrespective of the kind of metal ions involved. The ratios obtained in the present study are given in Table 3 together with the values reported in the literatures. From Table 3, it can be seen that the observed values are in an essential agreement with the calculated ones.

In the present and the previous[1] studies, the rate constants for the complex-forming reactions of Cu-NTA and Ni-NTA complexes were determined. If the rate constants for Cu-NTA complexes are denoted with $k^+_{\mathrm{IIIh}}(\mathrm{Cu})$ and $k^+_{\mathrm{IVh}}(\mathrm{Cu})$ and those for Ni-NTA complexes with $k^+_{\mathrm{IIIh}}(\mathrm{Ni})$ and $k^+_{\mathrm{IVh}}(\mathrm{Ni})$, the values of $k^+_{\mathrm{IIIh}}(\mathrm{Cu})/k^+_{\mathrm{IIIh}}(\mathrm{Ni})$ and $k^+_{\mathrm{IVh}}(\mathrm{Cu})/k^+_{\mathrm{IVh}}(\mathrm{Ni})$ were calculated to be 2×10^3 and 1×10^3, respectively. The values seem to be in an essential agreement with the ratio of the rate constants for the exchange of a water molecule from a hydrated copper(II) ion and a hydrated nickel(II) ion, which was reported by Eigen and Tamm,[10,11] and Connick and Stover.[12]

The authors wish to thank the Ministry of Education for the financial support granted for this research. Thanks are also due to the Teijin-Kumura Shogaku-kai for the scholarship granted to one of the authors (M. K.).

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[7] T. J. Bydalek and D. W. Margerum, *Inorg. Chem.*, **2**, 678 (1963).

[8] T. J. Bydalek and M. L. Blomster, *ibid.*, **3**, 667 (1964).

[9] N. Tanaka, K. Ebata, T. Takahari and T. Kumagai, This Bulletin, **35**, 1836 (1962).

[10] M. Eigen, *Z. Elektrochem.*, **64**, 115 (1960).

[11] M. Eigen and K. Tamm, *ibid.*, **66**, 93, 107 (1962).

[12] R. E. Connick and E. S. Stover, *J. Phys. Chem.*, **65**, 2075 (1961).