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# The Effect of Acetate Ion on the Rate of the Reaction between Cobalt(II) and Manganese(II)-Ethylenediaminetetraacetate Complexes

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The kinetics of the substitution reactions of cobalt(II) ions and manganese(II)-ethylenediaminetetraacetate complexes have been studied in acetate buffer solutions at 25°C and at ionic strength of 0.2. The reaction was treated as to proceed through both hydrated metal ions and monoacetato complexes. The rate constants for six elementary reaction paths, three of which involve hydrated cobalt(II) ions and the others, monoacetatocobalt(II) complexes, were determined. The values obtained indicate that all the reactions proceeding through monoacetatocobalt(II) complexes are about three times faster than the corresponding reactions proceeding through hydrated cobalt(II) ions.

In the previous papers on substitution reactions involving copper(II)-nitrilotriacetate (NTA) complexes[1] and lead(II)-ethylenediaminetetraacetate (EDTA) complexes,[2] it has been shown that monoacetatocopper(II) ions and monoacetatolead(II) ions react more slowly with NTA anions and EDTA anions respectively, than the corresponding hydrated metal ions do. However, recently, Tanaka and Kimura[3] have shown that monoacetatonickel(II) ions react with NTA anions faster than hydrated nickel(II) ions do. Tanaka and Sakuma,[4] and Bydalek,[5] who studied the effect of acetate ions on reactions involving nickel(II) ion, obtained results similar to those reported by Tanaka and Kimura.[3] It seemed to be important and interesting that the effect of acetate ions on the reactions involving nickel(II) ions is the reverse of that on the reactions involving copper(II) and lead(II) ions. This fact was considered to be due to the characteristics of acetatometal complexes, but not of NTA or EDTA; confirmation was sought in the present study. The behavior of the acetatocobalt(II) ions used in the present study was considered to be similar to that of acetatonickel(II) ions.

The substitution reactions between cobalt(II) ions and manganese(II)-ethylenediaminetetraacetate complexes have been investigated in acetate buffer solutions at an ionic strength of 0.2 at 25°C, and the rate constants of the paths by which the reactions proceed through hydrated cobalt(II) ions and monoacetatocobalt(II) complexes have been determined and compared with those of the corresponding reactions of other metal ions.

## Experimental

The solution of disodiumethylenediaminetetraacetate

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[1] N. Tanaka and M. Kimura, This Bulletin, **41**, 2375 (1968).

[2] N. Tanaka and H. Ogino, *ibid.*, **36**, 175 (1963).

[3] N. Tanaka and M. Kimura, *ibid.*, **40**, 2100 (1967).

[4] N. Tanaka and Y. Sakuma, *ibid.*, **32**, 578 (1959).

[5] T. J. Bydalek, *Inorg. Chem.*, **4**, 232 (1965).

was standardized by using a standard copper(II) solution by amperometric titration using a dropping-mercury electrode as the indicator electrode. A standard solution of manganese(II) nitrate was prepared from the guaranteed reagents and was standardized amperometrically by the standard solution of EDTA. The preparation and standardization of all the other chemicals and solutions used were the same as have been described in a previous paper.[3])

The rate of the reaction between cobalt(II) ions and manganese(II)-EDTA complexes was determined by measuring the polarographic limiting-diffusion current of cobalt(II) ions in acetate buffer solutions at 25°C and at an ionic strength of 0.2. The ionic strength was adjusted with potassium nitrate. Polyoxyethylene lauryl ether (LEO) ($2 \times 10^{-6}$ M) was added as a maximum suppressor. The pH of the solution was measured after polarographic measurements with a Hitachi-Horiba Model F-5 pH meter.

## Results and Discussion

In a solution containing acetate ions up to a concentration of 0.2 M, the overall substitution reaction of cobalt(II) ions and manganese(II)-EDTA complexes can be expressed as follows:

$$\left\{\begin{matrix} \mathrm{Co^{2+}} \\ \downarrow\uparrow \\ \mathrm{CoOAc^{+}} \end{matrix}\right\} + \mathrm{MnY^{2-}} \xrightleftharpoons{V^{+}_{0,\mathrm{app}}} \mathrm{CoY^{2-}} + \left\{\begin{matrix} \mathrm{Mn^{2+}} \\ \downarrow\uparrow \\ \mathrm{MnOAc^{+}} \end{matrix}\right\} \tag{1}$$

where $Y^{4-}$ denotes a tetravalent EDTA anion.

The apparent concentrations of cobalt(II) ions that can be determined polarographically, $[\mathrm{Co^{2+}}]_{\mathrm{app}}$ are give by

$$[\mathrm{Co^{2+}}]_{\mathrm{app}} = [\mathrm{Co^{2+}}] + [\mathrm{CoOAc^{+}}] \tag{2}$$

Under the present experimental conditions, the rate of the substitution reaction between Co(II) and Mn(II)-EDTA complexes was so slow that the apparent initial rates of the reactions, $-\Delta[\mathrm{Co^{2+}}]_{0,\mathrm{app}}/\Delta t$, could be measured accurately; the subscript 0 indicates the initial state.

The apparent initial rates of the forward reaction (1), $V^{+}_{0,\mathrm{app}}$ were obtained at various pH's with two different concentrations of Mn(II) and acetate ions. The plots of $V^{+}_{0,\mathrm{app}}/([\mathrm{Co^{2+}}]_{0,\mathrm{app}}[\mathrm{MnY^{2-}}]_0)$ *versus* $[\mathrm{H^+}]$ gave straight lines as is shown in Fig. 1.

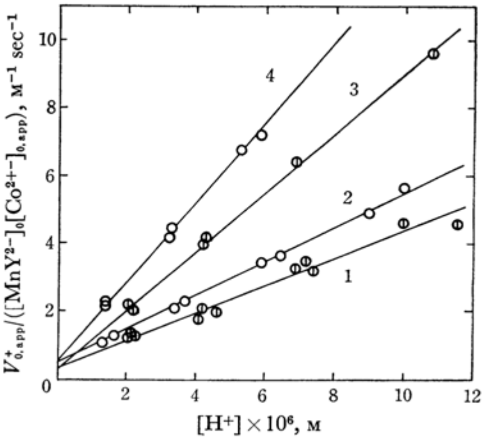

Fig. 1. $V^{+}_{0,\mathrm{app}}/([\mathrm{MnY^{2-}}]_0[\mathrm{Co^{2+}}]_{0,\mathrm{app}})$ as a function of hydrogen ion concentration in acetate buffer-potassium nitrate solutions of ionic strength 0.2 at 25°C.
Initial concentrations are $[\mathrm{MnY^{2-}}]_0 = 0.378$ mM; $[\mathrm{Co^{2+}}]_{0,\mathrm{app}} = 0.193$ mM; $[\mathrm{Mn^{2+}}]_{0,\mathrm{app}} = 4.875$ mM (cruves 3 and 4) and 12.04 mM (curves 1 and 2). Concentrations of acetate ions are 0.039 M for ⦶, and 0.168 M for ○.

On the basis of these facts, the following mechanisms can be suggested for reaction (1).

(i) $$\mathrm{Co^{2+}} + \mathrm{MnY^{2-}} \xrightleftharpoons{k^{+}_{\mathrm{I}h}} \mathrm{CoY^{2-}} + \mathrm{Mn^{2+}} \tag{3}$$

$$\mathrm{CoOAc^{+}} + \mathrm{MnY^{2-}} \xrightleftharpoons{k^{+}_{\mathrm{I}z}} \mathrm{CoY^{2-}} + \mathrm{MnOAc^{+}} \tag{3'}$$

(ii) $$\mathrm{MnY^{2-}} + \mathrm{H^{+}} \rightleftharpoons \mathrm{MnHY^{-}} \tag{4}$$

$$\mathrm{Co^{2+}} + \mathrm{MnHY^{-}} \xrightleftharpoons{k^{+}_{\mathrm{II}h}} \mathrm{CoHY^{-}} + \mathrm{Mn^{2+}} \tag{5}$$

$$\mathrm{CoOAc^{+}} + \mathrm{MnHY^{-}} \xrightleftharpoons{k^{+}_{\mathrm{II}z}} \mathrm{CoHY^{-}} + \mathrm{MnAOc^{+}} \tag{5'}$$

$$\mathrm{CoHY^{-}} \rightleftharpoons \mathrm{CoY^{2-}} + \mathrm{H^{+}} \tag{6}$$

(iii) $$\mathrm{MnY^{2-}} + \mathrm{H^{+}} \rightleftharpoons \mathrm{HY^{3-}} + \{\mathrm{Mn^{2+}} \rightleftharpoons \mathrm{MnOAc^{+}}\} \tag{7}$$

$$\mathrm{Co^{2+}} + \mathrm{HY^{3-}} \xrightleftharpoons{k^{+}_{\mathrm{III}h}} \mathrm{CoY^{2-}} + \mathrm{H^{+}} \tag{8}$$

$$\mathrm{CoOAc^{+}} + \mathrm{HY^{3-}} \xrightleftharpoons{k^{+}_{\mathrm{III}z}} \mathrm{CoY^{2-}} + \mathrm{H^{+}} + \mathrm{OAc^{-}} \tag{8'}$$

In the experimental treatment, it was assumed that the equilibria between hydrated ions and acetato complexes were maintained while the substitution reactions took place. From the same treatment in principle as in the previous papers,[1-3]) Eq. (9) was obtained as the rate equation of reaction (1).

$$\begin{aligned} V^{+}_{0,\mathrm{app}} = \frac{[\mathrm{Co^{2+}}]_{0,\mathrm{app}}[\mathrm{MnY^{2-}}]_0}{1 + \beta_{\mathrm{CoOAc}}[\mathrm{OAc^{-}}]} \Big\{ & k^{+}_{\mathrm{I}h} + k^{+}_{1z}[\mathrm{OAc^{-}}] \\ & + (k^{+}_{2h} + k^{+}_{2z}[\mathrm{OAc^{-}}])[\mathrm{H^{+}}] \\ & + (k^{+}_{3h} + k^{+}_{3z}[\mathrm{OAc^{-}}]) \frac{1 + \beta_{\mathrm{MnOAc}}[\mathrm{OAc^{-}}]}{[\mathrm{Mn^{2+}}]_{0,\mathrm{app}}}[\mathrm{H^{+}}] \Big\} \end{aligned} \tag{9}$$

$$\text{where: } k^{+}_{1z} = k^{+}_{\mathrm{I}z}\beta_{\mathrm{CoOAc}},\ k^{+}_{2h} = k^{+}_{\mathrm{II}h}K^{\mathrm{H}}_{\mathrm{MnHY}},$$
$$k^{+}_{2z} = k^{+}_{\mathrm{II}z}\beta_{\mathrm{CoOAc}}K^{\mathrm{H}}_{\mathrm{MnHY}},\ k^{+}_{3h} = k^{+}_{\mathrm{III}h}/(K_{\mathrm{MnY}}K_{\mathrm{HY}}),$$
$$k^{+}_{3z} = k^{+}_{\mathrm{III}z}\beta_{\mathrm{CoOAc}}/(K_{\mathrm{MnY}}K_{\mathrm{HY}}) \tag{9'}$$

$\beta_{\mathrm{CoOAc}}$ and $\beta_{\mathrm{MnOAc}}$ represent the overall formation constants of the acetatocobalt(II) and acetatomanganese(II) complexes respectively. $K^{\mathrm{H}}_{\mathrm{MnHY}}$ represents the equiliblium constant of reaction (4), $K_{\mathrm{MnY}}$ the formation constant of $\mathrm{MnY}^{2-}$, and $K_{\mathrm{HY}}$ the fourth dissociation constant of EDTA. In these equations, the changes in the initial concentrations during the measurements of the initial reaction rates were considered to be negligibly small under these experimental conditions.

The rate constants in Eq. (9) were obtained from an analysis of the plots in Fig. 1; they are given in Table 1.

TABLE 1. RATE CONSTANTS IN EQ. (9) OBTAINED AT IONIC STRENGTH 0.2 AT 25°C

| | Rate constant | |
|---|---|---|
| $k^{+}_{1h}$ | 0.3 | $l\,\mathrm{mol}^{-1}\mathrm{sec}^{-1}$ |
| $k^{+}_{1a}$ | 1.3 | $l^{2}\,\mathrm{mol}^{-2}\mathrm{sec}^{-1}$ |
| $k^{+}_{2h}$ | $\sim 6\times10^{4}$ | $l^{2}\,\mathrm{mol}^{-2}\mathrm{sec}^{-1}$ |
| $k^{+}_{2a}$ | $\sim 7\times10^{4}$ | $l^{3}\,\mathrm{mol}^{-3}\mathrm{sec}^{-1}$ |
| $k^{+}_{3h}$ | $3.3\times10^{3}$ | $l\,\mathrm{mol}^{-1}\mathrm{sec}^{-1}$ |
| $k^{+}_{3a}$ | $1.1\times10^{4}$ | $l^{2}\,\mathrm{mol}^{-2}\mathrm{sec}^{-1}$ |

The rate constants for reactions (3), (3′), (5), (5′), (8), and (8′) were calculated from the relations given in Eqs. (9′) and are given in Table 2. The values of $\beta_{\mathrm{CoOAc}}$,⁶⁾ $\beta_{\mathrm{MnOAc}}$,⁶⁾ $K_{\mathrm{MnY}}$,⁷⁾ $K_{\mathrm{HY}}$⁷⁾ and $K^{\mathrm{H}}_{\mathrm{MnHY}}$⁷⁾ which have been used in the calculation are 1.2, 1.6, $10^{13.79}$, $10^{-10.22}$, and $10^{3.1}$ respectively.

TABLE 2. RATE CONSTANTS FOR REACTIONS, (3), (3′), (5), (5′), (8) AND (8′) AT IONIC STRENGTH 0.2 AT 25°C

Rate constant, $l\,\mathrm{mol}^{-1}\mathrm{sec}^{-1}$

| $k^{+}_{\mathrm{I}h}$ | $k^{+}_{\mathrm{I}a}$ | $k^{+}_{\mathrm{II}h}$ | $k^{+}_{\mathrm{II}a}$ | $k^{+}_{\mathrm{III}h}$ | $k^{+}_{\mathrm{III}a}$ |
|---|---|---|---|---|---|
| 0.3 | 1.1 | —6—0 | ∼60 | $1\times10^{7}$ | $3\times10^{7}$ |

The rate constants in Table 2 indicate that all the reactions proceeding through $\mathrm{Co}^{2+}$ (hydrated ions) are slower than the corresponding reactions proceeding through $\mathrm{CoOAc}^{+}$ ions. Similar phenomena have been found in the complex-forming reactions of Ni(II)-NTA complexes³⁾ and Ni(II)-EDTA complexes,⁴⁾ and in substitution reactions between nickel(II) and copper(II)-EDTA complexes.⁵⁾ It is noteworthy that these phenomena are unlike those obtained in reactions involving copper(II) ions¹⁾ and lead(II) ions.²⁾

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6) H. Ogino, Ph. D. thesis, Tohoku University, (1965).

7) G. Schwarzenbach, R. Gut and G. Andereg, *Helv. Chim. Acta*, **37**, 937 (1954).