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Kinetics of the Ligand Substitution Reaction of the Cobalt(II)-(Ethylene glycol)bis(2-aminoethyl ether)-*N*,*N*,*N*′,*N*′-tetraacetate Complex with 4-(2-Pyridylazo)resorcinol

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The kinetics of the ligand substitution reaction of the cobalt(II)-(ethylene glycol)bis(2-aminoethyl ether)-*N*,*N*,*N*′,*N*′-tetraacetate complex (Co(II)-EGTA) with 4-(2-pyridylazo)resorcinol (PAR) have been studied photometrically in the pH range 8—9.4 at an ionic strength of 0.1 and at 25°C. The reaction proceeds simultaneously through two different reaction paths. Thus the rate law can be written as

$$\frac{d[CoR_2^-]}{dt} = k_1[CoY^{2-}][HR^-] + k_2[CoHY^-][HR^-]$$

where Y^{4-} and R^{2-} refer to tetravalent EGTA and divalent PAR respectively. Rate constants, k_1 and k_2 are $3.2\text{M}^{-1}\text{sec}^{-1}$ and $2.1\times10^4\text{M}^{-1}\text{sec}^{-1}$. Possible mechanism for the substitution is discussed. The stability constants for mercury(II)-EGTA complexes and cobalt(II)-EGTA complexes are determined by the mercury electrode method at $\mu=0.1$ and 25°C in order to analyze the substitution reaction: $K_{HgY}=10^{23.86\pm0.10}$, $K^{H}_{HgHY}=10^{3.06\pm0.10}$, $K_{CoY}=10^{12.3\pm0.1}$, $K^{H}_{CoHY}=10^{4.9\pm0.1}$, $K^{H}_{CoH_2Y}=10^{3.3\pm0.3}$.

In a previous paper,[1] the ligand substitution reaction of the zinc(II)-4-(2-pyridylazo)resorcinol complex (Zn(II)-PAR) with (ethylene glycol)-bis(2-aminoethyl ether)-*N*,*N*,*N*′,*N*′-tetraacetic acid (EGTA) has been reported. The reaction was found to proceed, under the experimental conditions, through one path involving predissociation equilibrium of the Zn(II)-PAR complex. The rate constants were determined and the possible mechanism was discussed.

Since it seemed worth while to extend the study to the substitution reaction involving the other metal ion, the ligand substitution reaction of the cobalt(II)-(ethylene glycol)bis(2-aminoethyl ether)-*N*,*N*,*N*′,*N*′-tetraacetate complex with 4(-2-pyridylazo)resorcinol:

$$\text{Co-EGTA} + \text{PAR} \rightleftharpoons \text{Co-PAR} + \text{EGTA} \qquad (1)$$

was undertaken, where EGTA and PAR represent (ethylene glycol)bis(2-aminoethyl ether)-*N*,*N*,*N*′,*N*′-tetraacetic acid and 4-(2-pyridylazo)resorcinol respectively, and are abbreviated as H_4Y (hexadentate) and H_2R (tridentate) respectively. This paper gives the results.

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[1] M. Tanaka, S. Funahashi and K. Shirai, *Inorg. Chem.*, **7**, 573 (1968).

Experimental

Reagents. *Cobalt(II) Perchlorate.* The reagent grade cobalt(II) chloride was recrystallized twice from distilled water. The recrystallized cobalt(II) chloride was then dissolved in perchloric acid, and hydrochloric acid and excess perchloric acid were expelled by an infrared lamp. The cobalt(II) perchlorate was recrystallized further from distilled water. The concentration of cobalt(II) ion was determined by a standard EDTA solution using xylenol orange as an indicator.

Mercuric Perchlorate. Mercuric perchlorate was prepared from mercuric nitrate by the same method as that for cobalt perchlorate. The solution was standardized against a standard EDTA solution using Erio T as an indicator.

Methods of preparation of all other reagents have been described previously.[1)]

Apparatus. The following instruments were used: a Horiba Model P pH meter; a Sharp Model TEB-10 thermoelectric circulating bath; a Beckman Model DU spectrophotometer with a thermostated cell compartment; a Jasco Model ORD/UV-5 optical rotatory dispersion recorder.

Determination of the Stability Constants of Cobalt(II)-EGTA Complexes. It is necessary to determine the stability constants of cobalt(II)-EGTA complexes in connection with the kinetic study of the substitution reaction. These stability constants were determined at ionic strength $\mu=0.1$ (sodium perchlorate) and 25°C.

Procedure of Measurements of Potential and pH. Potentials were measured by pH meter with the J shape tube mercury electrode using a saturated calomel electrode as a reference electrode. The latter was jacketted with a tube containing 1 M potassium nitrate solution in order to avoid contamination of chloride ion. The pH was varied by the dropwise addition of carbonate-free sodium hydroxide or perchloric acid in an atmosphere of nitrogen.

Calculation of Stability Constants of Mercury-(II)-EGTA Complexes. The potential of a mercury electrode at 25°C is given by the following equation:

$$E = E^{\circ}_{\mathrm{Hg}} + 0.0296 \log [\mathrm{Hg}^{2+}]. \qquad (2)$$

The value of the standard potential, E°_{Hg}, of the mercury electrode has been given by Latimer[2)] as 0.612 V *vs.* saturated calomel electrode at 25°C. The conditional stability constant, K'_{HgY}, of the mercury(II)-EGTA complex was determined from potential of the mercury electrode in a solution containing free EGTA and mercury(II)-EGTA complex. The potential is given by the relationship:

$$E = E^{\circ}_{\mathrm{Hg}} + 0.0296 \log \frac{[\mathrm{HgY}^{2-}]\alpha_{\mathrm{H(Y)}}}{[\mathrm{Y}']K'_{\mathrm{HgY}}}, \qquad (3)$$

where $[\mathrm{Y}']=[\mathrm{Y}^{4-}]\alpha_{\mathrm{H(Y)}}$ and $\alpha_{\mathrm{H(Y)}}$ is the side reaction coefficient taking into account the protonation of Y^{4-}. $K'_{\mathrm{HgY}}=[\mathrm{HgY}']/[\mathrm{Hg}^{2+}][\mathrm{Y}^{4-}]$ and $[\mathrm{HgY}']$ refers to the total concentration of normal and protonated complexes of mercury(II)-EGTA. As the concentration of EGTA added is about twice that of mercury ion added and the stability constant of mercury(II)-EGTA is very high, the following relationships hold with a good approximation:

$$[\mathrm{HgY}'] = C_{\mathrm{Hg}}, \quad [\mathrm{Y}']=C_{\mathrm{Y}}-C_{\mathrm{Hg}}, \qquad (4)$$

where C_{Hg} and C_{Y} are the total concentrations of added mercury ion and EGTA respectively. Thus we have

$$E = E^{\circ}_{\mathrm{Hg}} + 0.0296 \log \frac{C_{\mathrm{Hg}}\alpha_{\mathrm{H(Y)}}}{(C_{\mathrm{Y}}-C_{\mathrm{Hg}})K'_{\mathrm{HgY}}}. \qquad (5)$$

Therefore K'_{HgY} can be calculated from potential-pH measurements. Values of $\log K'_{\mathrm{HgY}}$ at various pH's are tabulated in Table 1.

TABLE 1. VALUES OF $\log K'_{\mathrm{HgY}}$ AT VARIOUS pH'S FOR DETERMINATION OF THE STABILITY CONSTANTS OF HgY^{2-} AND HgHY^{-}

$C_{\mathrm{Hg}}=2\times10^{-3}$ M, $C_{\mathrm{Y}}=4\times10^{-3}$ M, 25°C, $\mu=0.1$

pH	$\log K'_{\mathrm{HgY}}$	pH	$\log K'_{\mathrm{HgY}}$
2.69	24.35	4.28	23.83
2.82	24.33	4.94	23.85
3.09	24.15	6.20	23.92
3.24	25.08	8.32	23.88
3.54	23.98	8.52	23.88
3.94	23.93	9.29	23.80

Since the $\log K'_{\mathrm{HgY}}$-pH diagram gives a curve of a limiting slope of unity at lower pH, the presence of protonated complex of mercury(II)-EGTA is anticipated. Thus

$$K'_{\mathrm{HgY}} = \frac{[\mathrm{HgY}^{2-}]+[\mathrm{HgHY}^{-}]}{[\mathrm{Hg}^{2+}][\mathrm{Y}^{4-}]}$$

$$= (1+K^{\mathrm{H}}_{\mathrm{HgHY}}[\mathrm{H}^{+}])K_{\mathrm{HgY}}, \qquad (6)$$

where

$$K_{\mathrm{HgY}} = \frac{[\mathrm{HgY}^{2-}]}{[\mathrm{Hg}^{2+}][\mathrm{Y}^{4-}]} \text{ and } K^{\mathrm{H}}_{\mathrm{HgHY}} = \frac{[\mathrm{HgHY}^{-}]}{[\mathrm{HgY}^{2-}][\mathrm{H}^{+}]}.$$

In the pH range 5 to 9 K'_{HgY} is independent of hydrogen ion concentration. This value is obviously equal to K_{HgY} from the definition of K'_{HgY}. The following values are obtained: $\log K_{\mathrm{HgY}}=23.86\pm0.10$, $\log K^{\mathrm{H}}_{\mathrm{HgHY}}=3.06\pm0.10$. The value of $\log K_{\mathrm{HgY}}$ compares favorably with the value 23.8 reported by Holloway and Reilley.[3)]

Stability Constants of Cobalt(II)-EGTA Complexes. As the stability constant of HgY^{2-} is higher than that of CoY^{2-} and the total concentration of EGTA and that of cobalt ion added, C_{Y} and C_{Co}, are about twice that of mercury ion, the following relationships hold:

$$C_{\mathrm{Hg}} = [\mathrm{HgY}'] \qquad (7)$$

$$C_{\mathrm{Y}} - C_{\mathrm{Hg}} = [\mathrm{CoY}'] + [\mathrm{Y}'] \qquad (8)$$

$$[\mathrm{Co}'] = C_{\mathrm{Hg}} + C_{\mathrm{Co}} - C_{\mathrm{Y}} + [\mathrm{Y}'] = [\mathrm{Co}^{2+}]\alpha_{\mathrm{OH(Co)}} \qquad (9)$$

$$E = E^{\circ}_{\mathrm{Hg}} + 0.0296 \log \frac{K'_{\mathrm{CoY}}C_{\mathrm{Hg}}[\mathrm{Co}']}{K'_{\mathrm{HgY}}[\mathrm{CoY}']\alpha_{\mathrm{OH(Co)}}}. \qquad (10)$$

where $\alpha_{\mathrm{OH(Co)}}$ is the side reaction coefficient taking into account the hydrolysis of cobalt ion. We can calculate

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2) W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, New York (1952), p. 179.

3) J. H. Holloway and C. N. Reilley, *Anal. Chem.*, **32**, 249 (1960).

pY from the following equation:

$$E = E^{\circ}_{\mathrm{Hg}} + 0.0296 \log \frac{C_{\mathrm{Hg}}}{K'_{\mathrm{HgY}}} + 0.0296\,\mathrm{pY}. \quad (11)$$

Thus with a knowledge of [Y′], [CoY′] and [Co′] are obtained from Eqs. (8) to (9) respectively, and K'_{CoY} is calculated from Eq. (10). As shown in Fig. 1, the log K'_{CoY}-pH diagram tends to give a curve of limiting slope of 2 at lower pH. This fact points to the presence of CoY^{2-}, CoHY^{-} and $\mathrm{CoH_2Y}$ species. Then

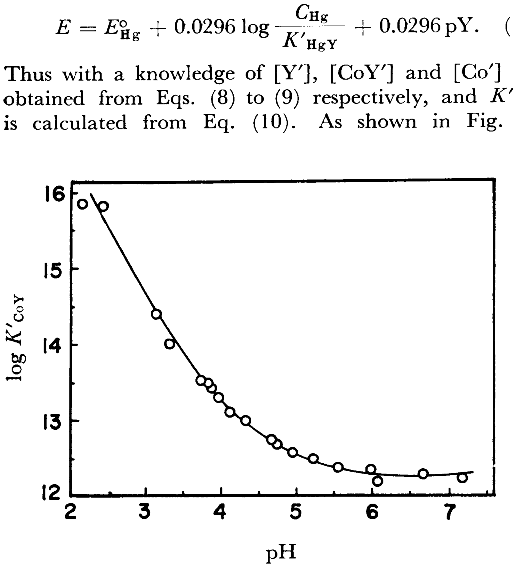

Fig. 1. Determination of the stability constants of CoY^{2-}, CoHY^{-} and $\mathrm{CoH_2Y}$. Solid line is the theoretical curve calculated with values obtained by means of the curve fitting. At $\mu=0.1$, 25°C.

$$K'_{\mathrm{CoY}} = \frac{[\mathrm{CoY}^{2-}]+[\mathrm{CoHY}^{-}]+[\mathrm{CoH_2Y}]}{[\mathrm{Co}^{2+}][\mathrm{Y}^{4-}]}$$

$$= K_{\mathrm{CoY}}(1+K^{\mathrm{H}}_{\mathrm{CoHY}}[\mathrm{H}^+]+K^{\mathrm{H}}_{\mathrm{Co_2HY}}K^{\mathrm{H}}_{\mathrm{CoHY}}[\mathrm{H}^+]^2), \quad (12)$$

where

$$K_{\mathrm{CoY}} = \frac{[\mathrm{CoY}^{2-}]}{[\mathrm{Co}^{2+}][\mathrm{Y}^{4-}]}, \quad K^{\mathrm{H}}_{\mathrm{CoHY}} = \frac{[\mathrm{CoHY}^{-}]}{[\mathrm{CoY}^{2-}][\mathrm{H}^+]}$$

and

$$K^{\mathrm{H}}_{\mathrm{Co_2HY}} = \frac{[\mathrm{CoH_2Y}]}{[\mathrm{CoHY}^{-}][\mathrm{H}^+]}.$$

By means of a "curve fitting" method the following results were obtained: log $K_{\mathrm{CoY}}=12.3\pm0.1$, log $K^{\mathrm{H}}_{\mathrm{CoHY}}=4.9\pm0.1$, log $K^{\mathrm{H}}_{\mathrm{CoH_2Y}}=3.3\pm0.3$. The value of log K_{CoY} compares favorably with the previous finding 12.3.[3] These constants are used in the analysis of the kinetic data.

Equilibrium. As seen from the values of stability constants of EGTA (log $K^{\mathrm{H}}_{\mathrm{HY}}=9.43$, log $K^{\mathrm{H}}_{\mathrm{H_2Y}}=8.85$, log $K^{\mathrm{H}}_{\mathrm{H_3Y}}=2.68$, log $K^{\mathrm{H}}_{\mathrm{H_4Y}}=2.07$[4]), Y^{4-}, HY^{3-}, and $\mathrm{H_2Y}^{2-}$ species may be present in the pH range 8 to 9.4 investigated. The 1 : 1 normal cobalt(II)-EGTA complex exists under these experimental conditions. In the pH range 8 to 9.4, the dominant species of PAR is found to be the monoionic species (HR^{-}) from the stability constants of PAR (log $K^{\mathrm{H}}_{\mathrm{H_3R}}=2.69$, log $K^{\mathrm{H}}_{\mathrm{H_2R}}=5.50$, log $K^{\mathrm{H}}_{\mathrm{HR}}=12.31$[5]). The monoionic species has maximum absorption at 410 nm and the absorbance of PAR is independent of pH in this pH range. The molar absorption coefficient is 8.14×10^2 at 510 nm. The molar ratio of cobalt to PAR in cobalt-PAR complex is 1 : 2.[6,7] Cobalt-PAR complex has maximum absorption at 510 nm and its molar absorption coefficient is 6.40×10^4 at 510 nm.

The equilibrium 1 is much favored to the right under the present experimental conditions, so that the reverse reaction can be neglected in the kinetic study. Therefore the stoichiometry of the present substitution reaction is expressed as

$$\mathrm{CoY}^{2-} + 2\mathrm{HR}^{-} \rightarrow \mathrm{CoR_2}^{-} + \mathrm{Y}', \quad (13)$$

where Y′ denotes nonmetallized EGTA.[8]

Procedure of Measurement of the Substitution Reaction Rate. pH of the cobalt-EGTA solution, prepared by mixing cobalt perchlorate solution with EGTA solution in excess, is buffered with borax and boric acid or sodium hydroxide and the ionic strength maintained constant ($\mu=0.1$) with sodium perchlorate. The cobalt-EGTA solution and the PAR solution are brought to the temperature equilibrium in a bath kept at 25±0.2°C. The velocity of the substitution reaction is sufficiently slow to be studied by manual mixing techniques. The reaction is commenced by mixing these two solutions. A portion of the reaction mixture is transferred to a spectrophotometer cell at different intervals, and the absorbance of cobalt-PAR complex is measured at 510 nm, a spectrophotometer being used with a thermostated cell compartment capable of temperature control ±0.3°C. All experiments are carried out in a room thermostated at 25±1°C.

Results

Beer's law is obeyed for the cobalt-PAR complex and the reaction(13) goes to completion. Therefore, if the substitution reaction of cobalt-EGTA with PAR in large excess is of the *p*th order with respect to cobalt-EGTA, the order of the reaction with respect to cobalt-EGTA is given by the slope, *p*, of the straight line obtained in a plot[1] of $\log \mathrm{d}(E_t-E_0)/\mathrm{d}t$ against $\log(E_\infty-E_t)$. The plot gave a straight line of slope 1. Therefore the reaction is of the first order in cobalt-EGTA. Thus for the reactions with a large excess of PAR the rate law is expressed as:

$$\frac{\mathrm{d}[\mathrm{CoR_2}^{-}]}{\mathrm{d}t} = k_{0(\mathrm{R,H})}[\mathrm{CoY}^{2-}], \quad (14)$$

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4) J. Bjerrum, G. Schwarzenbach and L. G. Sillén, Special Publication No. 6, The Chemical Society, London, 1957, Part I.

5) W. J. Geary, G. Nickless and F. H. Pollard, *Anal. Chim. Acta*, **27**, 71 (1962).

6) A. Corsini, Q. Fernando and H. Freiser, *Inorg. Chem.*, **2**, 224 (1963).

7) A. I. Busev, V. M. Ivanov and Zh. I. Nemtseva, *Zh. Neorg. Khim.*, **13**, 511 (1968).

8) We assume trivalent cobalt to be in the cobalt-PAR complex according to a previous finding (T. Iwamoto and M. Fujimoto, *Anal. Chim. Acta*, **29**, 282 (1963)). However, electron transfer does not seem to make any obstacle in studying the present ligand substitution reaction (see Discussion).

where $k_{0(R,H)}$ denotes the conditional rate constant[1] involving the concentration terms of PAR and hydrogen ion.

The kinetic studies performed with a 20—50-fold excess of the entering group PAR showed that the reaction was of the first order in PAR. The fact is also supported by the good linearity of the second order plots concerning cobalt-EGTA and PAR:

$$\frac{1}{C_{PAR}-2C_{Co}}\ln\frac{C_{Co}(C_{PAR}-2[CoR_2^-])}{C_{PAR}(C_{Co}-[CoR_2^-])}=k_{0(H)}t.$$

Typical second order plots are shown in Fig. 2.

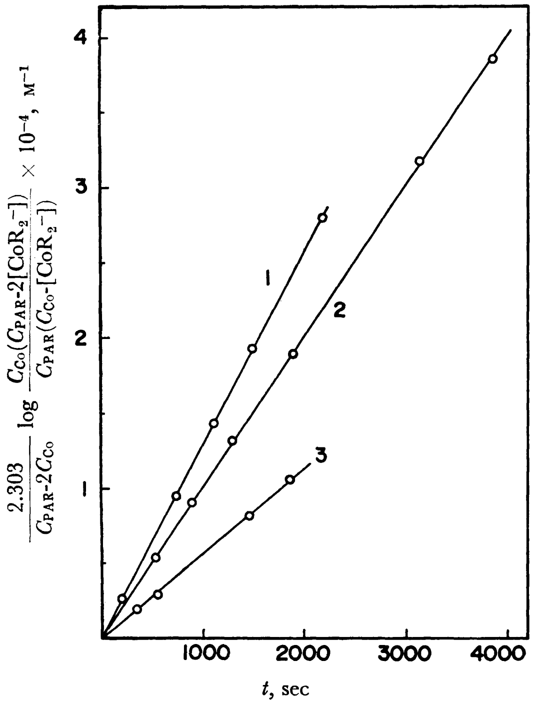

Fig. 2. Typical second order plots. For these runs the experimental conditions were as follows: $C_{Co}=1.09\times10^{-5}$M, $C_{PAR}=7.00\times10^{-5}$M, $C_Y=5.00\times10^{-5}$M, 1: pH=8.33; 2: pH=8.45; 3: pH=8.86, ionic strength=0.1M ($NaClO_4$), reaction temperature=25°C.

Under the experimental condition, predominant species of PAR is HR^- ($K^H_{HR}=10^{12.31}$ and $K^H_{H_2R}=10^{5.50}$).[5] Therefore, the rate law is expressed as

$$\frac{d[CoR_2^-]}{dt}=k_{0(H)}[CoY^{2-}][HR^-], \qquad (15)$$

where $k_{0(H)}$ refers to the conditional second order rate constant. The conditional rate constant $k_{0(H)}$ was determined at various pH's, concentrations of EGTA and concentrations of PAR.

Some results obtained are tabulated in Table 2. The values of $k_{0(H)}$ are plotted against the hydrogen ion concentration in Fig. 3, which indicates a linear relationship between $k_{0(H)}$ and $[H^+]$ within experimental error regardless of the concentration

TABLE 2. CONDITIONAL SECOND ORDER RATE CONSTANTS FOR THE SUBSTITUTION REACTION OF COBALT-EGTA WITH PAR

$\mu=0.1$, 25°C, $C_{Co}=9.78\times10^{-6}$M (Runs No. 1—14) or 1.09×10^{-5}M (Runs No. 15—23).

Run No.	C_{PAR} (M)	C_Y (M)	pH	$k_{0(H)}$ (M^{-1}sec^{-1})
1	4.00×10^{-4}	1.00×10^{-3}	8.32	11.7
2	4.00×10^{-4}	1.00×10^{-3}	8.44	9.58
3	4.00×10^{-4}	1.00×10^{-3}	9.13	4.17
4	4.00×10^{-4}	1.00×10^{-3}	9.37	4.00
5	4.00×10^{-4}	2.00×10^{-3}	8.22	13.3
6	4.00×10^{-4}	2.00×10^{-3}	8.28	10.9
7	4.00×10^{-4}	2.00×10^{-3}	8.39	9.38
8	4.00×10^{-4}	2.00×10^{-3}	9.08	4.22
9	4.00×10^{-4}	2.00×10^{-3}	9.29	3.75
10	2.00×10^{-4}	2.00×10^{-3}	8.00	19.0
11	2.00×10^{-4}	2.00×10^{-3}	8.04	19.8
12	2.00×10^{-4}	2.00×10^{-3}	8.09	16.6
13	2.00×10^{-4}	2.00×10^{-3}	8.12	16.8
14	2.00×10^{-4}	2.00×10^{-3}	8.25	12.8
15	7.00×10^{-5}	2.00×10^{-5}	8.63	7.82
16	7.00×10^{-5}	5.00×10^{-5}	8.33	12.9
17	7.00×10^{-5}	5.00×10^{-5}	8.45	10.1
18	7.00×10^{-5}	5.00×10^{-5}	8.86	5.60
19	7.00×10^{-5}	1.00×10^{-4}	8.62	7.85
20	7.00×10^{-5}	1.00×10^{-3}	8.52	8.88
21	7.00×10^{-5}	1.00×10^{-3}	8.18	14.5
22	7.00×10^{-5}	2.00×10^{-3}	8.11	15.9
23	7.00×10^{-5}	2.00×10^{-3}	8.37	9.39

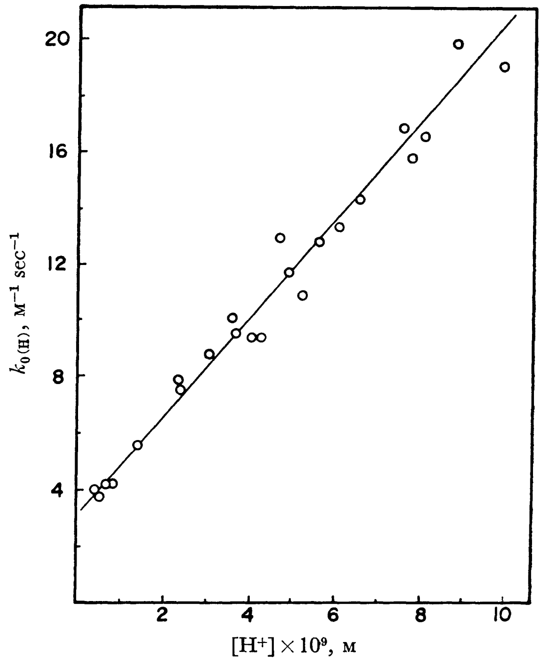

Fig. 3. $k_{0(H)}$ as a function of hydrogen ion concentration C_{Co}=about 10^{-5}M, $C_Y=2\times10^{-5}$ to 2×10^{-3}M, $C_{PAR}=7\times10^{-5}$ to 4×10^{-4}M, $\mu=0.1$, 25°C.

of EGTA. Thus we obtain the following rate expression:

$$\frac{d[CoR_2^-]}{dt}=k_1[CoY^{2-}][HR^-]+k_2'[H^+][CoY^{2-}][HR^-]. \quad (16)$$

From the intercept and slope in Fig. 3 k_1 and k_2' may be obtained: $k_1=3.2\text{M}^{-1}\,\text{sec}^{-1}$ and $k_2'=1.7\times10^9\text{M}^{-2}\,\text{sec}^{-1}$. The second term of Eq. (16) shows the participation of the proton complex $CoHY^-$. Thus substituting the stability constant of $CoHY^-$ determined in the present study, we have

$$\begin{aligned}\frac{d[CoR_2^-]}{dt}&=k_1[CoY^{2-}][HR^-]+\frac{k_2'}{K^{H}_{CoHY}}[CoHY^-][HR^-]\\&=k_1[CoY^{2-}][HR^-]+k_2[CoHY^-][HR^-]. \quad (17)\end{aligned}$$

The rate constants k_1 and k_2 at ionic strength $\mu=0.1$ and 25°C are $3.2\text{M}^{-1}\,\text{sec}^{-1}$ and $2.1\times10^4\text{M}^{-1}\cdot\text{sec}^{-1}$, respectively.

Discussion

Mechanism of the Present Ligand Substitution Reaction. PAR forms a 1 : 2 complex with cobalt and the formation of cobalt-PAR is of the first order in the concentration of PAR. The rate of the addition of the second PAR is much faster than the rate of addition of the first PAR.

The first step of complexation is in general rate-determining: the fact that the rate constants increase with increasing degree of association of ligand with metal has been provided by Hammes and Steinfeld[9] in successive substituion of nickel or cobalt with glycine. Honaker and Freiser[10] reported that the addition of the first ligand is rate controlling in the rate of extraction of zinc dithizonate from aqueous solution. Pearson and Ellgen[11] have shown that in the complex formation reactions of nickel(II) ion with dithioxalate or maleonitrile-dithiolate the formation of monoligand nickel(II) complex is rate-determining. Recently, the labilizing effect of a coordinated ligand in the substitution reaction has been quantitatively accounted for by a study of kinetics of the formation of nickel(II)-PAR complex from some monovalent monoacidopentaaquonickel(II) complexes.[12]

Proton transfer reactions are extremely rapid and the proton will tend to be in the position of the greatest basicity. Usually the reaction rate increases with decreasing pH if the protons are more attracted to the leaving group.[13]

It is suggested therefore that the first order dependence of the cleavage rate on hydrogen ion concentration is due to a rapid acid-base reaction preceding the rate-determining step. From this consideration, in the present case, the second term of Eq. (17) clearly shows the participation of a protonated complex $CoHY^-$ which is in equilibrium preceding the rate-determining step. From the stability constant K^{H}_{CoHY} of $10^{4.9}$ determined in the present study, the concentration of protonated complex $[CoHY^-]$ is found only 0.1 to 0.01% of that of the total cobalt-EGTA complex in the range of pH 8 to 9. Nevertheless the reaction path through the protonated complex is important in the present substitution reaction, because $CoHY^-$ is much more reactive than CoY^{2-}.

Margerum and Rosen[14] have recently shown a clear evidence for a series of intermediates in equilibrium with one another in the reaction of EDTA with mono- and bis(diethylenetriamine)-nickel(II) complexes. In the present case, there may be a successive dissociation of donor atoms in EGTA, before three sites of coordination at least are available for the incoming PAR. Thus the cleavage of nitrogen atom bonded to the central metal in the mixed ligand intermediates, RCoY and RCoHY, should be rate-determining.[1] The coordination of the second PAR molecule to the resulting 1 : 1 cobalt-PAR complex is fast.[12]

Reactions of CoY^{2-} and $CoHY^-$ with PAR are schematically given in Fig. 4. We assume the partial dissociation of cobalt-EGTA bonds (Steps K_I and K_I') followed by the incorporation of PAR to form the mixed ligand intermediates, RCoY and RCoHY (Steps K_{II} and K_{II}'). According to the proposed mechanism, the rate law (17) can be rewritten as

$$\begin{aligned}\frac{d[CoR_2^-]}{dt}&=k_1[CoY^{2-}][HR^-]+k_2[CoHY^-][HR^-]\\&=\frac{k_1}{K_IK_{II}}[RCoY]+\frac{k_2}{K_I'K_{II}'}[RCoHY]\\&=k_I[RCoY]+k_{II}[RCoHY],\end{aligned}$$

where $k_I=k_1/K_IK_{II}$ and $k_{II}=k_2/K_I'K_{II}'$. The estimation of the ratio k_I/k_{II} may be interesting. We have immediately.

$$\frac{k_I}{k_{II}}=\frac{k_1}{k_2}\,\frac{K_I'K_{II}'}{K_IK_{II}}$$

As it appears reasonable to assume that $K_I'/K_I=K_{CoY}/K^{HY}_{CoHY}$ and that the value of K_I does not differ appreciably from K_{II}', we put $K_{II}\simeq K_{II}'$. Then with the observed rate and formation con-

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[9] G. G. Hammes and J. I. Steinfeld, *J. Amer. Chem. Soc.*, **84**, 4639 (1962); *J. Phys. Chem.*, **67**, 528 (1963).

[10] C. B. Honaker and H. Freiser, *J. Phys. Chem.*, **66**, 127 (1962).

[11] R. G. Pearson and P. Ellgen, *Inorg. Chem.*, **6**, 1379 (1967).

[12] S. Funahashi and M. Tanaka, *ibid.*, **8**, 2159 (1969).

[13] J. D. Carr, R. A. Libbly and D. W. Margerum, *ibid.*, **6**, 1083 (1967).

[14] D. W. Margerum and H. M. Rosen, *ibid*, **7**, 299 (1968).

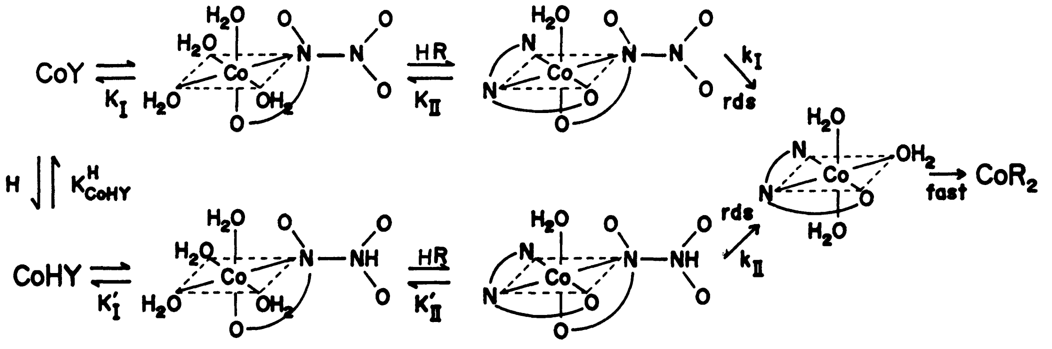

Fig. 4. Proposed mechanism of the substitution reactions of CoY and CoHY with PAR. EGTA and PAR are symbolized respectively as $\begin{smallmatrix}\mathrm{O} & & \mathrm{O}\\ & \mathrm{N{-}N} & \\ \mathrm{O} & & \mathrm{O}\end{smallmatrix}$ and N-N-O. Charges are omitted for simplicity.

stants, we obtain $k_{II}/k_I=5$, *i.e.*, k_I and k_{II} are of the same order of magnitude. In other words the difference between k_1 and k_2 is mostly determined by the difference between the overall formation constants of the mixed ligand intermediates, $K^R_{RCoY}=K_IK_{II}$ and $K^R_{RCoHY}=K_I'K_{II}'$. The ratio K_{CoY}/K^{HY}_{CoHY} would be a measure of k_2/k_1 in the proposed mechanism.

Oxidation State of Cobalt in the Product CoR_2 and in the Intermediate RCoY. 1-(2-Pyridiylazo)-2-naphthol (PAN) is similar to PAR and forms 1:2 cobalt-PAN complex. On mixing a cobalt(II) solution with an excess of PAN the color of the solution (pH 8) change gradually from red to green in a few minutes. This corresponds to the oxidation of the red cobalt(II)-PAN complex to the green cobalt(III) complex by atmospheric oxygen. On the other hand, mixing a cobalt(II) solution with a PAR solution results immediately in a red solution, which does not change in color. The trivalent state of cobalt in the green PAN complex and in the red PAR complex has been confirmed by magnetic susceptibility measurements.[15]

We studied qualitatively the rate of the acid dissociation reactions of cobalt-PAN and cobalt-PAR complexes. Solutions of red cobalt-PAN, green cobalt-PAN and red cobalt-PAR complexes were made acidic (pH 1 or lower) with 10 M perchloric acid. Then the color of the red cobalt-PAN complex changed immediately to reddish yellow which is the color of protonated PAN, while the color of the green cobalt-PAN and red cobalt-PAR complexes remained unchanged for at least a week. Similar experiments were carried out on nickel complexes. Upon acidification with perchloric acid, the color of the red nickel-PAN and nickel-PAR complexes changed to the color of a free ligand.

As expected from the inertness of trivalent cobalt complexes, the reaction of cobalt(III)-EDTA complex with PAN and that of cobalt(III)-PAN with EDTA do not proceed at all, for at least a week. Thus the cobalt in the labile red cobalt-PAN complex is divalent, while the cobalt in the inert (or thermodynamically very stable) green cobalt-PAN and the inert red cobalt-PAN complexes is trivalent. The result agrees with the previous conclusion drawn from the magnetic susceptibility of these complexes.[15] Trivalent state of cobalt seems to be more stabilized in the cobalt-PAR complex than in the corresponding PAN complex by the effect of the electron flow from the dissociated *para*-hydroxyl group of PAR into benzene ring. The same effect seems to be responsible for the fact that the cobalt(III)-PAR complex absorbs at a shorter wavelength than the cobalt(III)-PAN complex.

The rate of electron transfer in the system of tris(1,10-phenanthroline)-cobalt(II)——tris(1,10-phenanthroline)-cobalt(III) is faster by about five orders of magnitude than that of cobalt(II)-EDTA——cobalt(III)-EDTA. This fact has been explained on the basis of the difference in the ligand field strength.[16,17] If the cobalt in the intermediate RCoY were trivalent, the dissociation of EGTA from the intermediate would be impossible. Thus the cobalt in the intermediate RCoY should be divalent. Since the ligand field of PAR is stronger than that of EGTA, it seems reasonable that the oxidation of cobalt(II) occurs immediately after the incorporation of the second PAR molecule.

On the other hand, the substitution of nickel(II)-EGTA complex with PAR[18] is about 10 times slower than the corresponding reaction of cobalt(II) complexes studied in the present work. This is just as expected from the ligand field theory and

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agrees with a great number of experimental results.

It seems plausible that, in the step of the dissociation of EGTA from the intermediate RCoY, cobalt is divalent. The oxidation of cobalt(II) occurs after the dissociation of EGTA followed by the incorporation of the second PAR molecule.

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