Kinetics and Mechanism of the Ligand Substitution Reaction of the Mercury(II)-4-(2-pyridylazo)resorcinol Complex with 1,2-Cyclohexanediamine-*N*,*N*,*N*′,*N*′-tetraacetic Acid

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(Received December 7, 1970)

Kinetics and mechanism of the ligand substitution reaction of the mercury(II)-PAR complex with CyDTA were studied at 25°C in the presence of halogenide ion at an ionic strength of 0.1. The rate law can be written as

$$-\frac{d[\mathrm{Hg(par)_2}^{2-}]}{dt} = (k_1'[\mathrm{H^+}] + k_2' + k_{3,\mathrm{X}}'[\mathrm{H^+}][\mathrm{X^-}])\frac{[\mathrm{Hg(par)_2}^{2-}]}{[\mathrm{Hpar^-}]}[\mathrm{Hcydta^{3-}}]$$

where X^- refers to a halogenide ion (chloride, bromide, iodide). The rate constants k_1', k_2', and $k_{3,\mathrm{X}}'$ were determined as: $k_1' = (2.4\pm0.1)\times10^{7}\ \mathrm{M^{-1}\,sec^{-1}}$, $k_2' = (1.9\pm0.1)\times10^{-2}\ \mathrm{sec^{-1}}$, $k_{3,\mathrm{Cl}}' = (4.5\pm0.2)\times10^{9}\ \mathrm{M^{-2}\,sec^{-1}}$, $k_{3,\mathrm{Br}}' = (3.2\pm0.1)\times10^{11}\ \mathrm{M^{-2}\,sec^{-1}}$, $k_{3,\mathrm{I}}' = (5.6\pm0.2)\times10^{14}\ \mathrm{M^{-2}\,sec^{-1}}$. The rate constants for the paths involving mixed hydroxo and halogeno complexes (k_2' and $k_{3,\mathrm{X}}'$) are quantitatively accounted for in terms of electron donation of ligands OH^- and X^-.

The ligand substitution reactions of metal complexes with multidentate ligands have been extensively studied by many authors.[1-9] Some of these studies have shown that ligands coordinated to a central metal ion affect the rate of substitution. In the reaction of monoacidopentaaquonickel(II) complex with 4-(2-pyridylazo)resorcinol (PAR) it has been shown that the ligand coordinated to nickel(II) labilizes coordinated water molecules.[7] Hunt *et al.*[8] reported that the rate of water exchange of some nickel(II) complexes became faster with increasing extent of substitution. In the ligand substitution of the Ni(II)-EDDA complex and the Ni(II)-NTA complex with PAR,[9] it has been revealed that EDDA and NTA coordinated to nickel(II) labilize water molecules attached to nickel(II).

In the present study, the kinetics and mechanism of the ligand substitution reaction of the mercury(II)-PAR complex with CyDTA (1,2-cyclohexanediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid) were studied in the presence of halogenide ion. The reaction system is

$$\mathrm{Hg(II)\text{-}PAR + CyDTA \rightleftarrows Hg(II)\text{-}CyDTA + PAR} \qquad (1)$$

Primary purpose of this study is to elucidate the effect of monodentate ligands on the reaction.

Experimental

Reagents. *Mercury(II) Perchlorate*: Commercial G. R. mercury(II) oxide was dissolved in perchloric acid. Twice recrystallized sodium bicarbonate was added to the solution to obtain mercury carbonate. The mercury(II) perchlorate solution was prepared by dissolving mercury carbonate in a perchloric acid solution. The concentration of the mercury(II) solution was determined by a standard EDTA solution using xylenol orange as an indicator.

CyDTA: The acid form of CyDTA obtained from Dojindo Co., Ltd., was dissolved in a sodium hydroxide solution. CyDTA was then precipitated by addition of perchloric acid. The purified CyDTA was dissolved in 2 eq. of sodium hydroxide. The CyDTA solution was standardized complexometrically by a zinc(II) standard solution using Erio T as an indicator.

Sodium Chloride: Sodium chloride was obtained by addition of reagent grade hydrochloric acid to a saturated sodium chloride solution. Sodium chloride obtained was heated by an infrared lamp in order to expel excess hydrochloric acid.

Sodium Bromide: G. R. sodium bromide was recrystallized three times from distilled water. The bromide solution was standardized by a standard silver nitrate solution using eosine as an indicator.

Sodium Iodide: G. R. sodium iodide was recrystallized twice from distilled water. The precipitated sodium iodide was washed with ether and benzene, and then dried *in vacuo* at room temperature. The sodium iodide solution was standardized in the same way as the bromide solution.

Methods of preparation of all other reagents (sodium perchlorate, sodium hydroxide, PAR, borax and boric acid) have been described previously.[4]

Apparatus: The following instruments were used: Hitachi Perkin-Elmer 139 UV-VIS spectrophotometer, Hitachi Model QPD-53 recorder, Hirama Type 6 spectrophotometer, X-Y recorder Type UR-631 (Matsushita Communication Industrial Co., Yokohama), Radiometer PHM-4d (Copenhagen) with a Type G 202 B glass electrode and K 401 calomel electrode, Sharp Model TEB-10 thermoelectric circulating bath and a Coolnics circulator Type CTE-IB (Komatsu Solidate Co., Komatsu).

Procedure of Measurement of the Substitution Reaction Rate. Ionic strength was kept constant at 0.1 M with sodium perchlorate. A buffer solution of borate-boric acid was used. The mercury(II)-PAR solution containing PAR in excess was taken in a silica beaker with a light path of 5.3-cm or a quartz cell with a light path of 2.0-cm placed in the cell com-

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[1] D. W. Rogers, D. A. Aikens, and C. N. Reilley, *J. Phys. Chem.*, **66**, 1582 (1962).

[2] D. B. Rorabacher and D. W. Margerum, *Inorg. Chem.*, **3**, 382 (1964).

[3] W. H. Baddley and F. Basolo, *J. Amer. Chem. Soc.*, **88**, 2944 (1966).

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

[5] D. L. Rabenstein and R. J. Kula, *J. Amer. Chem. Soc.*, **91**, 2492 (1969).

[6] S. Funahashi, S. Yamada, and M. Tanaka, This Bulletin, **43**, 769 (1970).

[7] S. Funahashi and M. Tanaka, *Inorg. Chem.*, **8**, 2159 (1969).

[8] A. G. Desai, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, **92**, 798 (1970), and their papers cited therein.

[9] S. Funahashi and M. Tanaka, *Inorg. Chem.*, **9**, 2092 (1970).

partment thermostated at 25±0.2°C. The reaction was started by mixing the mercury(II)-PAR complex solution and the CyDTA solution. The reaction was followed automatically, the transmittance of the reaction system at 500 nm being recorded as a function of time. Molar absorption coefficients of $Hg(par)_2^{2-}$ and $Hpar^-$ at 500 nm are $\varepsilon_{Hg(par)_2}=6.50\times10^4$ and $\varepsilon_{Hpar}=1.31\times10^3$, respectively. All pH values were measured with a Radiometer PHM-4d which was carefully calibrated with a standard buffer solution (sodium borate 0.01 M) prepared as described by Bates.[10] All experiments were carried out at room temperature of 25±1°C.

Results

Substitution of the Mercury(II)-PAR Complex with CyDTA. The reaction of the mercury(II)-PAR complex with CyDTA was studied in the presence of a large excess of PAR over a pH range 8.5—9.1. Under the present experimental conditions the dominant species of CyDTA and PAR are the monoprotonated species $Hcydta^{3-}$ and $Hpar^-$, respectively, as apparent from stability constants: $K^{H}_{Hcydta}=10^{11.78}$, $K^{H}_{H2cydta}=10^{6.20}$, $K^{H}_{Hpar}=10^{12.31}$, $K^{H}_{H2par}=10^{5.48}$. The mercury(II)-PAR complex forms the 1 : 2 complex $Hg(par)_2^{2-}$. The mercury(II)-CyDTA complex is the 1 : 1 complex $Hg(cydta)^{2-}$ ($K_{Hg(cydta)}=10^{24.4}$[11], $K^{OH}_{Hg(cydta)OH}=10^{3.2}$[12]). Equilibrium (1) is much favored to the right so that the substitution reaction of the mercury(II)-PAR complex with CyDTA goes substantially to completion and the reverse reaction can be neglected. Thus the reaction system studied is described as

$$Hg(par)_2^{2-} + Hcydta^{3-} + H_2O \rightarrow$$
$$Hg(cydta)^{2-} + 2\,Hpar^- + OH^-$$

From the measurements of the initial rate, the rate of decrease of the mercury(II)-PAR complex is found to be first-order with respect to mercury(II)-PAR and to CyDTA. Thus the rate equation can be expressed as

$$-\frac{d[Hg(par)_2^{2-}]}{dt} = k_{0(H,PAR)}[Hg(par)_2^{2-}][Hcydta^{3-}] \qquad (2)$$

This equation is confirmed also from the linearity of the second order plots obtained by it. We have the following relationships

$$A_0 = \varepsilon_{Hg(par)_2}C_{Hg} + \varepsilon_{Hpar}(C_{PAR}-2C_{Hg}) \qquad (3)$$

$$A_t = \varepsilon_{Hg(par)_2}[Hg(par)_2^{2-}] + \varepsilon_{Hpar}(C_{PAR}-2C_{Hg}+2[Hg(cydta)^{2-}]) \qquad (4)$$

$$A_\infty = \varepsilon_{Hpar}C_{PAR} \qquad (5)$$

where A_0, A_t, and A_∞ are the absorbances of the reaction system at reaction time 0, t and ∞, respectively, and C_{Hg} and C_{PAR} denote the total concentration of mercury(II) and of PAR, respectively. Substitution of Eqs. (3), (4) and (5) into the integrated form of Eq. (2) leads to

Table 1. Conditional rate constants for the reaction between the mercury(II)-PAR complex and CyDTA at 25°C and $\mu=0.1$ ($NaClO_4$)

$C_{Hg}\times10^6$ M	$C_{PAR}\times10^4$ M	$C_{CyDTA}\times10^5$, M	pH	$k_{0(H,PAR)}\times10^{-2}$ $M^{-1}sec^{-1}$
0.984	1.50	1.93	8.94	2.9
1.97	1.50	1.93	8.62	5.5
1.97	1.50	1.93	8.78	4.1
1.97	1.50	1.93	8.92	3.2
1.97	1.50	1.93	8.93	2.9
1.97	1.50	1.93	9.07	2.6
1.97	2.00	1.93	8.64	3.7
1.97	2.00	1.93	8.79	2.8
1.97	1.98	1.93	8.88	2.5
1.97	2.00	1.93	9.07	2.0
1.97	4.00	1.93	8.62	1.9
1.97	4.00	1.93	8.78	1.3
1.97	4.00	1.93	8.87	1.2
1.97	1.50	0.771	8.93	3.0
1.97	1.50	2.70	8.94	3.0
1.97	1.50	3.85	8.93	3.0
2.95	1.50	1.93	8.92	3.0

Table 2. Conditional rate constants $k_{0(H,PAR,X)}$ for the reaction of the mercury(II)-PAR complex with CyDTA in the presence of halogenide ions at 25°C and $\mu=0.1$ ($NaClO_4$)
$C_{Hg}=1.97\times10^{-6}$ M, $C_{CyDTA}=1.93\times10^{-5}$ M,
$C_{PAR}=2.00\times10^{-4}$ M

$[I^-]\times10^8$, M	pH	$k_{0(H,PAR,I)}\times10^{-2}$, $M^{-1}sec^{-1}$
2.16	8.77	3.8
2.16	8.87	3.2
2.16	8.88	3.1
2.16	9.05	2.4
4.28	8.89	3.7
8.85	8.90	5.2
10.69	8.90	5.6

$[Br^-]\times10^4$, M	pH	$k_{0(H,PAR,Br)}\times10^{-2}$, $M^{-1}sec^{-1}$
0.94	8.46	9.8
0.94	8.82	4.5
0.94	8.74	5.2
0.94	9.01	3.8
1.98	8.84	7.8
3.96	8.83	11.9
5.95	8.83	17.0
7.93	8.82	21.8

$[Cl^-]\times10^2$, M	pH	$k_{0(H,PAR,Cl)}\times10^{-2}$, $M^{-1}sec^{-1}$
1.00	8.54	12.0
1.00	8.71	8.2
1.00	8.84	6.5
1.00	8.89	5.4
0.50	8.83	4.9
1.59	8.84	8.0

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[10] R. G. Bates, "Determination of pH, Theory and Practice," John Wiley & Sons, Inc., New York (1964), p. 76.

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

[12] D. L. Janes and D. W. Margerum, *Inorg. Chem.*, **5**, 1135 (1966).

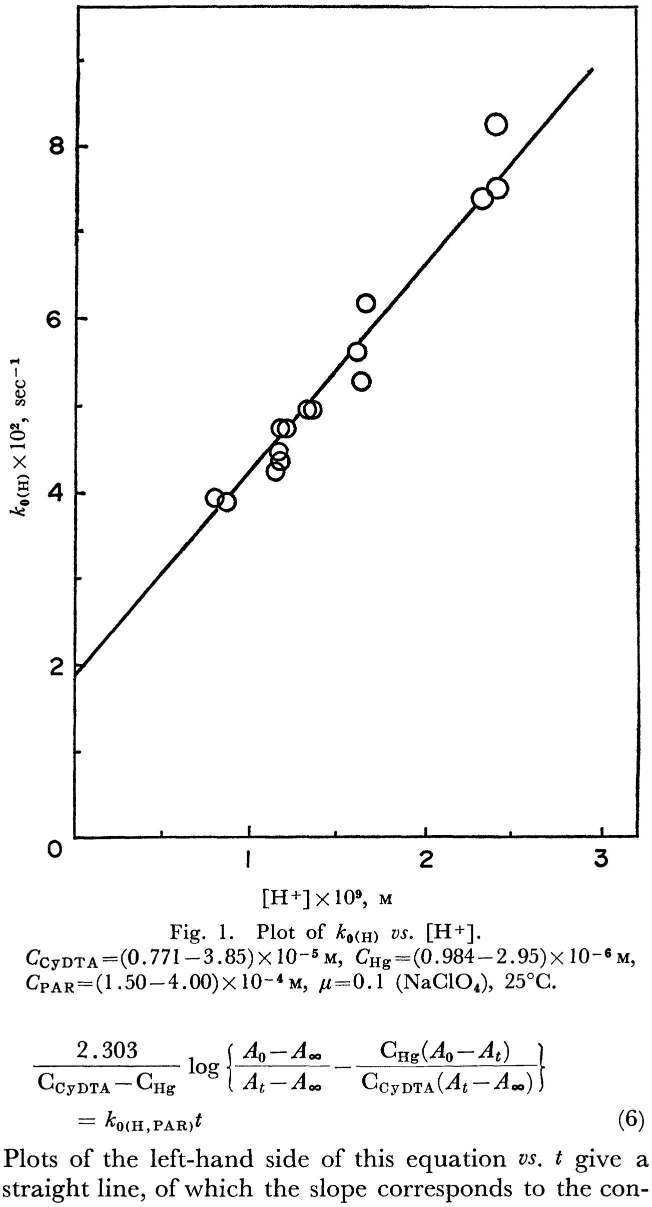

Fig. 1. Plot of $k_{0(\mathrm{H})}$ *vs.* [H$^+$].
$C_{\mathrm{CyDTA}}=(0.771-3.85)\times10^{-5}$ M, $C_{\mathrm{Hg}}=(0.984-2.95)\times10^{-6}$ M, $C_{\mathrm{PAR}}=(1.50-4.00)\times10^{-4}$ M, $\mu=0.1$ (NaClO$_4$), 25°C.

$$\frac{2.303}{C_{\mathrm{CyDTA}}-C_{\mathrm{Hg}}}\log\left\{\frac{A_0-A_\infty}{A_t-A_\infty}-\frac{C_{\mathrm{Hg}}(A_0-A_t)}{C_{\mathrm{CyDTA}}(A_t-A_\infty)}\right\} = k_{0(\mathrm{H,PAR})}t \tag{6}$$

Plots of the left-hand side of this equation *vs.* t give a straight line, of which the slope corresponds to the conditional rate constant $k_{0(\mathrm{H,PAR})}$. Conditional rate constants are summarized in Table 1. The data indicate the linear relationship between $k_{0(\mathrm{H,PAR})}$ and the reciprocal concentration of PAR with the zero intercept. Values of $k_{0(\mathrm{H,PAR})}[\mathrm{Hpar}^-]$ (*i.e.* $k_{0(\mathrm{H})}$) are plotted against the concentration of hydrogen ion in Fig. 1, from which we can derive the following relationship:

$$k_{0(\mathrm{H,PAR})}[\mathrm{Hpar}^-] = k_1'[\mathrm{H}^+] + k_2' \tag{7}$$

The rate equation of the substitution of the mercury(II)-PAR complex with CyDTA is

$$-\frac{d[\mathrm{Hg(par)_2}^{2-}]}{dt} = (k_1'[\mathrm{H}^+]+k_2')\frac{[\mathrm{Hg(par)_2}^{2-}][\mathrm{Hcydta}^{3-}]}{[\mathrm{Hpar}^-]} \tag{8}$$

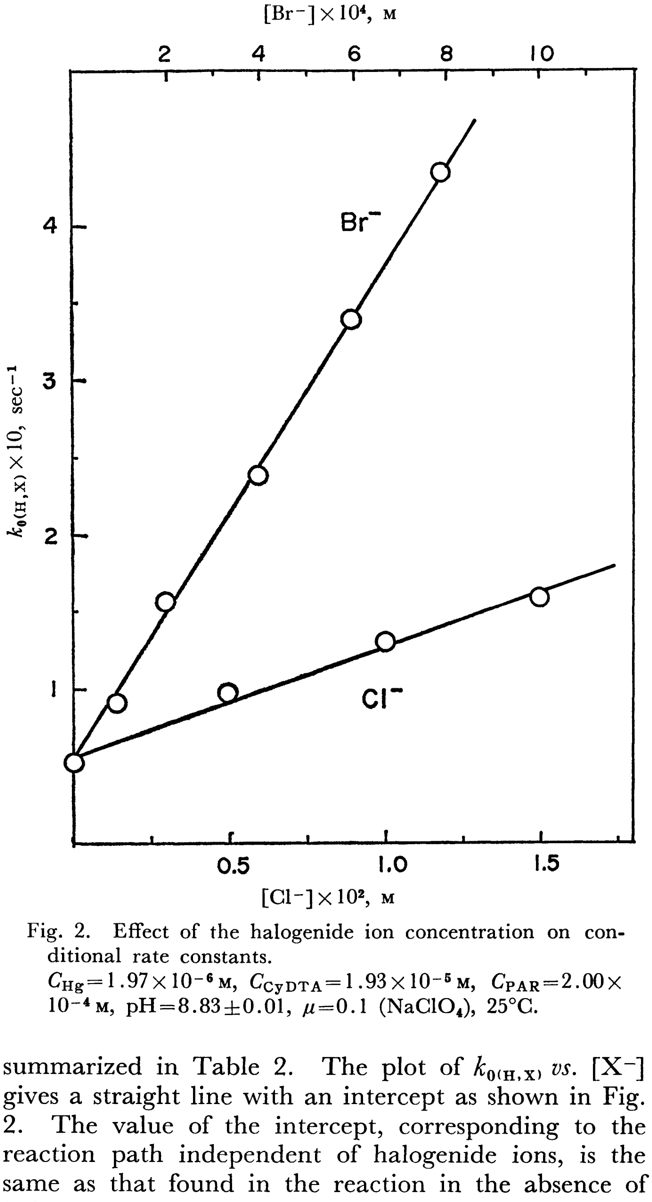

Fig. 2. Effect of the halogenide ion concentration on conditional rate constants.
$C_{\mathrm{Hg}}=1.97\times10^{-6}$ M, $C_{\mathrm{CyDTA}}=1.93\times10^{-5}$ M, $C_{\mathrm{PAR}}=2.00\times10^{-4}$ M, pH=8.83±0.01, $\mu=0.1$ (NaClO$_4$), 25°C.

Substitution of the Mercury(II)-PAR Complex with CyDTA in the Presence of Halogenide Ions. A halogenide ion accelerates the substitution of the mercury(II)-PAR complex with CyDTA. Conditional rate constants $k_{0(\mathrm{H,PAR,X})}$ under various conditions are summarized in Table 2. The plot of $k_{0(\mathrm{H,X})}$ *vs.* [X$^-$] gives a straight line with an intercept as shown in Fig. 2. The value of the intercept, corresponding to the reaction path independent of halogenide ions, is the same as that found in the reaction in the absence of halogenide at the same pH (*i.e.* $[\mathrm{H}^+]=(1.5\pm0.1)\times10^{-9}$, see Fig. 1.). Hence, we have the following relationship:

$$k_{0(\mathrm{H,X})} = k_1'[\mathrm{H}^+] + k_2' + k_3'{}_{(\mathrm{H})}[\mathrm{X}^-] \tag{9}$$

The values of conditional rate constants in the presence of iodide, bromide, and chloride are plotted against hydrogen ion concentrations in Fig. 3. It is evident that $k_{0(\mathrm{H,X})}$ is linearly related to the hydrogen ion concentration. Thus Eq. (9) can be written as

$$k_{0(\mathrm{H,X})} = k_1'[\mathrm{H}^+] + k_2' + k_{3,\mathrm{X}}'[\mathrm{H}^+][\mathrm{X}^-] \tag{10}$$

From these results we obtain the following rate equation for the ligand substitution reaction of the mercury(II)-PAR complex with CyDTA in the presence of halogenide ion:

$$-\frac{d[\mathrm{Hg(par)_2}^{2-}]}{dt} = (k_1'[\mathrm{H}^+] + k_2' + k_{3,\mathrm{X}}'[\mathrm{H}^+][\mathrm{X}^-]) \times \frac{[\mathrm{Hg(par)_2}^{2-}][\mathrm{Hcydta}^{3-}]}{[\mathrm{Hpar}^-]} \tag{11}$$

The rate constants k_1', k_2', $k_{3,\mathrm{Cl}}'$, $k_{3,\mathrm{Br}}'$, and $k_{3,\mathrm{I}}'$ at 25°C and $\mu=0.1$ are tabulated in Table 3.

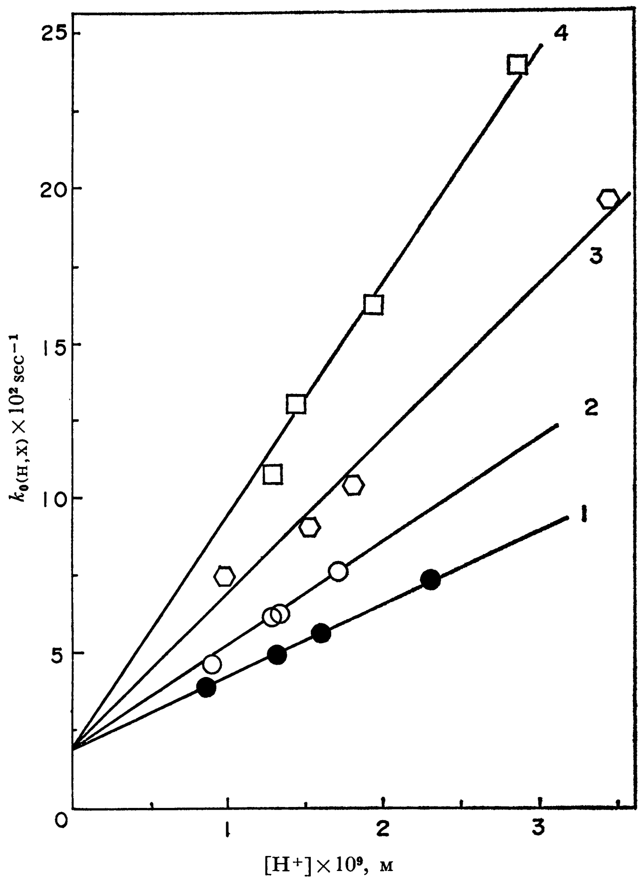

Fig. 3. Effect of the hydrogen ion concentration on conditional rate constants in the presence of halogenide ions. 1: $[\mathrm{X}^-]=0$ M, 2: 2.16×10^{-8} M, 3: $[\mathrm{Br}^-]=0.94\times10^{-4}$ M, 4: $[\mathrm{Cl}^-]=1.00\times10^{-2}$ M, $C_{\mathrm{Hg}}=1.97\times10^{-6}$ M, $C_{\mathrm{CyDTA}}=1.93\times10^{-5}$ M, $C_{\mathrm{PAR}}=2.00\times10^{-4}$ M, $\mu=0.1$ ($\mathrm{NaClO_4}$), 25°C.

TABLE 3. RATE CONSTANTS FOR THE LIGAND SUBSTITUTION REACTION OF THE MERCURY(II)-PAR COMPLEX WITH CyDTA IN THE PRESENCE OF HALOGENIDE ION AT 25°C AND $\mu=0.1$ ($\mathrm{NaClO_4}$)

k_1'	$(2.4\pm0.1)\times10^{7}\ \mathrm{M}^{-1}\,\mathrm{sec}^{-1}$
k_2'	$(1.9\pm0.1)\times10^{-2}\ \mathrm{sec}^{-1}$
$k_{3,\mathrm{Cl}}'$	$(4.5\pm0.2)\times10^{9}\ \mathrm{M}^{-2}\,\mathrm{sec}^{-1}$
$k_{3,\mathrm{Br}}'$	$(3.2\pm0.1)\times10^{11}\ \mathrm{M}^{-2}\,\mathrm{sec}^{-1}$
$k_{3,\mathrm{I}}'$	$(5.6\pm0.2)\times10^{14}\ \mathrm{M}^{-2}\,\mathrm{sec}^{-1}$

Discussion

The rate of the reaction of the mercury(II)-PAR complex with CyDTA is suppressed by the increased PAR concentration, and is first-order with respect to the hydrogen ion concentration. The predominant species of PAR is the mono-protonated form Hpar^-. CyDTA can not react directly with the 1 : 2 mercury(II)-PAR complex $\mathrm{Hg(par)_2}^{2-}$ but with the 1 : 1 mercury(II)-PAR complex Hg(par) formed by the dissociation of a PAR. Thus it seems reasonable to consider Equilibrium (12) to precede the rate-determining step (13).

$$\mathrm{Hg(par)_2}^{2-} + \mathrm{H}^+ \rightleftarrows \mathrm{Hg(par)} + \mathrm{Hpar}^- \tag{12}$$

$$\mathrm{Hg(par)} + \mathrm{Hcydta}^{3-} \longrightarrow \mathrm{Hg(cydta)}^{2-} + \mathrm{Hpar}^- \tag{13}$$

Such a predissociation equilibrium has been observed also in the ligand substitution reactions of the zinc(II)-PAR complex[4] and the copper(II)-PAR complex[6] with (ethyleneglycol)bis(2-aminoethylether)-*N*,*N*,-*N*'-tetraacetic acid. When the equilibrium constant of Reaction (12) is taken into consideration, the following equation can be derived from Eq. (11).

$$-\frac{\mathrm{d}[\mathrm{Hg(par)_2}^{2-}]}{\mathrm{d}t} = \left(\frac{k_1' K^{\mathrm{par}}_{\mathrm{Hg(par)_2}}}{K^{\mathrm{H}}_{\mathrm{Hpar}}} + \frac{k_2' K^{\mathrm{par}}_{\mathrm{Hg(par)_2}}}{K^{\mathrm{H}}_{\mathrm{Hpar}}}[\mathrm{H}^+]^{-1} + \frac{k_{3,\mathrm{X}}' K^{\mathrm{par}}_{\mathrm{Hg(par)_2}}}{K^{\mathrm{H}}_{\mathrm{Hpar}}}[\mathrm{X}^-]\right)[\mathrm{Hg(par)}][\mathrm{Hcydta}^{3-}] \tag{14}$$

where $K^{\mathrm{H}}_{\mathrm{Hpar}}=[\mathrm{Hpar}^-]/[\mathrm{par}^{2-}][\mathrm{H}^+]$ and $K^{\mathrm{par}}_{\mathrm{Hg(par)_2}}=[\mathrm{Hg(par)_2}^{2-}]/[\mathrm{Hg(par)}][\mathrm{par}^{2-}]$.

In the presence of halogenide ions the following equilibrium should be operative in the present ligand substitution.

$$\mathrm{Hg(par)} + \mathrm{X}^- \rightleftarrows \mathrm{Hg(par)X}^- \tag{15}$$

PAR has three coordinate sites (N in pyridine, N in azo and O in resorcinol). The 1 : 1 mercury(II)-PAR complex will accept another ligand. The third term on the right-hand side of Eq. (14) corresponds to the reaction path through the mixed halogeno complex. The second term on the right-hand side of Eq. (14) involves the reciprocal concentration of hydrogen ion. This suggests a reaction path through a mixed hydroxo complex similar to the mixed halogeno complex. Protolytic reaction of mercury(II) ion is sufficiently fast, and the following equilibrium precedes the rate-determining step.

$$\mathrm{Hg(par)} \rightleftarrows \mathrm{Hg(par)OH}^- + \mathrm{H}^+ \tag{16}$$

With constants for Equilibria (15) and (16), Eq. (14) is rewritten as

$$\begin{aligned}-\frac{\mathrm{d}[\mathrm{Hg(par)_2}^{2-}]}{\mathrm{d}t} &= \frac{k_1' K^{\mathrm{par}}_{\mathrm{Hg(par)_2}}}{K^{\mathrm{H}}_{\mathrm{Hpar}}}[\mathrm{Hg(par)}] \\ &+ \frac{k_2'}{K_{\mathrm{W}}}\frac{K^{\mathrm{par}}_{\mathrm{Hg(par)_2}}}{K^{\mathrm{OH}}_{\mathrm{Hg(par)OH}}K^{\mathrm{H}}_{\mathrm{Hpar}}}[\mathrm{Hg(par)OH}^-] \\ &+ \frac{k_{3,\mathrm{X}}' K^{\mathrm{par}}_{\mathrm{Hg(par)_2}}}{K^{\mathrm{X}}_{\mathrm{Hg(par)X}}K^{\mathrm{H}}_{\mathrm{Hpar}}}[\mathrm{Hg(par)X}^-])[\mathrm{Hcydta}^{3-}] \\ &= (k_1[\mathrm{Hg(par)}] + k^{\mathrm{OH}}[\mathrm{Hg(par)OH}^-] \\ &+ k^{\mathrm{X}}[\mathrm{Hg(par)X}^-])[\mathrm{Hcydta}^{3-}]\end{aligned} \tag{17}$$

Some related constants are defined as follows:

$$K_{\mathrm{W}} = [\mathrm{H}^+][\mathrm{OH}^-] \tag{18}$$

$$K^{\mathrm{OH}}_{\mathrm{Hg(par)OH}} = \frac{[\mathrm{Hg(par)OH}^-]}{[\mathrm{Hg(par)}][\mathrm{OH}^-]} \tag{19}$$

$$K^{\mathrm{X}}_{\mathrm{Hg(par)X}} = \frac{[\mathrm{Hg(par)X}^-]}{[\mathrm{Hg(par)}][\mathrm{X}^-]} \tag{20}$$

$$k_1 = k_1'\left(\frac{K^{\mathrm{par}}_{\mathrm{Hg(par)_2}}}{K^{\mathrm{H}}_{\mathrm{Hpar}}}\right) \tag{21}$$

$$k^{\mathrm{OH}} = \frac{k_2'}{K_{\mathrm{W}}}\frac{1}{K^{\mathrm{OH}}_{\mathrm{Hg(par)OH}}}\left(\frac{K^{\mathrm{par}}_{\mathrm{Hg(par)_2}}}{K^{\mathrm{H}}_{\mathrm{Hpar}}}\right) \tag{22}$$

$$k^{\mathrm{X}} = k_{3,\mathrm{X}}'\frac{1}{K^{\mathrm{X}}_{\mathrm{Hg(par)X}}}\left(\frac{K^{\mathrm{par}}_{\mathrm{Hg(par)_2}}}{K^{\mathrm{H}}_{\mathrm{Hpar}}}\right) \tag{23}$$

The proposed reaction mechanism of the mercury(II)-PAR complex with CyDTA in the presence of halogenide ions is as follows:

$$\mathrm{Hg(par)_2}^{2-} + \mathrm{H}^+ \rightleftarrows \mathrm{Hg(par)} + \mathrm{Hpar}^-$$

$$\begin{tikzcd}
\mathrm{Hg(par)OH}^- + \mathrm{Hcydta}^{3-} \arrow[r, "k^{\mathrm{OH}}"] \arrow[d, shift right, "\mathrm{H}^+"'] & \mathrm{Hg(cydta)}^{2-} + \mathrm{Hpar}^- + \mathrm{OH}^- \\
\mathrm{Hg(par)} + \mathrm{Hcydta}^{3-} \arrow[r, "k_1"] \arrow[u, shift right] \arrow[d, shift right, "\mathrm{X}^-"'] & \mathrm{Hg(cydta)}^{2-} + \mathrm{Hpar}^- \\
\mathrm{Hg(par)X}^- + \mathrm{Hcydta}^{3-} \arrow[r, "k^{\mathrm{X}}"] \arrow[u, shift right] & \mathrm{Hg(cydta)}^{2-} + \mathrm{Hpar}^- + \mathrm{X}^-
\end{tikzcd}$$

The equilibria between $\mathrm{Hg(par)_2}^{2-}$ and Hg(par), and between Hg(par) and $\mathrm{Hg(par)X}^-$ precede the rate-determining steps. CyDTA reacts with Hg(par), $\mathrm{Hg(par)OH}^-$, and $\mathrm{Hg(par)X}^-$ formed through the equilibrium processes.

It is necessary to determine $K^{\mathrm{par}}_{\mathrm{Hg(par)_2}}$, $K^{\mathrm{OH}}_{\mathrm{Hg(par)OH}}$ and $K^{\mathrm{X}}_{\mathrm{Hg(par)X}}$ in order to estimate the values of k_1, k^{OH}, and k^{X}. Unfortunately, these stability constants could not be successfully determined because of hydrolysis and precipitation of complexes. As apparent from Fig. 4, the plot of $\log(k_{3,\mathrm{X}}'/k_{3,\mathrm{H_2O}}')$ *vs.* E_n values of ligands (halogenide and hydroxide ions) gives a good straight line with a slope of 6.1, where $k_{3,\mathrm{H_2O}}'$ corresponds to $k_1'/55.5$ and E_n refers to the electron donor constant of a ligand.[13] Since $k_{3,\mathrm{X}}'/k_{3,\mathrm{H_2O}}' = (55.5/k_1) \times k^{\mathrm{X}} K^{\mathrm{X}}_{\mathrm{Hg(par)X}}$ from Eqs. (21)—(23), $\log k^{\mathrm{X}} K^{\mathrm{X}}_{\mathrm{Hg(par)X}}$ has a linear relationship with E_n's of ligands. Therefore, either $\log k^{\mathrm{X}}$ or $\log K^{\mathrm{X}}_{\mathrm{Hg(par)X}}$ or both are proportional to E_n of X. In fact, the following results have been reported in some systems. In the case of the reaction between $\mathrm{Ni(H_2O)A}^+$ and PAR there is an excellent correlation between E_n values of ligands and formation rate constants (where A denotes F^-, $\mathrm{N_3}^-$, $\mathrm{CH_3COO}^-$, OH^-, and $\mathrm{H_2O}$[7])). For the mixed complex of $\mathrm{Hg(cydta)X}^{3-}$, log stability constant $\log K^{\mathrm{X}}_{\mathrm{Hg(cydta)X}}$ is related to E_n of X by a straight line with a slope of 4.[12] The plot of $\log K^{\mathrm{X}}_{\mathrm{HgX_4}}$ *vs.* E_n gives a straight line with a slope of 1.5,[14] $K^{\mathrm{X}}_{\mathrm{HgX_4}}$ being defined as follows: $K^{\mathrm{X}}_{\mathrm{HgX_4}} = [\mathrm{HgX_4}^{2-}]/[\mathrm{HgX_3}^-][\mathrm{X}^-]$. For the mixed complex of the type $\mathrm{Hg(CN)_3X}^{2-}$, the slope of the plot of $\log K^{\mathrm{X}}_{\mathrm{Hg(CN)_3X}}$ *vs.* E_n of X^- has been found to be 2.[15] These facts being taken into account, the slope of the plot of $\log K^{\mathrm{X}}_{\mathrm{Hg(par)X}}$ *vs.* E_n is expected to be smaller than 6.1. This suggests that the rate constant (k^{X}) also depends on the E_n value of a ligand (X^-) coordinated to the mercury(II)-PAR complex; a ligand having larger E_n value tends to weaken the bond of mercury(II) with PAR. When a ligand coordinated to a central metal donates to a greater extent, the bond of the central metal with the leaving ligand will be weakened and more easily broken.

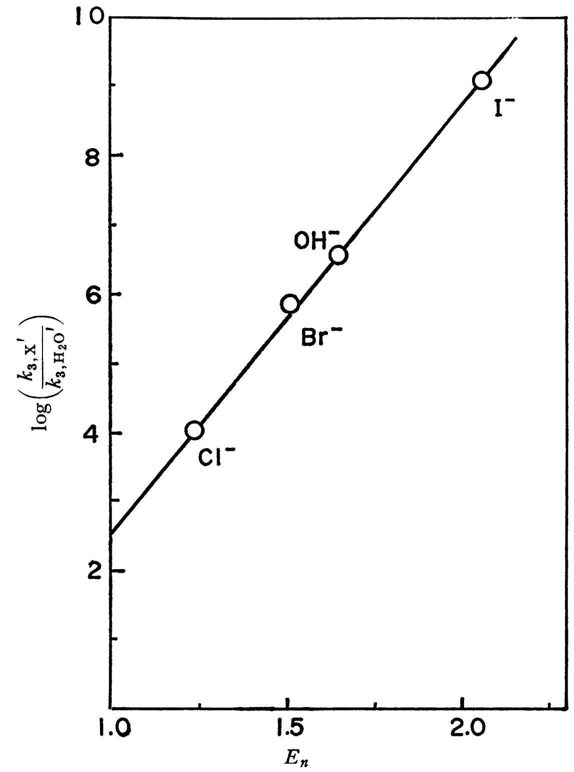

Fig. 4. Plot of $\log(k_{3,\mathrm{X}}'/k_{3,\mathrm{H_2O}}')$ *vs.* E_n.

The financial support given by the Ministry of Education is gratefully acknowledged.

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[13] J. O. Edwards, *J. Amer. Chem. Soc.*, **76**, 1540 (1954).

[14] L. G. Sillén, *Acta Chem. Scand.*, **3**, 539 (1949).

[15] L. Newman and D. N. Hume, *J. Amer. Chem. Soc.*, **83**, 1795 (1961).