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Kinetics and Mechanism of the Ligand-Substitution Reaction of the Copper(II)–4-(2-Pyridylazo)resorcinol Complex with *trans*-1,2-Diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetraacetic Acid with Special Reference to the Effect of Unidentate Ligands

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Received September 18, 1977

The kinetics of the ligand-substitution reaction of the copper(II)–4-(2-pyridylazo)resorcinol complex (Cu^{II}-PAR) with *trans*-1,2-diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetraacetic acid (CyDTA) has been studied spectrophotometrically in the presence of unidentate ligands ($L = NH_3, CH_3COO^-, N_3^-, SCN^-, Cl^-, Br^-$, and I^-) and in the pH range 9.0–10.0 at $I = 1.0$ ($NaClO_4$) and at 25 °C. The rate of the substitution reaction is expressed as $-d[Cu(par)_2{}^{2-}]/dt = k_1[Cu(par)][cydta'] + k_{OH}\cdot[Cu(par)OH^-][cydta'] + k_L[Cu(par)L][cydta']$, where cydta′ denotes CyDTA not combined with copper ion, and $k_1 = 1.57 \pm 0.03$ mol^{-1} dm^3 s^{-1}, $k_{OH} = 0.491 \pm 0.034$ mol^{-1} dm^3 s^{-1}, $k_{NH_3} = 1.73 \pm 0.014$ mol^{-1} dm^3 s^{-1}, $k_{CH_3COO} = 0.183 \pm 0.006$ mol^{-1} dm^3 s^{-1}, $k_{N_3} = 0.672 \pm 0.020$ mol^{-1} dm^3 s^{-1}, $k_{SCN} = 0.303 \pm 0.008$ mol^{-1} dm^3 s^{-1}, $k_{Cl} = 0.26 \pm 0.11$ mol^{-1} dm^3 s^{-1}, $k_{Br} = 0.70 \pm 0.18$ mol^{-1} dm^3 s^{-1}, and $k_I = 1.33 \pm 0.07$ mol^{-1} dm^3 s^{-1}, all at 25 °C and $I = 1.0$. The reactivity of the mixed-ligand complex (Cu(par)L) is discussed in terms of the electron donation from L.

Introduction

The ligand-substitution reaction often proceeds through an intermediate mixed-ligand complex, in which the central metal ion is simultaneously bonded to both leaving and entering ligands. The rate-determining step of the reaction is the cleavage of the bonds of the metal ion and leaving group. For instance, Ni(edda) and $Ni(nta)^-$ react with PAR to give intermediate mixed-ligand complexes $Ni(edda)par^{2-}$ and $Ni(nta)par^{3-}$, respectively[2] ($edda^{2-}$ = ethylenediamine-*N*,*N'*-diacetate, nta^{3-} = nitrilotriacetate, PAR = 4-(2-pyridylazo)resorcinol (H_2par)). The reaction of $Ni(dien)^{2+}$ and EDTA gives $Ni(dien)edta^{2-}$ as a fast step (dien = diethylenetriamine).[3] Furthermore, a third ligand being incorporated in the mixed-ligand intermediates, the reaction rates are sometimes dramatically accelerated by added ligands.[4-8] Thus, the formation of the mixed-ligand intermediate plays an important thermodynamic and kinetic role in the overall reaction processes.

The kinetic effect of coordinated ligands in the mixed-ligand complexes has also been reported for the dissociation reaction of various nickel(II)–malonate mixed-ligand complexes by Hoffmann and Yeager,[9] and a correlation, except for some ligands, has been found between the dissociation rate and the observed spectral shift of the d–d orbital transition of the mixed-ligand complex.

Zinto et al.,[10] in a study of the aquation of a series of substituted acetatopentaammine chromium complexes ($Cr(NH_3)_5(RCOO)^{2+}$, R = CCl_3, $CHCl_2$, CH_2Cl, CH_3), have related the rate of aquation of NH_3 with the basicity of $RCOO^-$ and suggested the hydrogen bond formation between acetate and NH_3 in the cis position. According to them, the stronger the hydrogen bond, the faster is the rate of ammonia dissociation. However, the increased rate of aquation with increasing basicity of $RCOO^-$ may alternatively be attributable to the increased electron donation from carboxylates.

Nakagawa and Wada[11] have found an accelerating effect of 1,10-phenanthroline (phen) in the ligand-substitution reaction of $Cu(pan)^+$ (pan = 1-(2-pyridylazo)-2-naphthol) with EDTA. They have explained the kinetic data in terms of the structural property of the distorted octahedral mixed-ligand complex Cu(pan)phen.

In previous papers,[7,8] we have reported on the acceleration of the ligand-substitution reaction of certain mercury(II) complexes with *trans*-1,2-diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetraacetic acid (CyDTA) in the presence of halide ions or of ammonia. In this reaction we have mixed halogeno- or hydroxo or ammine complexes of mercury(II). The reaction rate (k_0) is formulated as the product of the formation constant of the mixed-ligand complex (K_M) and the dissociation rate constant (k_d); $k_0 = K_M k_d$. We wish to understand the extent of these two effects. To this end the formation constants of the mixed-ligand complexes of Cu^{II}–PAR with unidentate ligands ($L = NH_3$, pyridine, CH_3COO^-, N_3^-, SCN^-, Cl^-, Br^-, I^-) have been determined by spectrophotometry.[12] The logarithmic formation constant has been related with both the electron-donor constant (E_n) and the basicity constant (H) of the unidentate ligand. The present paper describes the kinetic results on the substitution reaction

$$Cu^{II}\text{–PAR} + \text{CyDTA} \rightleftharpoons Cu^{II}\text{–CyDTA} + \text{PAR}$$

in the presence of these unidentate ligands.

Experimental Section

Reagents. Methods of preparation and standardization of the reagents (copper(II) perchlorate, unidentate ligands, CyDTA, sodium perchlorate, and sodium hydroxide) have been described previously.[12]

Measurements. The kinetics of the substitution reaction was studied spectrophotometrically by recording the change of absorbance of Cu^{II}–PAR complex at 500 nm as a function of the reaction time with a Toa EPR-100A recorder. The absorbance was measured with a Hitachi 139 UV–vis spectrophotometer with a thermostated 10-mm

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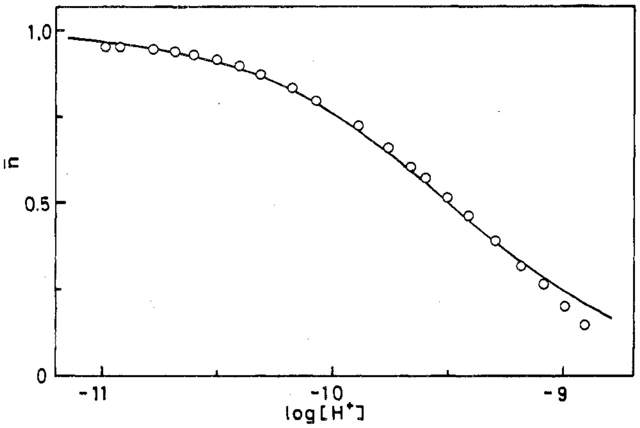


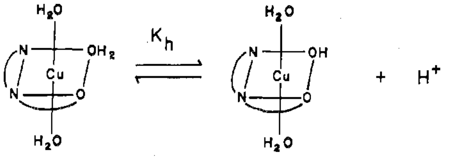
Figure 1. Determination of the formation constant of Cu(par)OH$^-$ at 25 °C and $I = 1.0$ (NaClO$_4$). Initial concentration of Cu^{II}–PAR complex is 1.01×10^{-3} mol dm^{-3}.

cell. The reaction was started by mixing two solutions, i.e., one containing Cu^{II}–PAR complex, unidentate ligand, borate buffer, and sodium perchlorate, and the other containing CyDTA, borate buffer, and sodium perchlorate.

pH was varied by addition of buffer solution of sodium borate and boric acid or of sodium borate and sodium hydroxide. The pH was determined by a Toa digital pH meter HM-15A with a calomel electrode filled with saturated sodium chloride. A 1.002×10^{-2} mol dm^{-3} perchloric acid solution containing 0.99 mol dm^{-3} sodium perchlorate was employed as a standard of hydrogen ion concentration ($-\log [H^+] = 2.001$). From pH meter readings at various hydrogen ion concentrations at an ionic strength of 1.0 (H, Na)(ClO$_4$), the glass electrode was calibrated to read the hydrogen ion concentration.

All experiments were carried out at 25.0 ± 0.1 °C and an ionic strength of 1.0 (NaClO$_4$).

Formation Constant of the Hydroxo Mixed-Ligand Complex Cu(par)OH$^-$. It is necessary to determine the formation constant of the hydroxo mixed-ligand complex Cu(par)OH$^-$ to elucidate the equilibria involved in the ligand-substitution reaction. At pH higher than 5, the species Cu(par) prevails ($K^H_{Cu(Hpar)} = [Cu(Hpar)^+]\cdot[Cu(par)]^{-1}[H^+]^{-1} = 10^{5.00}$[13]). The 1:1 Cu^{II}–PAR complex hydrolyzes at higher pH:



(1)

where par is symbolized as N–N–O. The formation constant defined as $K_h = [Cu(par)OH^-][H^+]/[Cu(par)]$ was determined by pH titration. Alkaline Cu^{II}–PAR solution containing 1.01×10^{-3} mol dm^{-3} Cu(ClO$_4$)$_2$, 1.01×10^{-3} mol dm^{-3} PAR, and 1.00 mol dm^{-3} NaClO$_4$ was titrated with 3.21×10^{-2} mol dm^{-3} HClO$_4$ solution containing 0.97 mol dm^{-3} NaClO$_4$. The titration was carried out under nitrogen atmosphere at 25 °C. The formation constant, K_h, was calculated by using the formation function $\bar{n}$ defined as follows:

$$\bar{n} = [Cu(par)OH^-]/([Cu(par)] + [Cu(par)OH^-]) = K_h[H^+]^{-1}/(1 + K_h[H^+]^{-1})$$

The plot of $\bar{n}$ vs. log [H$^+$] is shown in Figure 1. Using a set of normalized curves, $x = -\log v$, $y = v/(1 + v)$, we obtained the value of $\log K_h = -9.49 \pm 0.03$. In Figure 1, the solid curve is calculated with the obtained constant. The experimental values deviate from the solid curve at lower pH because of the precipitation of the neutral 1:1 Cu(par) complex.

Protonation Constants of CyDTA. The protonation constants of CyDTA, especially the first protonation constant defined as $K^H_{Hcydta} = [Hcydta^{3-}]/[cydta^{4-}][H^+]$, are affected by cations used in constant ionic medium.[14] Therefore, the protonation constants were determined by potentiometry at an ionic strength of 1.0 (NaClO$_4$) and 25 °C.

CyDTA solution containing 9.38×10^{-3} mol dm^{-3} CyDTA, 9.43×10^{-3} mol dm^{-3} NaOH, and 0.99 mol dm^{-3} NaClO$_4$ was titrated with 9.80×10^{-2} mol dm^{-3} HClO$_4$ containing 0.99 mol dm^{-3} NaClO$_4$. In the basic solution where Hcydta^{3-} and H$_2$cydta^{2-} are prevailing, the average number of H$^+$ bonded to cydta^{4-} is expressed as follows:

$$\bar{n} = ([Hcydta^{3-}] + 2[H_2cydta^{2-}])/([cydta^{4-}] + [Hcydta^{3-}] + [H_2cydta^{2-}]) = (K^H_{Hcydta}[H^+] + 2K^H_{Hcydta}K^H_{H_2cydta}[H^+]^2)/(1 + K^H_{Hcydta}[H^+] + K^H_{Hcydta}K^H_{H_2cydta}[H^+]^2)$$

Using a set of normalized curves, $x = \log v$, $y = (pv + 2v^2)/(1 + pv + v^2)$, we were able to obtain K^H_{Hcydta} and $K^H_{H_2cydta}$ as 9.28 ± 0.02 and 5.96 ± 0.02, respectively. These values compare favorably with the previous values at $I = 1.0$ (NaClO$_4$) and 20 °C.[15]

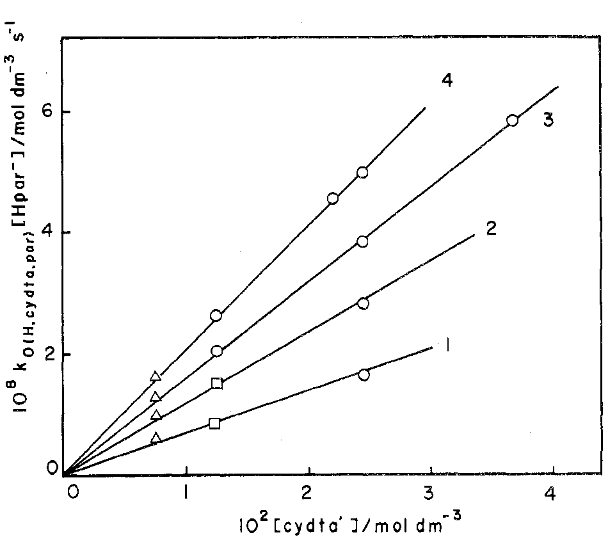


Figure 2. Plot of $k_{0(H,par,cydta)}$[Hpar$^-$] vs. [cydta′] at 25 °C and $I = 1.0$. $C_{Cu} = 7.36 \times 10^{-6}$ mol dm^{-3}. 10^4C_{PAR}/mol dm^{-3} = 1.61 (△), 2.05 (○), and 4.10 (□), at pH 9.80 (1), 9.55 (2), 9.39 (3), 9.24 (4).

Results

The reaction of the Cu^{II}–PAR complex with CyDTA was studied in the presence of a large excess of PAR, CyDTA, and unidentate ligand compared to copper(II) at pH from 9.0 to 10.0. Under the present experimental conditions, the predominant species of Cu^{II}–PAR complex and PAR are the 1:2 complex Cu(par)$_2^{2-}$ and the monoprotonated species Hpar$^-$, respectively,[16] and the species of CyDTA is Na(cydta)$^{3-}$ and Hcydta^{3-} (vide infra). Thus the substitution reaction is written as

$$Cu(par)_2^{2-} + cydta' \rightarrow Cu(cydta)^{2-} + 2Hpar^-$$

where cydta′ denotes CyDTA not combined with copper ion. The reaction goes substantially to completion and the reverse reaction can be neglected.

For the reaction with a large excess of CyDTA, PAR, and unidentate ligand the rate equation can be expressed as

$$-d[Cu(par)_2^{2-}]/dt = k_{0(H,par,cydta,L)}[Cu(par)_2^{2-}]$$

where $k_{0(H,par,cydta,L)}$ denotes the conditional rate constant containing concentrations of hydrogen ion, PAR, CyDTA, and unidentate ligand. The first-order plot $\ln [(A_0 - A_\infty)/(A_t - A_\infty)]$ vs. t gave a good straight line (A_0, A_t, and A_∞ are the absorbances of the reaction system at reaction times 0, t, and ∞, respectively). Then the conditional rate constant $k_{0(H,par,cydta,L)}$ was determined from the slope of the straight line. $k_{0(H,par,cydta)}$ is linearly related with the reciprocal PAR concentration with zero intercept. Thus in Figure 2, values of $k_{0(H,par,cydta)}$[Hpar$^-$] are plotted against the concentration of CyDTA at constant pH. The plots fall along straight lines with zero intercept. In Figure 3, values of $k_{0(H,par,cydta)}$ determined at various pH's and concentrations of CyDTA and PAR are plotted against the hydrogen ion concentration. Figure 3 indicates clearly a linear relationship between $k_{0(H,par,cydta)}$ and the hydrogen ion concentration with nonzero

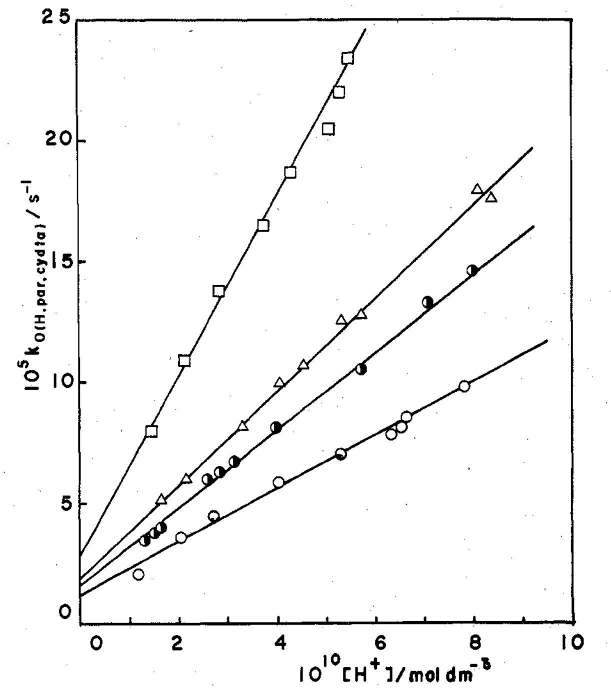


Figure 3. Plot of $k_{0(\mathrm{H,par,cydta})}$ vs. $[\mathrm{H}^+]$ at 25 °C and $I = 1.0$ ($\mathrm{NaClO_4}$). $C_{\mathrm{Cu}} = 7.36 \times 10^{-6}$ mol dm^{-3}. $10^2 C_{\mathrm{CyDTA}}$/mol dm^{-3} = 1.23 (○), 0.750 (◐), 1.23 (△), and 2.45 (□). $10^4 C_{\mathrm{PAR}}$/mol dm^{-3} = 4.10 (○), 1.61 (◐), 2.05 (△), and 2.05 (□).

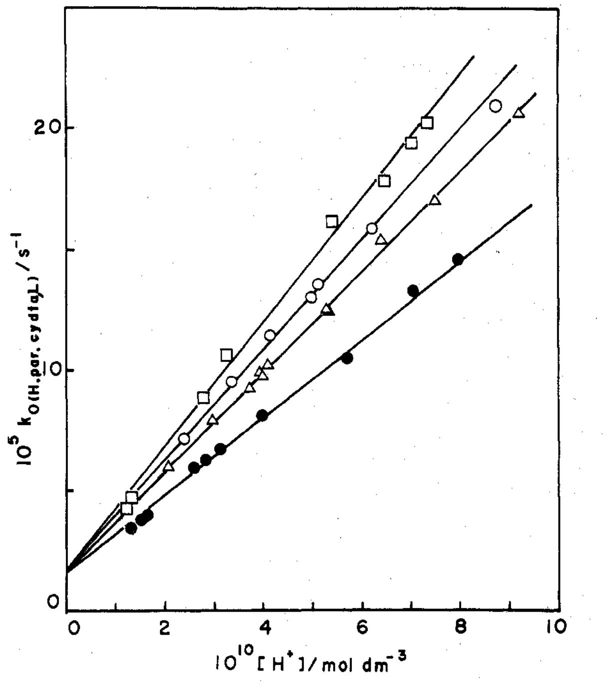


Figure 4. Plot of $k_{0(\mathrm{H,par,cydta,L})}$ vs. $[\mathrm{H}^+]$ at 25 °C and $I = 1.0$. Concentrations of unidentate ligands are as follows (in mol dm^{-3}): [L] = 0 (●), $[\mathrm{N_3}^-] = 1.06 \times 10^{-2}$ (△), $[\mathrm{CH_3COO}^-] = 0.100$ (○), $[\mathrm{I}^-] = 0.937$ (□). $C_{\mathrm{Cu}} = 7.36 \times 10^{-6}$ mol dm^{-3} for all but iodide where $C_{\mathrm{Cu}} = 1.10 \times 10^{-5}$ mol dm^{-3}. $C_{\mathrm{PAR}} = 1.61 \times 10^{-4}$ mol dm^{-3} and $C_{\mathrm{CyDTA}} = 7.50 \times 10^{-3}$ mol dm^{-3} for all but acetate where $C_{\mathrm{PAR}} = 2.05 \times 10^{-4}$ mol dm^{-3} and $C_{\mathrm{CyDTA}} = 1.23 \times 10^{-2}$ mol dm^{-3}.

intercept. The nonzero intercept suggests a rate expression involving the $[\mathrm{H}^+]$-independent term. Thus the conditional rate constant is expressed by

$$\begin{aligned} k_{0(\mathrm{H,par,cydta})} &= k_{0(\mathrm{H})}[\mathrm{cydta}']/[\mathrm{Hpar}^-] \\ &= (k_1'[\mathrm{H}^+] + k_2')[\mathrm{cydta}']/[\mathrm{Hpar}^-] \quad (2) \end{aligned}$$

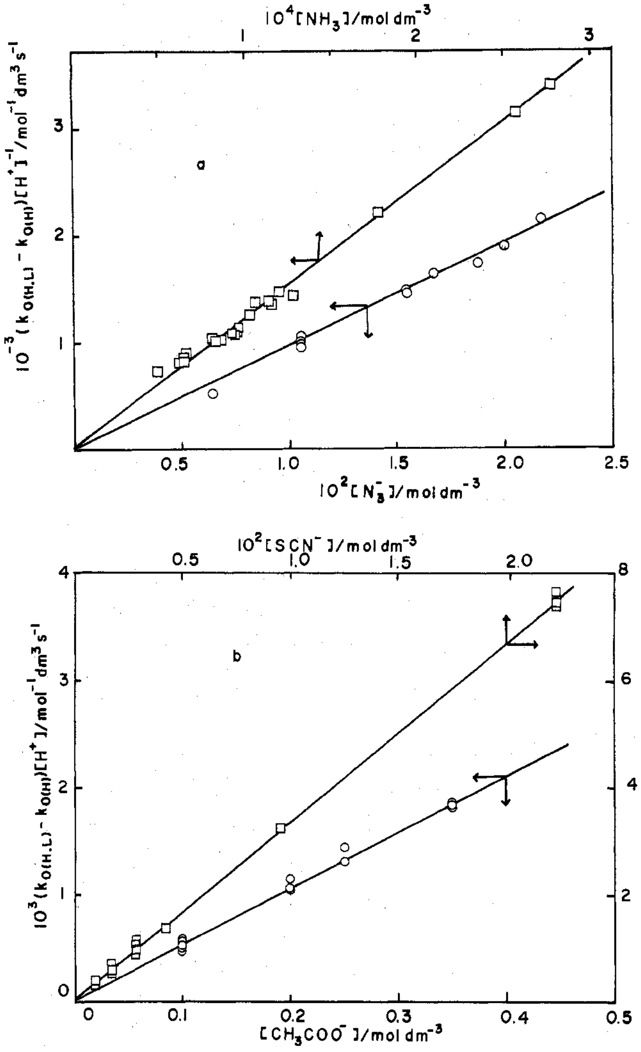


Figure 5. Plot of $(k_{0(\mathrm{H,L})} - k_{0(\mathrm{H})})/[\mathrm{H}^+]$ vs. [L]. Concentrations of copper(II), PAR, and CyDTA are as follows (in mol dm^{-3}): $C_{\mathrm{Cu}} = 7.36 \times 10^{-6}$, $C_{\mathrm{PAR}} = 1.61 \times 10^{-4}$, and $C_{\mathrm{CyDTA}} = 7.50 \times 10^{-3}$ for azide (○) and ammonia (□) in (a), $C_{\mathrm{Cu}} = 7.36 \times 10^{-6}$, $C_{\mathrm{PAR}} = 2.05 \times 10^{-4}$, and $C_{\mathrm{CyDTA}} = 1.23 \times 10^{-2}$ for acetate (○) in (b), and $C_{\mathrm{Cu}} = 6.48 \times 10^{-6}$, $C_{\mathrm{PAR}} = 2.13 \times 10^{-4}$, and $C_{\mathrm{CyDTA}} = 9.90 \times 10^{-3}$ for thiocyanate (□) in (b).

Ligand Substitution Reaction in the Presence of Unidentate Ligands. Unidentate ligands accelerate the substitution reaction of the $\mathrm{Cu^{II}}$–PAR complex with CyDTA. The conditional rate constants in the presence of unidentate ligands are plotted against hydrogen ion concentrations in Figure 4. The rate constants are linearly related to the hydrogen ion concentration. The intercept corresponding to the reaction path independent of the hydrogen ion concentration is the same as that found in the reaction without unidentate ligand. Hence, we have the following relationship:

$$k_{0(\mathrm{H,par,cydta,L})}[\mathrm{Hpar}^-]/[\mathrm{cydta}'] = k_{0(\mathrm{H,L})} = k_{0(\mathrm{H})} + k_{0(\mathrm{L})}[\mathrm{H}^+] \quad (3)$$

In Figure 5, the value of $(k_{0(\mathrm{H,L})} - k_{0(\mathrm{H})})/[\mathrm{H}^+]$ is plotted against the concentration of the unidentate ligand. The plot gives a straight line. Thus eq 3 can be rewritten as

$$k_{0(\mathrm{H})} = (k_{0(\mathrm{H,L})} - k_{0(\mathrm{H})})/[\mathrm{H}^+] = k'_{3,\mathrm{L}}[\mathrm{L}] \quad (4)$$

From eq 2–4 we obtain the following rate equation for the substitution reaction in the presence of unidentate ligand:

$$\begin{aligned} -\mathrm{d}[\mathrm{Cu(par)_2}^{2-}]/\mathrm{d}t &= k_{0(\mathrm{H,par,cydta,L})}[\mathrm{Cu(par)_2}^{2-}] = \\ k_{0(\mathrm{H,L})}[\mathrm{Cu(par)_2}^{2-}][\mathrm{cydta}'][\mathrm{Hpar}^-]^{-1} &= (k_1'[\mathrm{H}^+] + k_2' + \\ k_{3,\mathrm{L}}'[\mathrm{H}^+][\mathrm{L}])[\mathrm{Cu(par)_2}^{2-}]&[\mathrm{cydta}'][\mathrm{Hpar}^-]^{-1} \quad (5) \end{aligned}$$

Scheme I

$$\begin{array}{l}
\mathrm{Cu(par)_2}^{2-} + \mathrm{H}^+ \rightleftharpoons \mathrm{Cu(par)} + \mathrm{Hpar}^- \\
\mathrm{Cu(par)OH}^- + \mathrm{cydta}' \xrightarrow{k_2} \mathrm{Cu(cydta)}^{2-} + \mathrm{Hpar}^- \\
\quad \Updownarrow -\mathrm{H}^+ \\
\mathrm{Cu(par)} + \mathrm{cydta}' \xrightarrow{k_1} \mathrm{Cu(cydta)}^{2-} + \mathrm{Hpar}^- \\
\mathrm{L} \Updownarrow \\
\mathrm{Cu(par)L} + \mathrm{cydta}' \xrightarrow{k_{3,\mathrm{L}}} \mathrm{Cu(cydta)}^{2-} + \mathrm{Hpar}^- + \mathrm{L}
\end{array}$$

The rate of the reaction of the $\mathrm{Cu^{II}}$–PAR complex with CyDTA decreases with increasing PAR concentration. The reaction is first order with respect to CyDTA and hydrogen ion concentration. CyDTA cannot react directly with the 1:2 $\mathrm{Cu^{II}}$–PAR complex but it reacts with the 1:1 $\mathrm{Cu^{II}}$–PAR complex. Thus equilibrium 6 precedes rate-determining step 7. Such a predissociation equilibrium has been observed also

$$\mathrm{Cu(par)_2}^{2-} + \mathrm{H}^+ \rightleftharpoons \mathrm{Cu(par)} + \mathrm{Hpar}^- \tag{6}$$

$$\mathrm{Cu(par)} + \mathrm{cydta}' \rightarrow \mathrm{Cu(cydta)}^{2-} + \mathrm{Hpar}^- \tag{7}$$

in the ligand-substitution reactions of $\mathrm{Cu^{II}}$–PAR complex with (ethylene glycol)bis(2-aminoethyl ether)-*N*,*N*,*N'*,*N'*-tetraacetic acid (EGTA)[17] and $\mathrm{Hg^{II}}$–PAR complex with CyDTA.[7] In the presence of unidentate ligand, the following equilibrium should also precede the rate-determining step

$$\mathrm{Cu(par)} + \mathrm{L} \rightleftharpoons \mathrm{Cu(par)L} \tag{8}$$

The formation constant of the mixed-ligand complex has been determined for several unidentates.[12] The third term on the right-hand side of eq 5 corresponds to the reaction path through the mixed-ligand complex containing unidentate ligand. The second term on the right-hand side of eq 5 is independent of hydrogen ion concentration. This suggests a reaction path through a mixed hydroxo complex $\mathrm{Cu(par)OH^-}$ produced by eq 1 preceding the rate-determining step. When the equilibrium constants of reactions 1, 6, and 8 are taken into consideration, the following rate equation is derived from eq 5:

$$\begin{aligned}
-\mathrm{d}[\mathrm{Cu(par)_2}^{2-}]/\mathrm{d}t &= (k_1'[\mathrm{Cu(par)}] + k_2'K_\mathrm{h}^{-1}[\mathrm{Cu(par)OH^-}] + \\
&\qquad k_{3,\mathrm{L}}'(K^{\mathrm{L}}{}_{\mathrm{Cu(par)L}})^{-1}[\mathrm{Cu(par)L}])K^{\mathrm{Hpar}}{}_{\mathrm{Cu(par)_2}}[\mathrm{cydta}'] \\
&= k_1[\mathrm{Cu(par)}][\mathrm{cydta}'] + k_2[\mathrm{Cu(par)OH^-}][\mathrm{cydta}'] + \\
&\qquad k_{3,\mathrm{L}}[\mathrm{Cu(par)L}][\mathrm{cydta}']
\end{aligned} \tag{9}$$

where $K^{\mathrm{Hpar}}{}_{\mathrm{Cu(par)_2}} = [\mathrm{Cu(par)_2}^{2-}][\mathrm{H^+}]/[\mathrm{Cu(par)}][\mathrm{Hpar^-}]$, $K_\mathrm{h} = [\mathrm{Cu(par)OH^-}][\mathrm{H^+}]/[\mathrm{Cu(par)}]$, and $K^{\mathrm{L}}{}_{\mathrm{Cu(par)L}} = [\mathrm{Cu(par)L}]/[\mathrm{Cu(par)}][\mathrm{L}]$. These equilibrium constants being determined independently, we are able to determine values of k_1, k_2, and $k_{3,\mathrm{L}}$, which are summarized in Table I.

The proposed reaction mechanism of the $\mathrm{Cu^{II}}$–PAR complex with CyDTA in the presence of unidentate ligand is as shown in Scheme I. Rapid formation of Cu(par), $\mathrm{Cu(par)OH^-}$ and Cu(par)L precedes the rate-determining step. CyDTA reacts with Cu(par), $\mathrm{Cu(par)OH^-}$, and Cu(par)L yielding the common product $\mathrm{Cu(cydta)^{2-}}$.

Discussion

Under the present experimental conditions the dominant species of CyDTA are $\mathrm{Na(cydta)^{3-}}$ and $\mathrm{Hcydta^{3-}}$ as apparent from the protonation constant $K^{\mathrm{H}}{}_{\mathrm{Hcydta}} = 10^{9.28\pm0.02}$. However, we observe no variation of the rate varying extent of protonation of CyDTA (Figure 3). The substitution reaction of some metal complexes of $\mathrm{cydta^{4-}}$ is faster than that with $\mathrm{Hcydta^{3-}}$.[18,19] However, the substitution reaction with $\mathrm{Na(cydta)^{3-}}$ is nearly the same as with $\mathrm{Hcydta^{3-}}$.

The ligand-substitution reaction of $\mathrm{Cu^{II}}$–PAR complex with EGTA has been reported and the reaction mechanism is the same as that of the present study.[17] The rate constant is 8.8 × 10^2 $\mathrm{mol^{-1}\,dm^3\,s^{-1}}$ at 25 °C and an ionic strength of 0.1 ($\mathrm{NaClO_4}$). For the substitution reaction of $\mathrm{Cu^{II}}$–PAN complex with EDTA the rate constant is 1.7 × 10^3 $\mathrm{mol^{-1}\,dm^3\,s^{-1}}$.[11] The reacting site of PAN is similar to PAR. The rate of substitution of $\mathrm{Cu^{II}}$–PAR or $\mathrm{Cu^{II}}$–PAN complex with EGTA or EDTA is about 1000 times as high as that of the $\mathrm{Cu^{II}}$–PAR complex with CyDTA. Slower substitution reaction of CyDTA compared to EDTA has been observed by some authors.[20-22] The rate constant for CyDTA substitution of $\mathrm{Pb(edta)^{2+}}$ complex is approximately 160 times slower than that for EDTA.[20,21] Likewise, the rate constant for CyDTA substitution of Ni(hida) complex ($\mathrm{hida^{2-}}$ denotes 2-hydroxyethyliminodiacetate) is approximately five times slower than that for EDTA.[22]

Table I. Rate Constants for Substitution Reaction and Formation Constants of Mixed-Ligand Complexes Cu(par)L at 25 °C and I = 1.0

ligand	$k_{3,\mathrm{L}}$/mol^{-1} dm^3 s^{-1}	log $K^{\mathrm{L}}{}_{\mathrm{Cu(par)L}}$[a]	E_n[b]
H_2O	1.57 ± 0.03		0.00
OH^-	0.491 ± 0.034	4.31 ± 0.03[c]	1.65
NH_3	1.73 ± 0.014	3.51 ± 0.08	1.84
CH_3COO^-	0.183 ± 0.006	1.12 ± 0.08	0.95
N_3^-	0.672 ± 0.020	1.81 ± 0.09	1.58
SCN^-	0.303 ± 0.008	1.70 ± 0.04	1.83
Cl^-	0.26 ± 0.11	−0.35 ± 0.07	1.24
Br^-	0.70 ± 0.18	−0.42 ± 0.06	1.51
I^-	1.33 ± 0.07	−0.15 ± 0.05	2.06

[a] In $\mathrm{mol^{-1}\,dm^3}$. Tabata, M.; Tanaka, M. *J. Inorg. Nucl. Chem.* 1976, 38, 1529. [b] Electron donor constant, Edwards, J. O. *J. Am. Chem. Soc.* 1954, 76, 1540. [c] K_W is $10^{13.80}$ at 25 °C and I = 1.0: "Stability Constants of Metal-Ion Complexes", Supplement No. 1; The Chemical Society: London, 1971.

As reported previously,[7,17,23] in the ligand-substitution reaction of metal complex with multidentate ligand, the rate-determining step is the loss of a leaving group from the intermediate involving the leaving and entering groups. Thus the reaction of these copper complexes with aminopolycarboxylates is given by

$$\mathrm{CuR} + \mathrm{Y} \xrightleftharpoons{K^{\mathrm{Y}}{}_{\mathrm{CuRY}}} \mathrm{CuRY} \xrightarrow{k^{-\mathrm{R}}{}_{\mathrm{CuRY}}} \mathrm{CuY} + \mathrm{R}$$

where R and Y denote a chromogenic reagent such as PAR and PAN and an aminopolycarboxylate such as CyDTA, EGTA, and EDTA, respectively, and $K^{\mathrm{Y}}{}_{\mathrm{CuRY}}$ (=[CuRY]/[CuR][Y]) is the formation constant of the intermediate in which aminopolycarboxylate is partly coordinated to Cu(II) with its segment. The experimentally determined rate constant k is expressed as $k = k^{-\mathrm{R}}{}_{\mathrm{CuRY}}K^{\mathrm{Y}}{}_{\mathrm{CuRY}}$, where $k^{-\mathrm{R}}{}_{\mathrm{CuRY}}$ denotes the rate constant for copper(II)–R bond rupture. The steric hindrance of cyclohexane ring for CyDTA seems to be operative in the formation of the intermediate as well as in the bond rupture. The experimental $K^{\mathrm{Y}}{}_{\mathrm{CuRY}}$ value not being available for the present system, the value is estimated from the formation constant of the mixed-ligand complex of Cu(par) complex with a ligand having segments of aminopolycarboxylate.

The formation constants of the related mixed-ligand complexes are given in Table II. As apparent from Table II, the cyclohexyl substitution (*N*-cyclohexyliminodiacetic acid (CyIDA) and *N*-methyl-*N*-cyclohexylglycine (MCG)) increases the basicity of the ligand nitrogen as compared to that of NH_3 or Gly or iminodiacetic acid (IDA). However, the formation constant of the mixed-ligand complex of $\mathrm{Cu(par)cyida^{2-}}$ or $\mathrm{Cu(par)mcg^-}$ is nearly equal to that of $\mathrm{Cu(par)NH_3}$ or Cu(pan)gly. This suggests that these ligands are bonded to copper ion through amine nitrogen in the mixed-ligand complexes and that the axial bond of copper with

Table II. Formation Constants of Mixed-Ligand Complexes of Cu(par)A or Cu(pan)A

A	$\log K^{\mathrm{H}}{}_{\mathrm{HA}}$[c]	$\log K^{\mathrm{A}}{}_{\mathrm{CuRA}}$[d]	ref
		Cu(par)A	
CyIDA[a]	10.71 ± 0.01	3.70 ± 0.04	*e*
MCG[b]	10.96 ± 0.01	3.76 ± 0.05	*e*
NH_3	9.47	3.51 ± 0.08	*f*
		Cu(pan)A	
Gly	9.40	3.40	*g*
IDA	9.50	4.69	*g*

[a] *N*-Cyclyhexyliminodiacetic acid. [b] *N*-Methyl-*N*-cyclohexylglycine. [c] $K^{\mathrm{H}}{}_{\mathrm{HA}} = [\mathrm{HA}]/[\mathrm{H}^+][\mathrm{A}]$. [d] $K^{\mathrm{A}}{}_{\mathrm{CuRA}} = [\mathrm{CuRA}]/[\mathrm{CuR}][\mathrm{A}]$ and R denotes PAR or PAN. [e] At $I = 1.0$ ($NaClO_4$) and 25 °C, and details will be reported elsewhere. [f] Tabata, M.; Tanaka, M. *J. Inorg. Nucl. Chem.* 1976, 38, 1529. [g] At $I = 0.1$ and 25 °C. Wada, H.; Ikuta, K.; Nakagawa, G. *Bull. Chem. Soc. Jpn.*, in press.

acetate is weak. On the other hand, the formation constant of mixed-ligand complex Cu(pan)ida$^-$ is ca. 10 times higher than those of the other mixed-ligand complexes. It seems likely that, in the mixed-ligand complexes, CuRY, CyDTA, and EDTA are bonded to Cu(II) as are CyIDA and IDA, respectively. Thus, CyDTA forms a weaker intermediate mixed-ligand complex Cu(par)cydta^{4-} as compared to Cu(par)edta^{4-}.

Furthermore, the formation constant of sodium complex with CyDTA is much larger than that of EGTA or EDTA. The value is as follows: $K^{\mathrm{Na}}{}_{\mathrm{Na(cydta)}} = 10^{4.66}$ at 25 °C and $I = 0.5$,[14] $K^{\mathrm{Na}}{}_{\mathrm{Na(egta)}} = 10^{1.38}$ at 25 °C and $I = 1.5$,[23] and $K^{\mathrm{Na}}{}_{\mathrm{Na(edta)}} = 10^{1.66}$ at 20 °C and $I = 0.1$.[24] The sodium complex would reduce the formation of the intermediate complex Cu(par)cydta^{4-}. Thus the lower rate of substitution reaction with CyDTA with EDTA or EGTA is partly attributable to the decreased formation of the intermediate mixed-ligand complex.

Kinetic Effect of Unidentate Ligands. As described above, the Cu$^{\mathrm{II}}$–PAR complex forms an intermediate complex Cu(par)cydta^{4-} before the rate-determining step. In the presence of a unidentate ligand L, the equatorial coordination sites of copper ion are filled with PAR and L. Therefore, entering ligand CyDTA has to coordinate weakly through carboxylate at the axial position in the reaction intermediate Cu(par)L(cydta).[25]

The rate of the reaction through the mixed-ligand intermediate Cu(par)L(cydta) is given by

$$\begin{aligned}\text{rate} &= k^{-\mathrm{par}}[\mathrm{Cu(par)L(cydta)}]\\ &= k^{-\mathrm{par}}K^{\mathrm{cydta}}{}_{\mathrm{Cu(par)L(cydta)}}K^{\mathrm{L}}{}_{\mathrm{Cu(par)L}}[\mathrm{Cu(par)}][\mathrm{L}][\mathrm{cydta'}]\\ &= k'_{3,\mathrm{L}}K^{\mathrm{Hpar}}{}_{\mathrm{Cu(par)_2}}[\mathrm{Cu(par)}][\mathrm{L}][\mathrm{cydta'}] \qquad (10)\end{aligned}$$

where $k^{-\mathrm{par}}$ denotes the rate of dissociation of PAR from Cu(par)L(cydta). From eq 10 it follows

$$k'_{3,\mathrm{L}} = k^{-\mathrm{par}}K^{\mathrm{cydta}}{}_{\mathrm{Cu(par)L(cydta)}}K^{\mathrm{L}}{}_{\mathrm{Cu(par)L}}(K^{\mathrm{Hpar}}{}_{\mathrm{Cu(par)_2}})^{-1}$$

Of the rate and equilibrium constants involved in $k'_{3,\mathrm{L}}$, $K^{\mathrm{cydta}}{}_{\mathrm{Cu(par)L(cydta)}}$ does not seem to be sensitive to the kind of L. Thus the effect of L on the rate constant $k'_{3,\mathrm{L}}$ comes from the rate constant $k^{-\mathrm{par}}$ and the equilibrium constant $K^{\mathrm{L}}{}_{\mathrm{Cu(par)L}}$. The latter constant has previously been related with the electron-donating ability of L, $E(\mathrm{L})$, and the Brønsted basicity of L, $H(\mathrm{L})$:[12]

$$\log K^{\mathrm{L}}{}_{\mathrm{Cu(par)L}} = \log K_{\mathrm{os(Cu(par),L)}} + \alpha E(\mathrm{L}) + \beta H(\mathrm{L})$$

According to the postulation in the mechanistic consideration,[26] $\log k^{-\mathrm{par}}$ should be proportional to the electron-donating ability of L, $E(\mathrm{L})$. As a measure of $E(\mathrm{L})$, E_n values have been proposed by Edwards.[27] E_n is a redox potential for the process $2\mathrm{L}^- = \mathrm{L}_2 + 2\mathrm{e}$. The plot of $\log k_{3,\mathrm{L}}$ ($k_{3,\mathrm{L}} = k'_{3,\mathrm{L}} \times K^{\mathrm{Hpar}}{}_{\mathrm{Cu(par)_2}}(K^{\mathrm{L}}{}_{\mathrm{Cu(par)L}})^{-1}$) vs. E_n is given in Figure 6.[28] The plot lies along a straight line. When a ligand coordinated to copper(II) donates an electron to copper(II), the bond of copper(II) with PAR will become weaker. The effect of the coordinated unidentate ligands on the reactivity of the mixed-ligand complexes Cu(par)L is quantitatively accounted for by the electron donation from the unidentate ligand as shown in Figure 6.

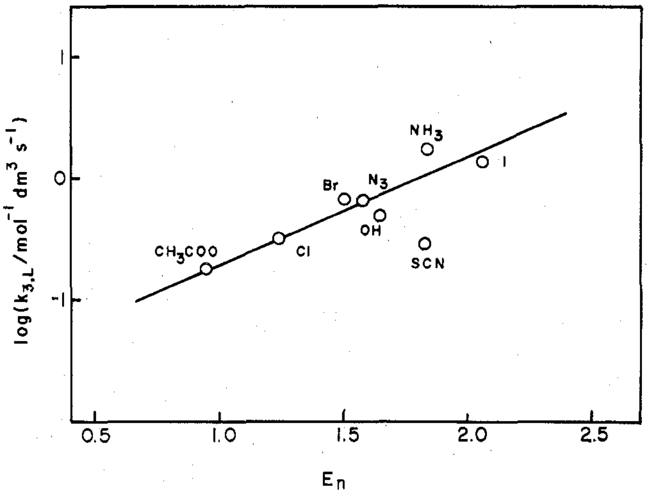


Figure 6. Correlation of logarithmic rate constant with electron donor constant E_n.

Such an approach can be extended to explain trends observed by Hague and Kinley[29] for the dissociation rate of 5-nitrosalicylic acid (NSA) from Ni(II) mixed-ligand complexes. In this case, the dissociation rate of NSA increased as follows: $\mathrm{Ni(aq)}^{2+} < \mathrm{Ni(ida)} \simeq \mathrm{Ni(nta)}^- < \mathrm{Ni(edda)} < \mathrm{Ni(dien)}^{2+} < \mathrm{Ni(trien)}^{2+} \simeq \mathrm{Ni(tren)}^{2+}$, where ida^{2-}, nta^{3-}, edda^{2-}, dien, trien, and tren denote iminodiacetate, nitrilotriacetate, ethylenediamine-*N,N'*-diacetate, diethylenetriamine, triethylenetetramine, and 2,2′,2″-triaminotriethylamine, respectively. These authors interpreted this trend in terms of the number of binding nitrogen and oxygen atoms. In these mixed-ligand complexes, electron donation of ligands will play an important role for the dissociation rate. Then we assume the following additivity for E_n values of the following ligands: $E_{\mathrm{ida}} = E_{\mathrm{NH_3}} + 2E_{\mathrm{CH_3COO}} = 3.74$, $E_{\mathrm{nta}} = E_{\mathrm{NH_3}} + 3E_{\mathrm{CH_3COO}} = 4.69$, $E_{\mathrm{dien}} = 3E_{\mathrm{NH_3}} = 5.52$, $E_{\mathrm{edda}} = 2E_{\mathrm{NH_3}} + 2E_{\mathrm{CH_3COO}} = 5.58$, $E_{\mathrm{trien}} = 4E_{\mathrm{NH_3}} = 7.36$, and $E_{\mathrm{tren}} = 4E_{\mathrm{NH_3}} = 7.36$. The rates of the dissociation of NSA from the mixed-ligand complexes are linearly related with the estimated values of electron-donating ability: the more extensive the electron donation from coordinated ligand, the faster becomes the dissociation rate of NSA. The activation enthalpy is better correlated with E_n.

Registry No. $\mathrm{Cu(par)_2}^{2-}$, 67464-24-8; CyDTA, 13291-61-7; $\mathrm{Cu(par)OH(OH_2)_2}^-$, 67464-32-8; OH^-, 14280-30-9; NH_3, 7664-41-7; CH_3COO^-, 71-50-1; N_3^-, 14343-69-2; SCN^-, 302-04-5; Cl^-, 16887-00-6; Br^-, 24959-67-9; I^-, 20461-54-5.

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Reactions of Hydrogen Peroxide with Metal Complexes.[1] 3. Thermodynamic and Kinetic Studies on the Formation, Dissociation, and Decomposition of Peroxochromium(VI) Complexes in Acid Media

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Received November 30, 1977

The stoichiometry and kinetics of the formation and dissociation of the peroxochromium(VI) complex, so-called perchromic acid, and of the decomposition of the latter to yield Cr(III) have been studied spectrophotometrically by using a stopped-flow technique at an ionic strength of 3.0 M (H, $NaClO_4$) over the range of hydrogen ion concentration 0.01–3.0 M at temperatures between 15 and 35 °C. The formation constant of chromic acid is $K^{\mathrm{H}} = [\mathrm{H_2CrO_4}][\mathrm{HCrO_4}^-]^{-1}[\mathrm{H}^+]^{-1} = 0.16 \pm 0.02\ \mathrm{M}^{-1}$ (25 °C) ($\Delta H = 0 \pm 1$ kJ mol^{-1} and $\Delta S = -15 \pm 2$ J K^{-1} mol^{-1}). The measurement of evolved oxygen gas confirmed the following stoichiometry: $2\mathrm{HCrO_4}^- + 8\mathrm{H}^+ + 3\mathrm{H_2O_2} \rightleftharpoons 2\mathrm{Cr}^{3+} + 3\mathrm{O_2} + 8\mathrm{H_2O}$. The stoichiometry for the formation of the oxodiperoxochromium(VI) complex is consistent with the expression: $\mathrm{HCrO_4}^- + \mathrm{H}^+ + 2\mathrm{H_2O_2} \rightleftharpoons \mathrm{CrO(O_2)_2} + 3\mathrm{H_2O}$ with $K_{\mathrm{f}} = [\mathrm{CrO(O_2)_2}][\mathrm{HCrO_4}^-]^{-1}[\mathrm{H}^+]^{-1}[\mathrm{H_2O_2}]^{-2} = (2.0 \pm 0.2) \times 10^7\ \mathrm{M}^{-3}$ (25 °C) and the corresponding thermodynamic parameters $\Delta H = -58 \pm 10$ kJ mol^{-1} and $\Delta S = -55 \pm 30$ J K^{-1} mol^{-1}. The protonation constant of the oxodiperoxochromium(VI) complex was determined to be $0.15 \pm 0.02\ \mathrm{M}^{-1}$ (25 °C) ($\Delta H = 27 \pm 10$ kJ mol^{-1} and $\Delta S = 76 \pm 35$ J K^{-1} mol^{-1}). The formation rate of the peroxochromium(VI) complexes is expressed as $\mathrm{d}[\mathrm{CrO_5}']/\mathrm{d}t = k_1[\mathrm{H_2CrO_4}][\mathrm{H_2O_2}] - k_{-1}'[\mathrm{CrO(O_2)_2}][\mathrm{H_2O_2}]^{-1}$, where $[\mathrm{CrO_5}']$ indicates the sum of the concentrations of $\mathrm{CrO(O_2)_2}$ and $\mathrm{Cr(OH)(O_2)_2}^+$, k_1 (25 °C) = $(9.3 \pm 0.2) \times 10^4\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ ($\Delta H_1^\ddagger = 17 \pm 1$ kJ mol^{-1} and $\Delta S_1^\ddagger = -93 \pm 5$ J K^{-1} mol^{-1}), and a rate constant for the reverse reaction, i.e., dissociation of the peroxochromium(VI) $k_{-1}'(25\ °\mathrm{C}) = (6.1 \pm 0.2) \times 10^{-4}\ \mathrm{M\ s}^{-1}$ ($\Delta H_{-1}^\ddagger = 80 \pm 5$ kJ mol^{-1} and $\Delta S_{-1}^\ddagger = -36 \pm 20$ J K^{-1} mol^{-1}). The rate law for decomposition of the peroxochromium(VI) complexes is $-\mathrm{d}[\mathrm{CrO_5}']/\mathrm{d}t = k_2[\mathrm{CrO(O_2)_2}][\mathrm{H}^+] + k_3[\mathrm{Cr(OH)(O_2)_2}^+][\mathrm{H}^+]$ with $k_2(25\ °\mathrm{C}) = 0.25 \pm 0.02\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ ($\Delta H_2^\ddagger = 81 \pm 5$ kJ mol^{-1} and $\Delta S_2^\ddagger = 17 \pm 15$ J K^{-1} mol^{-1}) and $k_3(25\ °\mathrm{C}) = 1.8 \pm 0.3\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ ($\Delta H_3^\ddagger = 73 \pm 15$ kJ mol^{-1} and $\Delta S_3^\ddagger = 6 \pm 50$ J K^{-1} mol^{-1}). Mechanisms for the formation and decomposition of the peroxochromium(VI) complexes are presented and discussed.

Introduction

Although there have been numerous studies on transition-metal peroxides,[2] the kinetic behavior of the peroxy species has been little investigated. Peroxides, besides having an intrinsic interest of their own, are of considerable and growing importance in relation to the catalytic oxidation involving hydrogen peroxide or dioxygen, the catalytic decomposition of hydrogen peroxide itself, and the storage and use of oxygen in biological systems.

The decomposition of hydrogen peroxide by chromium(VI) species occurs over a wide range of pH.[3-5] Especially, it has been well-known that when chromic acid solutions are treated with hydrogen peroxide, a deep blue color rapidly appears but does not persist long. In acid solution, complexity arises, not only because of the protonation of $\mathrm{CrO_4}^{2-}$ giving rise to $\mathrm{HCrO_4}^-$ and $\mathrm{H_2CrO_4}$ but also because of the condensation of chromium(VI) anions yielding dichromate and possibly larger condensed molecules. Furthermore, the reduction of chromium(VI) by hydrogen peroxide at various concentration levels can lead to greater complexity.

We have studied the reaction of hydrogen peroxide with chromium(VI) at the chromium concentration as low as possible and at the large excess hydrogen peroxide concentration in order to avoid complexity of the reaction. We have also elucidated the protonation equilibria of $\mathrm{HCrO_4}^-$, the stoichiometry of blue perchromic acid formation, and the overall reaction of hydrogen peroxide and hydrogen chromate anion.

Experimental Section

Reagents. Chromic acid solutions were prepared by dissolving primary standard grade potassium dichromate which was dried for 3 h at 110 °C. Sixty percent hydrogen peroxide containing no stabilizing agent (Mitsubishi Edogawa Kagaku Co., Tokyo, Japan) was distilled under reduced pressure. The stock solutions of about 10^{-2} M hydrogen peroxide were standardized with a standard potassium permanganate solution. A spontaneous decomposition of ca. 10^{-2} M hydrogen peroxide at room temperature was ca. 0.5% for 1 month. Reagent grade perchloric acid was used for perchloric acid solutions which were standardized by titration against weighed quantities of sodium carbonate. Sodium perchlorate was prepared by neutralizing reagent grade 60% perchloric acid with reagent grade sodium carbonate. Impurities of heavy-metal ions in the sodium perchlorate solution were removed together with active carbon as hydroxides at pH 8.5. Sodium perchlorate was then recrystallized twice from distilled water.

0020-1669/78/1317-2784$01.00/0