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Effects of Perchlorate Ion on the Hydrolysis of Glycine Esters Initiated by a Cobalt(III)-Chelate Formation

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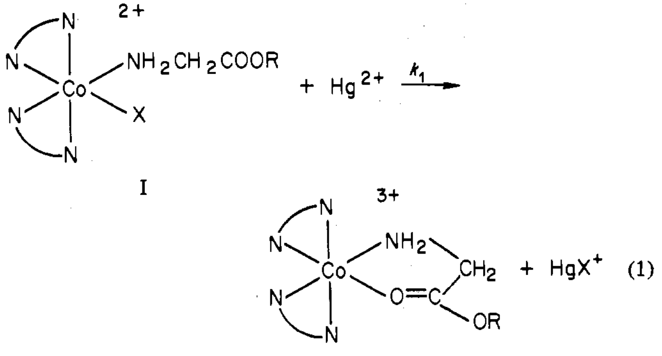
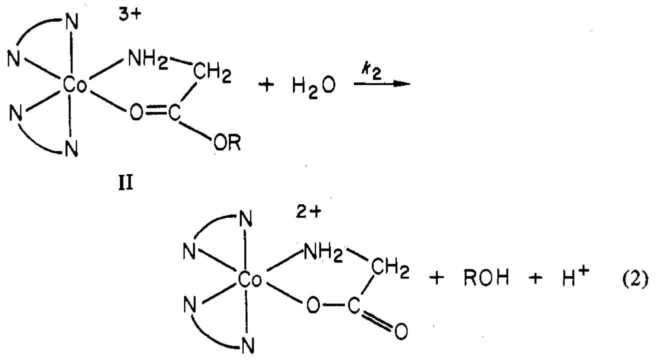
The hydrolysis of coordinated glycine ester in *cis*-[$CoX(en)_2(NH_2CH_2COOR)$] (X: halide, en: ethylenediamine) is initiated by the formation of a glycine ester chelate upon extraction of the coordinated halide by mercury(II) ion. The extraction reaction of the coordinated halide by mercury(II) ion is accelerated in high concentrations of perchlorate ion. However, the hydrolysis of coordinated glycine ester initiated by adding mercury(II) ion remarkably decreases its rate in high concentrations of perchlorate ion. This was interpreted as follows: The hydrolysis of the chelated glycine ester is rather independent of the concentration of perchlorate ion in solution, whereas the extraction reaction of coordinated halide by mercury(II) ion in high concentrations of perchlorate ion causes the formation of an intermediate aquo complex with the monodentate glycine ester *cis*-[$CoH_2O(en)_2(NH_2CH_2COOR)$], which is so inert that it takes much time to form the chelate ring necessary for the hydrolysis to be achieved.

Alexander and Busch identified a metal-ion promoted process in the hydrolysis of coordinated glycine ester employing an inert cobalt(III) complex.[1,2] The glycine ester in



I

II



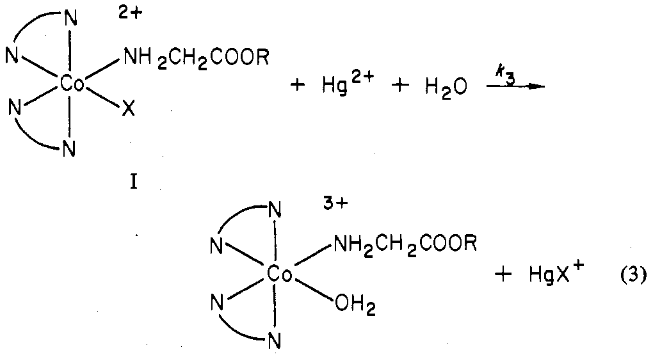
II

III

N N = ethylenediamine (en); X = halide ion

complex I is not readily hydrolyzed. When X is extracted by mercury(II) ion, the glycine ester forms an inert chelate ring with cobalt(III) ion and then the chelated glycine ester in complex II is readily hydrolyzed. In the bromo complex, process 1 is very fast and thus process 2 is rate determining, whereas in the chloro complex both processes 1 and 2 are of comparable rate.[1]

In low concentrations of perchlorate ion, the extraction reaction of coordinated halide by mercury(II) ion results in the formation of the chelate in process 1 and then the hydrolysis of the chelated glycine ester. In high concentrations of perchlorate ion, the extraction reaction is accelerated; however, the rate of the hydrolysis of coordinated glycine ester initiated by adding mercury(II) ion remarkably decreases. In the present paper, we show experimental evidences that the hydrolysis of the chelated glycine ester is rather independent of the concentration of perchlorate ion in solution; however, in high concentrations of perchlorate ion a mercury-ion induced substitution reaction of coordinated halide by a water molecule takes place as in (3) rather



I

IV

than the chelate formation in process 1, and an intermediate aquo complex thus formed is so inert that it takes much time to form the chelate necessary for the hydrolysis of coordinated glycine ester to be achieved.

$$\mathrm{IV} \xrightarrow{k_4} \mathrm{II} \qquad (4)$$

Experimental Section

Materials. The perchlorates *cis*-[$CoX(en)_2(NH_2CH_2COOC_2H_5)$]($(ClO_4)_2$, where X is chloride or bromide, and *cis*-[$CoCl(en)_2NH_3$]($(ClO_4)_2$ were prepared by the methods in the literature with some modifications.[2,3] Visible and infrared absorption spectra of the complexes were in good agreement with those given in the literature.[1,2] Elemental analyses of the perchlorates are summarized as follows.

Anal. Calcd for $Co(C_8H_{25}N_5O_{10}Cl_3)$: C, 18.60; H, 4.88; N, 13.56. Found: C, 18.39; H, 5.40; N, 13.75.

Anal. Calcd for $Co(C_8H_{25}N_5O_{10}BrCl_2)$: C, 17.13; H, 4.49; N, 12.48. Found: C, 17.18; H, 5.02; N, 13.14.

Anal. Calcd for $Co(C_4H_{29}N_5O_{13}Cl_3)$: C, 9.22; H, 5.57; N, 13.45. Found: C, 9.13; H, 5.56; N, 13.59.

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(1) M. D. Alexander and D. H. Busch, *J. Amer. Chem. Soc.*, **88**, 1130 (1966).

(2) M. D. Alexander and D. H. Busch, *Inorg. Chem.*, **5**, 602 (1966).

(3) A. Ablov, *Bull. Soc. Chim. Fr.*, [5] 4, 1783 (1937).

cis-$[CoH_2O{\cdot}NH_3(en)_2](ClO_4)_3$ was prepared by the method described by Werner.[4]

Kinetic Measurements. A Shimadzu recording spectrophotometer Model MPS-50 equipped with its thermostated cell compartment was used for kinetic measurements. Solutions for the kinetic studies were prepared according to the methods given in the literature by Alexander and Busch.[1] Without using buffer solutions, the hydrogen-ion concentration (pH 1.0) and the concentration of perchlorate ion were adjusted by mixing the stock solutions of sodium hydroxide, perchloric acid, and sodium perchlorate.

Nmr Measurements. Nmr spectra were recorded at room temperature on a 100-MHz Japan Electron Optics Laboratory spectrometer Model JNM 4H-100. Sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was used as internal reference.

Results and Discussion

Reaction of Mercury(II) Ion with *cis*-$[CoBr(en)_2(NH_2CH_2COOC_2H_5)]^{2+}$. Since process 1 for the bromo complex is very fast, the rate-determining process 2 can be traced by an increase of absorbance at 487 nm. The rates of formation of III were measured for a variety of concentrations of perchlorate ion, 0.66–6.00 *M*; the results are summarized in Table I. The rate constant decreases with increase in the concentration of perchlorate ion.

Reaction of Mercury(II) Ion with *cis*-$[CoCl(en)_2(NH_2CH_2COOC_2H_5)]^{2+}$. Process 1 for the chloro complex is not as fast as for the bromo complex; it can be followed experimentally without employing fast reaction techniques. The rates of disappearance of I were obtained by absorbance measurements at 535 nm for a variety of concentrations of perchlorate ion; the results are summarized in Table II. This process is well described by pseudo-first-order kinetics for the initial concentrations $[Hg^{2+}]_0 \gg [complex]_0$.[5] The second-order rate constants in Table II were evaluated from the pseudo-first-order rate constants. The disappearance rate constant of I increases with an increase in the concentration of perchlorate ion. The rate constants are described as a linear function of the concentration of perchlorate ion: $k_{obsd} = k_a + k_b [ClO_4^-]$, where k_a and k_b are constants. Similar linear relationships were also obtained at various temperatures (Figure 1). In the case of the chloro complex in low concentrations of perchlorate ion, the concentrations of I, II, and III are reproduced as functions of time by a consecutive reaction of processes 1 and 2 using the disappearance rate constant of I and the formation rate constant of III (Figure 2). The latter was obtained from the runs of the bromo complex. Hydrolysis of the chelated methyl glycinate is retarded upon addition of a small amount of methanol, whereas it is not changed unless there is a large addition of ethanol. On the other hand, hydrolysis of the chelated ethyl glycinate is retarded by ethanol but not by methanol. This implies that the hydrolysis of the chelated glycine esters has a reversible character. When extra alcohol is not added, however, the reverse reaction can be ignored as long as the reaction percentage is less than several per cent.[5] The rate of process 2 was determined only from the initial stage of the hydrolysis. Since *cis*-$[CoH_2O(en)_2NH_3]^{3+}$ did not form any amount of *cis*-$[CoCl(en)_2NH_3]^{2+}$ in the presence of $HgCl^+$ as discussed later, the analogous reverse reaction of process 1 was assumed to be ignored. An observed isosbestic point is shifted during the course of reaction from the isosbestic point of the initial reactant I and the final product III at 518 nm. This indicates the existence of an intermediate. In the case of low concentrations of perchlorate ion, a change of the concentration of the intermediate for a period of time could not be traced by absorbance measurements at 518 nm. In an appreciably high concentration of perchlorate ion, however, it could directly be measured.

Table I. The Rates of Formation of Complex III at 25° Obtained by Absorbance Measurements at 487 nm for a Variety of Concentrations of ClO_4^- Ion[a]

$[ClO_4^-]$, mol l.$^{-1}$	0.66	0.89	1.34	1.56	1.78	2.00	4.00	6.00
k_{obsd}, min^{-1}	0.36	0.39	0.33	0.33	0.30	0.28	0.09	0.03

[a] [Complex III] = $(3.56 \pm 0.18) \times 10^{-3}$ mol l.$^{-1}$, $[Hg^{2+}] = 0.189$ mol l.$^{-1}$.

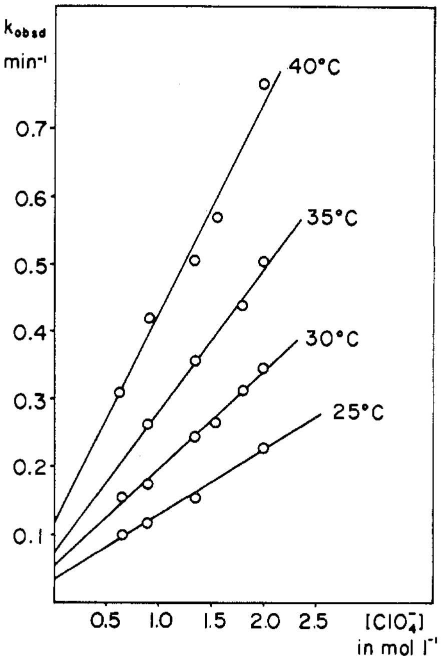
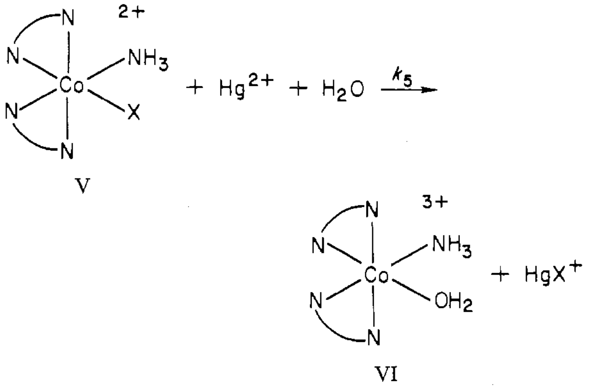


Figure 1. The rates of disappearance of *cis*-$[CoCl(en)_2(NH_2CH_2COOC_2H_5)]^{2+}$ as a function of concentration of ClO_4^- ion: [complex I] = 3.87×10^{-3} mol l.$^{-1}$; $[Hg^{2+}] = 0.189$ mol l.$^{-1}$.

Reaction of Mercury(II) Ion with *cis*-$[CoCl(en)_2NH_3]^{2+}$. *cis*-$[CoCl(en)_2NH_3]^{2+}$ has a structure analogous to *cis*-$[CoCl(en)_2(NH_2CH_2COOC_2H_5)]^{2+}$ except that the ligand NH_3 makes no chelate formation upon extraction of coordinated halide by mercury(II) ion. Reaction of mercury(II) ion with *cis*-$[CoCl(en)_2NH_3]^{2+}$ was traced by absorbance measurements at 525 nm under the exact same conditions employed in determining the rate of the reaction with *cis*-$[CoCl(en)_2(NH_2CH_2COOC_2H_5)]^{2+}$. The results are shown in Table III. The rate constant k_{obsd} increases with an increase in the concentration of perchlorate ion. Plots of k_{obsd} *vs.*



V

VI

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Table II. The Rates of Disappearance of *cis*-$[CoCl(en)_2(NH_2CH_2COOC_2H_5)]^{2+}$ Obtained by Absorbance Measurements at 535 nm for a Variety of Concentrations of ClO_4^- Ion[a]

	Temp, °C	$[ClO_4^-]$, mol l.$^{-1}$ 0.66	0.89	1.34	1.56	1.78	2.00	$k_{obsd} = k_a + k_b[ClO_4^-]$ k_a, l. mol^{-1} min^{-1}	k_b, l.^{2} mol^{-2} min^{-1}	k_a/k_b
k_{obsd}, l. mol^{-1} min^{-1}	25	0.529	0.619	0.805	0.852	1.085	1.191	0.178	0.488	0.365
	30	0.815	0.921	1.281	1.387	1.641	1.810	0.278	0.752	0.369
	35		1.371	1.869	2.049	2.292	2.626	0.380	1.092	0.346
	40		2.197	2.631	2.970		3.997	0.609	1.616	0.377

[a] [Complex] = $(3.87 \pm 0.19) \times 10^{-3}$ mol l.$^{-1}$, $[Hg^{2+}] = 0.189$ mol l.$^{-1}$.

Table III. The Rates of Disappearance of *cis*-$[CoCl(en)_2NH_3]^{2+}$ upon Reaction with Mercury(II) Ion Obtained by Absorbance Measurements at 525 nm[a]

	Temp, °C	$[ClO_4^-]$, mol l.$^{-1}$ 0.66	1.78	2.00	4.00	k_5,[b] l.^{2} mol^{-2} min^{-1}
k_{obsd}, l. mol^{-1} min^{-1}	25	0.307		0.856	1.683	0.412
	30	0.471		0.911	2.679	0.678
	35		1.572	1.699	3.949	1.092

[a] [Complex] = $(4.65 \pm 0.24) \times 10^{-3}$ mol l.$^{-1}$, $[Hg^{2+}] = 0.189$ mol l.$^{-1}$. [b] $k_{obsd} = k_5[ClO_4^-]$.

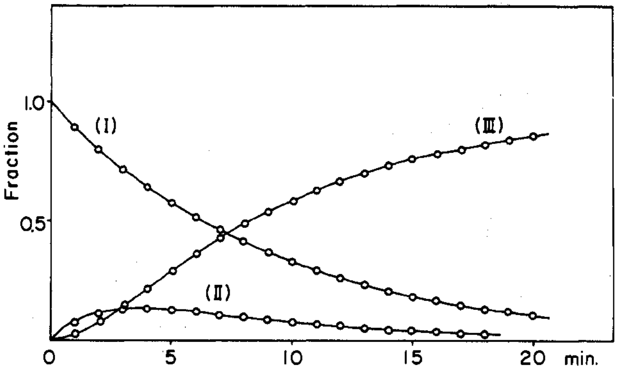


Figure 2. Changes with time of the concentrations of complexes I, II, and III in the case of the chloro complex: [complex I] = 3.87×10^{-3} mol l.$^{-1}$; $[Hg^{2+}] = 0.189$ mol l.$^{-1}$; $[ClO_4^-] = 0.66$ mol l.$^{-1}$.

the concentrations of perchlorate ion give a straight line passing through the origin: $k_{obsd} = k_5[ClO_4^-]$, where k_5 is a constant. The value of k_5 is very close to a value obtained for k_b in the case of *cis*-$[CoCl(en)_2(NH_2CH_2COOC_2H_5)]^{2+}$. When various concentrations of $HgCl^+$ were added to the separately prepared aqueous solution of $[CoH_2O(en)_2NH_3]^{3+}$, no spectral change was observed in the visible region. Thus, no reverse reaction of process 5 actually occurs.

Changes of Nmr Spectra in the Course of Reaction of Mercury(II) Ion with *cis*-$[CoCl(en)_2(NH_2CH_2COOC_2H_5)]^{2+}$. Proton nmr spectra of *cis*-$[CoCl(en)_2(NH_2CH_2COOC_2H_5)]^{2+}$ in D_2O exhibit a characteristic triplet at 1.27 ppm ($J = 7$ Hz) and a quartet at 4.2–4.3 ppm ($J = 7$ Hz), which are assigned to CH_3 and CH_2 protons, respectively, of the ethyl group in the glycine ethyl ester of I.

In the course of reaction of mercury(II) ion with *cis*-$[CoCl(en)_2(NH_2CH_2COOC_2H_5)]^{2+}$, the molecular environment of the ethyl group of the glycine ethyl ester makes a change from the monodentate coordination state through bidentate and then to free ethanol. The chemical shift of the CH_3 proton resonance is remarkably dependent on the molecular environment.

When the concentration of perchlorate ion is 0.66 mol l.$^{-1}$, the 1.27-ppm signal of glycine ethyl ester in *cis*-$[CoCl(en)_2(NH_2CH_2COOC_2H_5)]^{2+}$ is appreciably diminished in 13–15 min after initiation of the reaction by adding mercury(II) ion, and it becomes actually undetectable by 20 min. A new triplet appears at 1.16 ppm about 10 min after initiation of the reaction and then increases its intensity for 1 hr. The triplet at 1.16 ppm is assigned to the CH_3 protons in the reaction product ethanol. A signal appears at 1.20 ppm about 3–6 min after initiation of the reaction. This is assigned to the CH_3 protons in the chelated glycine ester. When the concentration of perchlorate ion is 4.0 mol l.$^{-1}$, the 1.27-ppm signal is not diminished in 20 min after initiation of the reaction and the signals at 1.27, 1.20, and 1.10 ppm are of comparable intensity. The signal at 1.10 ppm arising from ethanol increases its intensity continuously but slowly. Separate nmr measurements identified a shift of the ethanol signal depending upon the concentration of perchlorate ion in aqueous solution. The 1.27-ppm signal of monodentate coordinated glycine ethyl ester can be observed even 1 hr after initiation of the reaction. A typical change of nmr spectrum during the reaction of mercury(II) ion with *cis*-$[CoCl(en)_2(NH_2CH_2COOC_2H_5)]^{2+}$ in aqueous solution containing perchlorate ion is shown in Figure 3.

Competitive Aquation and Chelate Formation upon Extraction of Coordinated Halide by Mercury(II) Ion. The rate of disappearance of I determined by absorbance measurements increases with an increase in the concentration of perchlorate ion in aqueous solution. At 20 min after initiation of the reaction, monodentate coordinated glycine ester is not detected by nmr when $[ClO_4^-] = 0.66$ mol l.$^{-1}$, whereas the monodentate ester is still present even 1 hr after the initiation when $[ClO_4^-] = 4.0$ mol l.$^{-1}$. These facts are seemingly contradictory. However, it must be noted that the nmr spectrum makes no distinction between monodentate esters in I and IV, while the visible absorption spectrum detects a difference between I and IV. On the other hand, the visible absorption spectrum makes no distinction between the oxygen-donating II and IV, while the nmr spectrum detects a difference between the monodentate glycine ester in IV and the bidentate chelated glycine ester in II.

In low concentrations of perchlorate ion, the disappearance of I detected by visible absorbance measurements is due to chelate formation of the coordinated glycine ester upon extraction of coordinated halide by mercury(II) ion as described in eq 1. The rate of encounter of the counterions which participate in the extraction reaction might be increased in the presence of indifferent electrolytes. Because of the solubility of mercury(II) ion in aqueous solution containing indifferent electrolytes, we could study a variety of concentrations of sodium perchlorate. The rate of the disappearance of I is dependent upon the concentration of perchlorate ion rather than the concentration of sodium perchlorate and increases with an increase in the concentration of perchlorate ion. In high concentrations of perchlorate ion, however, the disappearance of I becomes faster, forming a complex with monodentate-coordinated glycine ethyl ester rather than II with chelated glycine ethyl ester. The intermediate complex with monodentate-coordinated glycine ethyl ester is detected by an absorption spectrum different from that of I, while it shows the 1.27-ppm nmr signal of monodentate-coordinated glycine ethyl ester as observed in I. Thus, the intermediate complex is assigned to an aquo complex such as that denoted IV. In fact, the absorption spectrum is close to that of oxygen-donating II. IV is inert and thus it forms the chelate ring rather slowly. The 1.27-ppm signal of monodentate-coordinated glycine ethyl ester, in fact, very slowly disappears. Since the reverse reaction of process 3 can be ignored, as evidenced by the reverse reaction of process 5, the disappearance of IV is due to chelate formation.

At high concentrations of perchlorate ion, chelate formation process 1 and aquation process 3 are competitive. In the case of reaction of mercury(II) ion with *cis*-$[CoBr(en)_2(NH_2CH_2COOC_2H_5)]^{2+}$, the competitive chelate formation and aquation occur very rapidly upon extraction of the coordinated bromide by mercury(II) ion. At low concentrations of perchlorate ion, however, only process 1 occurs very rapidly. The disappearance of I in the case of the bromo complex is too fast to be detected without employing a fast reaction technique, but the aquation (3) is more promoted by the presence of perchlorate ion as in the case of the chloro complex. The hydrolysis of glycine ester in the intermediate aquo complex is inhibited, since the inert aquo complex takes much time to form the chelate ring necessary for the hydrolysis of glycine ester to be achieved. Thus, perchlorate ion gives rise to a retardation of the formation of III and ethanol. The rate of formation of III obtained by absorbance measurements is coincident within experimental error with the rate for formation of ethanol obtained from nmr measurements.

Reaction Scheme. A system of consecutive reactions is shown in Scheme I. The observed values of k_b and k_5 agree within experimental error. Thus, the processes for the rate constant k_a and k_b most likely correspond to the process of chelate formation upon extraction of coordinated chloride and that of aquation, respectively. A computer simulation assuming that $k_a = k_1$, $k_b = k_2$, and the rate of hydrolysis of the chelated glycine ester itself is not influenced by perchlorate ion present in aqueous solution can reproduce well the changes of both the visible absorption spectrum and the nmr spectrum for a self-consistent value $k_4 = 0.03 \pm 0.01$ min^{-1} and predicts that hydrolysis of the glycine ester in IV occurs only after process 4 is achieved.

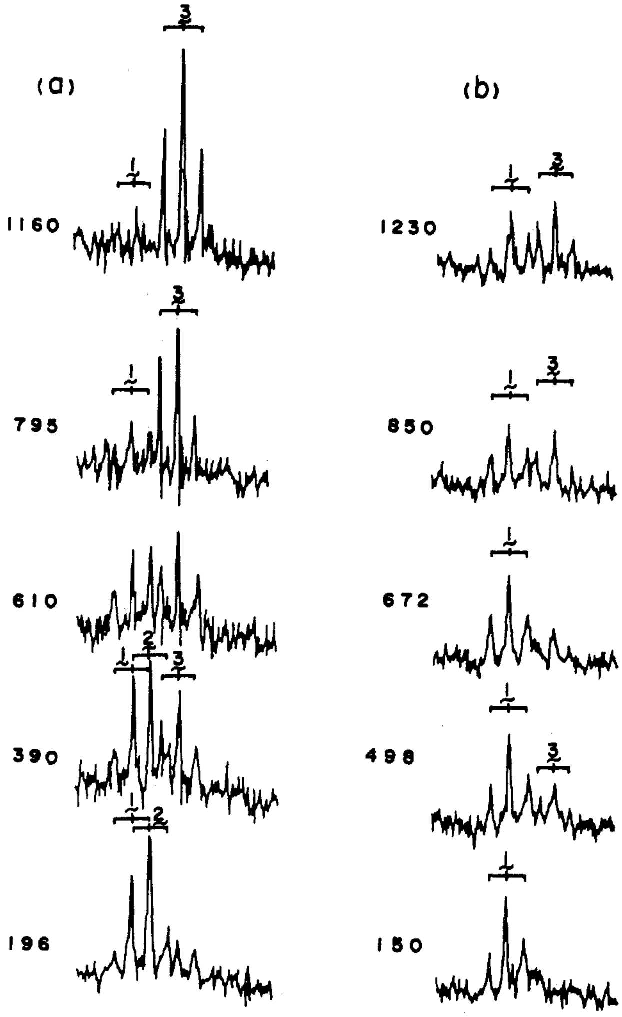
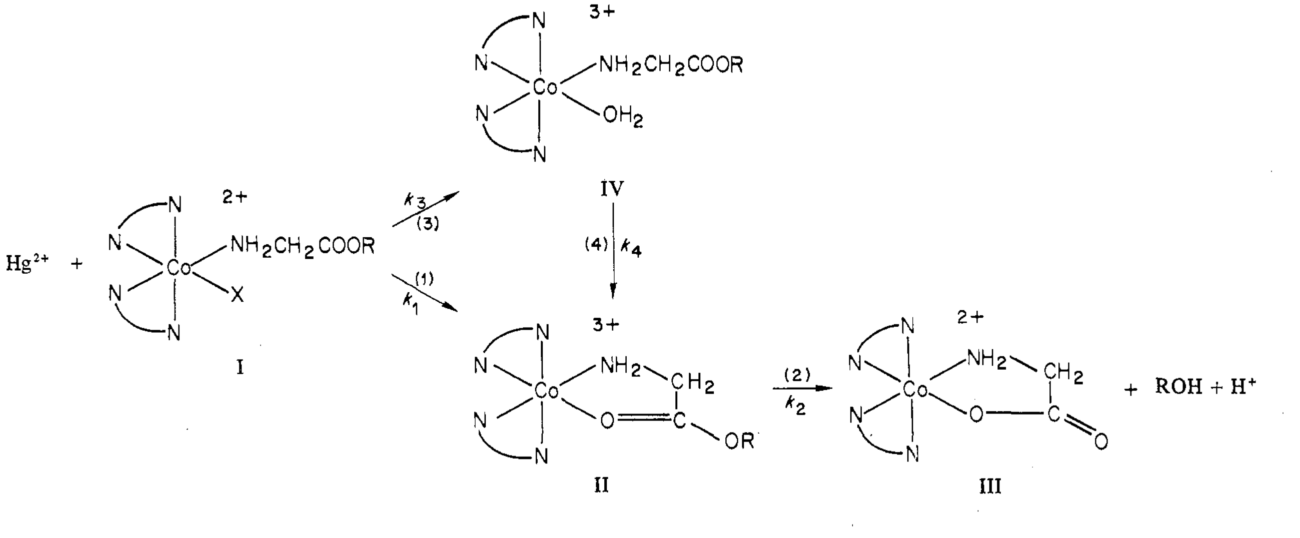


Figure 3. Changes of the nmr triplet of the ethyl CH_3 protons during the reaction of mercury(II) ion with *cis*-$[CoCl(en)_2(NH_2CH_2COOC_2H_5)]^{2+}$ in aqueous solution containing ClO_4^- (pH 1.0). (a) $[ClO_4^-] = 0.66$ mol l.$^{-1}$; (1) monodentate coordinated glycine ester (1.27 ppm); (2) chelated glycine ester (1.20 ppm); (3) ethanol (1.16 ppm). (b) $[ClO_4^-] = 4.0$ mol l.$^{-1}$; (1) monodentate coordinated glycine ester (1.27 ppm); (3) ethanol (1.10 ppm). The figures on the left-hand side indicate the time in seconds after mixing the solutions.

As stated before, processes 1 and 3 for the bromo complex are very fast. However, process 3 is promoted by per-

Scheme I.



chlorate ion present in aqueous solution. An enhanced formation of IV inhibits hydrolysis of the coordinated glycine ester. The simulation can also reproduce the retarded hydrolysis of glycine ester of the bromo complex in high concentrations of perchlorate ion.

Thermodynamic Data of Activation. Measurements of the rate constants at various temperatures make it possible to evaluate the activation enthalpy, $\Delta H^{\ddagger}$, and entropy, $\Delta S^{\ddagger}$. Thermodynamic data of activation were obtained for chelate formation process 1 and aquation process 3 as summarized in Table IV. The activation enthalpy is not as different in processes 1 and 3; however, the activation entropy is a little higher in process 1. The activation process is mainly involved in the extraction reaction of coordinated halide by mercury(II) ion prior to the chelate formation or the aquation. Perchlorate ion, however, when present in aqueous solution causes a change in mechanism from chelate formation in process 1 to aquation in process 3. The concentrations of perchlorate ion used in the present work were so high that the activity of perchlorate ion could not be described in terms of ionic strength, a concept applicable only to dilute aqueous solutions. In the presence of sufficient concentration of perchlorate ion, however, the rate of the mercury-ion induced aquation linearly increases with an increase in the concentration of perchlorate ion. The thermodynamic data of activation were obtained from the rates divided by the concentration of perchlorate ion.

Microdynamic Effects of Perchlorate Ion. The microscopic structure of solvent water is changed by the presence of perchlorate ion in aqueous solution.[6-11] An nmr observation that the substitution reaction of water molecules in the hydration sphere of hydrated sodium ion is accelerated by the presence of perchlorate ion in solution has been interpreted in terms of the structure-breaking effect due to perchlorate ion in aqueous solution.[6,7] Laser Raman and near-infrared spectra furnish evidences that an equilibrium between the mobile water molecules in liquid water and the ordered water molecules in the "iceberg" is shifted to melt the iceberg structure in the presence of perchlorate ion.[8-11]

Table IV. Thermodynamic Data of Activation of Chelate Formation Process 1 and Aquation Process 3

	$\Delta G^{\ddagger}$ at 298° K, kcal mol^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}
Step 1	17.09	14.22	−9.66
Step 3	16.50	14.11	−8.02

A change of the microscopic structure in solvent water may give rise to an effect in such reactions as the solvent water molecules are participating. Effects of perchlorate ion observed in the present work are interpreted by a participation of labile waters set free from the iceberg structure broken by perchlorate ions. The near-infrared and also nmr studies show that the water-structure-breaking effect by perchlorate ion is equivalent to the effect arising from an increase in temperature.[11,12] If this is the case, the rates of processes 1, 2, and 3 should be simultaneously enhanced as if the temperature is elevated. However, only the rate of process 3 increases with an increase in the concentration of perchlorate ion.

It should be noted that the solvent-participating aquation in process 3 is lower in activation energy than the chelate formation in process 1; however, the aquation occurs only when perchlorate ion in aqueous solution furnishes labile water molecules.

Registry No. *cis*-$[CoCl(en)_2(NH_2CH_2COOC_2H_5)](ClO_4)_2$, 23242-62-8; *cis*-$[CoBr(en)_2(NH_2CH_2COOC_2H_5)](ClO_4)_2$, 49567-52-4; *cis*-$[CoCl(en)_2NH_3](ClO_4)_2$, 15280-85-0; Hg^{2+}, 14302-87-5; ClO_4^-, 14797-73-0; *cis*-$[Co(H_2O)(en)_2(NH_2CH_2COOC_2H_5]^{3+}$, 49567-53.5; *cis*-$[Co(en)_2(NH_2CH_2COOEt)]^{3+}$, 42481-57-2.

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