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Ligand Substitution Reaction of (Carbonato)bis(ethylenediamine)cobalt(III) Complex with Ethylenediamine

HIROYUKI FUSHIMI, KEN-ICHI OKAMOTO, JINSAI HIDAKA

Department of Chemistry, University of Tsukuba, Sakura, Niihari, Ibaraki 305, Japan

and HISAHIKO EINAGA*

Institute of Materials Science, University of Tsukuba, Sakura, Niihari, Ibaraki 305, Japan

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Abstract

Substitution reaction of the coordinated carbonate ligand in $[Co(CO_3)(en)_2]^+$ in alkaline aqueous solution of 1.0 mol dm^{-3} chloride at 55 ℃ under the pesudo-first-order kinetic condition with respect to ethylenediamine has been studied, by employing the electronic absorption and circular dichroism spectral methods for the racemate and the optically active isomers. The reaction proceeded stepwise with two rate-determining steps. Δ-(−)$_{589}$-$[Co(CO_3)(en)_2]^+$ changed *via* two parallel pathways principally with racemization to $[Co(OCO_2)(OH)(en)_2]$, which subsequently changed to $[Co(en)_3]^{3+}$ through $[Co(OCO_2)(en\text{-}N)(en)_2]^+$; where $OCO_2{}^{2-}$ and en-*N* denote unidentate carbonate and ethylenediamine, respectively. Some stereoselectivity was noticed in the first base-catalyzed hydrolysis step. A substitution reaction mechanism was discussed.

Introduction

Studies on the nucleophilic substitution reaction of cobalt(III) complexes with chelate ligands have hitherto been centered around aquation, acid or base hydrolysis and anation [1]. There have been few studies on the substitution reaction of the coordinated chelate ligand with another chelate ligand in these substitution-inert complexes; although these cobalt(III) complexes are presumed to proceed through the dissociative (D), or dissociative interchange (I_d), mechanism. Moreover, an elucidation of the mechanism of the cobalt(III) complexes, whose intermediate is more emphatic, is useful for substitution-labile complexes such as the aluminum(III) group [2–4].

The present paper is concerned with the substitution reaction of the coordinated carbonate ligand in the racemic and optically active $[Co(CO_3)(en)_2]^+$ complex, with ethylenediamine (en).

Experimental

$[Co(CO_3)(en)_2]Cl$ was prepared from *trans*-$[CoCl_2(en)_2]Cl$ according to a literature procedure [5]. It was characterized by elemental analysis and absorption spectra. Optical resolution was made by using (+)$_{589}$-$[Co(ox)_2(en)]^-$ (ox^{2-}, oxalate) as a resolving agent [6]. In this work the resolution was carried out by using $K_2[Sb_2\text{-}(d\text{-}(+)\text{-}tart)_2]\cdot H_2O$ as follows (tart^{4-}, tartrate). A solution containing 1.09 g of $[Co(CO_3)(en)_2]Cl$ in 40 cm^3 of warm water (40 ℃) was mixed with a solution containing 1.2 g of $K_2[Sb_2(d\text{-}(+)\text{-}tart)_2]\cdot H_2O$ in 7 cm^3 of water. The resulting solution was cooled in an ice bath, ethanol was added until crystals of the less soluble diastereomer, (−)$_{589}$-$[Co(CO)_3(en)_2]_2[Sb_2(d\text{-}(+)\text{-}tart)_2]$, began to appear, and the aqueous ethanol solution was refrigerated for a few hours. The precipitated diastereomer was filtered and washed with ethanol and ether and then dissolved in a minimal amount of water. The resulting solution was poured onto a small column of QAE-Sephadex A-25 (Cl$^-$ form) to remove the resolving agent. Elution was made with water and the eluate was evaporated to near-dryness with a rotary evaporator. The product, Δ-(−)$_{589}$-$[Co(CO_3)(en)_2]Cl$, was recrystallized from aqueous ethanol and was characterized by elemental analysis and the absorption and circular dichroism (CD) spectra. The Λ-(+)$_{589}$-isomer was obtained from the filtrate of the less soluble diastereomer.

$[Co(en)_3]Cl_3\cdot 3H_2O$ was prepared according to a literature procedure [7].

Analytical grade reagents of ethylenediamine and hydrochloric acid were used throughout the experiments. The former was distilled before use when necessary.

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*Author to whom correspondence should be addressed.

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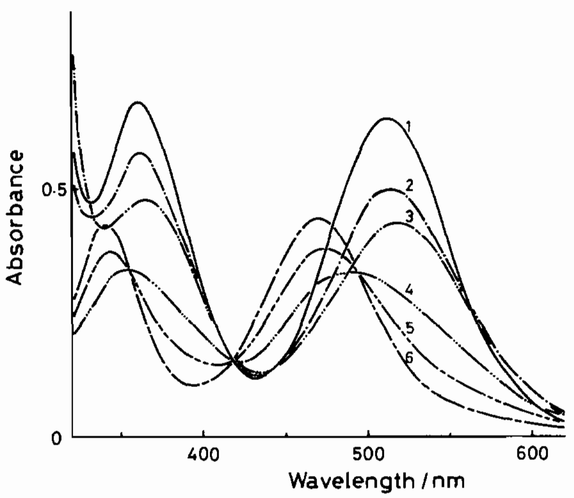

Fig. 1. Absorption spectral change with time of $[Co(CO_3)(en)_2]^+$. $[[Co(CO_3)(en)_2]^+]$, 1.00×10^{-2} mol dm^{-3}; [en], 2.00 mol dm^{-3}; $[OH^-]$, 3.55×10^{-3} mol dm^{-3}; and $[Cl^-]$, 1.0 mol dm^{-3}. 55.4 °C. Time/min.: 1, 0; 2, 40; 3, 80; 4, 240; 5, 360; and 6, 540.

The absorption and CD spectra were recorded on a JASCO Spectrophotometer, model UVIDEC-1, and a JASCO Spectropolarimeter, model J-500C, respectively. Hydroxide ion concentration was determined (using a Horiba pH meter, model F7-SS, with glass and 3.33 mol dm^{-3} aqueous potassium chloride calomel electrodes) by defining the hydroxide ion concentration of a solution containing 0.0100 mol dm^{-3} sodium hydroxide and 0.9900 mol dm^{-3} sodium chloride as $-\log [OH^-] \equiv 2.00$.

Runs were made under the pseudo-first-order kinetic condition with respect to ethylenediamine in the buffered hydroxide ion concentration range 1×10^{-3}–2×10^{-2} mol dm^{-3} and the temperature range 45.2–65.4 °C at 1.0 mol dm^{-3} aqueous chloride solution. The solution, which contained more than 0.5 mol dm^{-3} ethylenediamine above pH 11, had sufficiently high buffer capacity as to the hydroxide ion concentration. No measurable changes in the hydroxide ion concentration were noticed before and after the kinetic runs. The temperature was regulated at a specified value within ±0.1 °C. The reactions were monitored with absorbance change at 513 nm for the racemate and with CD change at 530 nm for the optically active isomer, from which the pseudo-first-order rate constants were calculated.

Results

Kinetic of The Racemate

Figure 1 shows absorption spectra in the *d–d* transition region of $[Co(CO_3)(en)_2]^+$ with time, in an alkaline aqueous solution under the pseudo-first-order kinetic condition with respect to ethylenediamine. The absorption spectrum of $[Co(CO_3)(en)_2]^+$ (λ_{max}, 512 and 360 nm) changes, with two isosbestic points at 450 and 420 nm, to an intermediate spectrum (Curve 4 in Fig. 1). This further changes, with isosbestic points at 500, 420, and 355 nm, to a final spectrum characteristic of $[Co(en)_3]^{3+}$ (λ_{max}, 470 and 340 nm). This spectral evidence can be interpreted in terms of stepwise, biphasic substitution reaction kinetics of $[Co(CO_3)(en)_2]^+$ through an intermediate complex to $[Co(en)_3]^{3+}$. This mechanistic feature was supported by logarithmic absorbance change *vs.* time plots, which were composed of two linear portions.

In the case where the first and the second rate-determining steps are given by the rate constants, k_1 and k_2, with S, I, and P being the starting, the intermediate and the final complexes,

$$S \xrightarrow{k_1} I \xrightarrow{k_2} P,$$

the rate equation is expressed as follows.

$$A_t = B_1\exp(-k_1 t) + B_2\exp(-k_2 t) + A_\infty$$

$$B_1 \equiv [S]_0\{\epsilon_S(k_1 - k_2) - \epsilon_I k_1 + \epsilon_P k_2\}/(k_1 - k_2)$$

$$B_2 \equiv [S]_0\{(\epsilon_I - \epsilon_P)k_1\}/(k_1 - k_2). \qquad (1)$$

Here, $[S]_0$ is the initial concentration of the starting complex, ϵ_S, ϵ_I, and ϵ_P are molar absorption coefficients of the corresponding complexes, and A_t and A_∞ are absorbances at the fixed wavelength at time t and at equilibrium, respectively. When k_2 is considerably smaller than k_1, these two exponential terms become separated from each other to give two linear portions in the ln $(A_t - A_\infty)$ *vs.* t plots. Hence k_2 can be obtained from the second linear portion of this logarithmic absorbance change *vs.* time plots, and k_1 from a slope of the $\ln\{A_t - B_2\exp(-k_2 t) - A_\infty\}$ *vs.* t plots, by using the $B_2\exp(-k_2 t)$ term estimated by extrapolation of the second linear portion of the ln $(A_t - A_\infty)$ *vs.* t plots.

Figures 2 and 3 show the hydroxide ion and ethylenediamine concentration dependences of the observed rate constants, k_{obsd}, of the first and the second rate-determining steps. The first step depends uniquely on the hydroxide ion concentration, whilst the second step depends uniquely on the ethylenediamine concentration. The following relations can be deduced from Figs. 2 and 3.

$$\left.\begin{aligned} k^1_{obsd} &= k^1_{H_2O} + k^1_{OH}[OH^-] \\ k^2_{obsd} &= k^2_{en}[en] \end{aligned}\right. \qquad (2)$$

Here, $k^1_{H_2O}$, k^1_{OH}, and k^2_{en} denote the rate constants for the aquation, the base hydrolysis, and the ethylenedimaine coordination pathways, respectively.

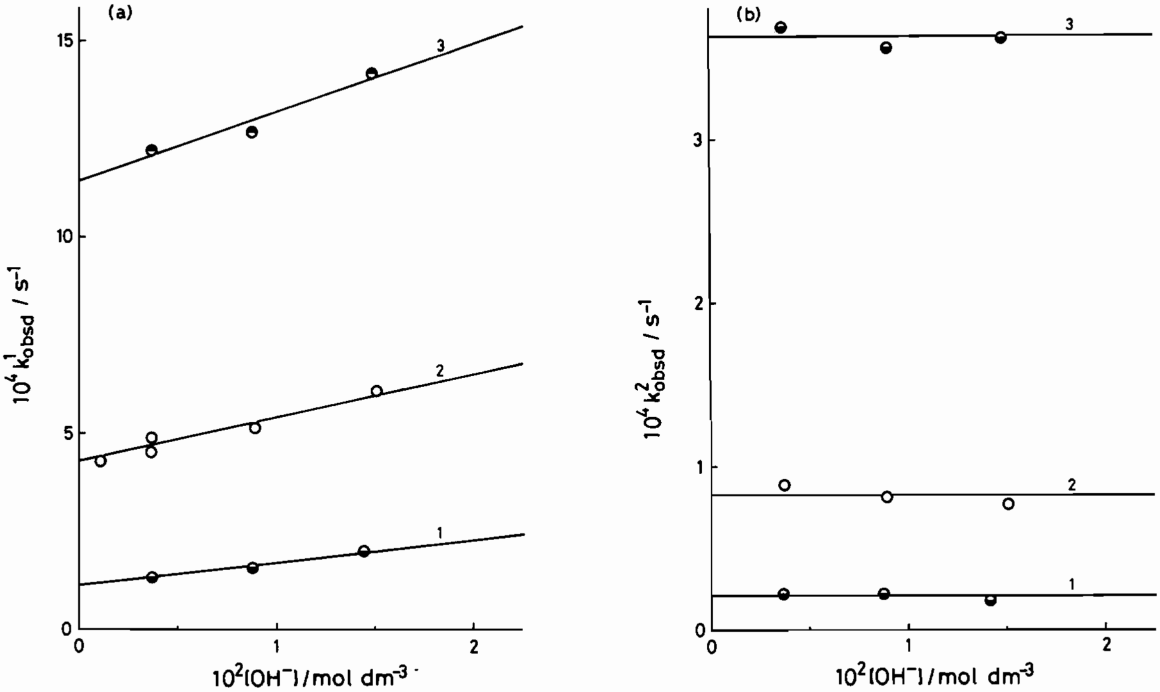

Fig. 2. Relation between $k_{obsd}^{1(or2)}$ and [OH$^-$]. (a), k^1_{obsd} and (b), k^2_{obsd}. [[Co(CO$_3$)(en)$_2$]$^+$], 1.00 × 10^{-2} mol dm^{-3}; [en], 2.00 mol dm^{-3}; and [Cl$^-$], 1.0 mol dm^{-3}. Temp./°C: 1, 45.2; 2, 55.4; and 3, 65.4.

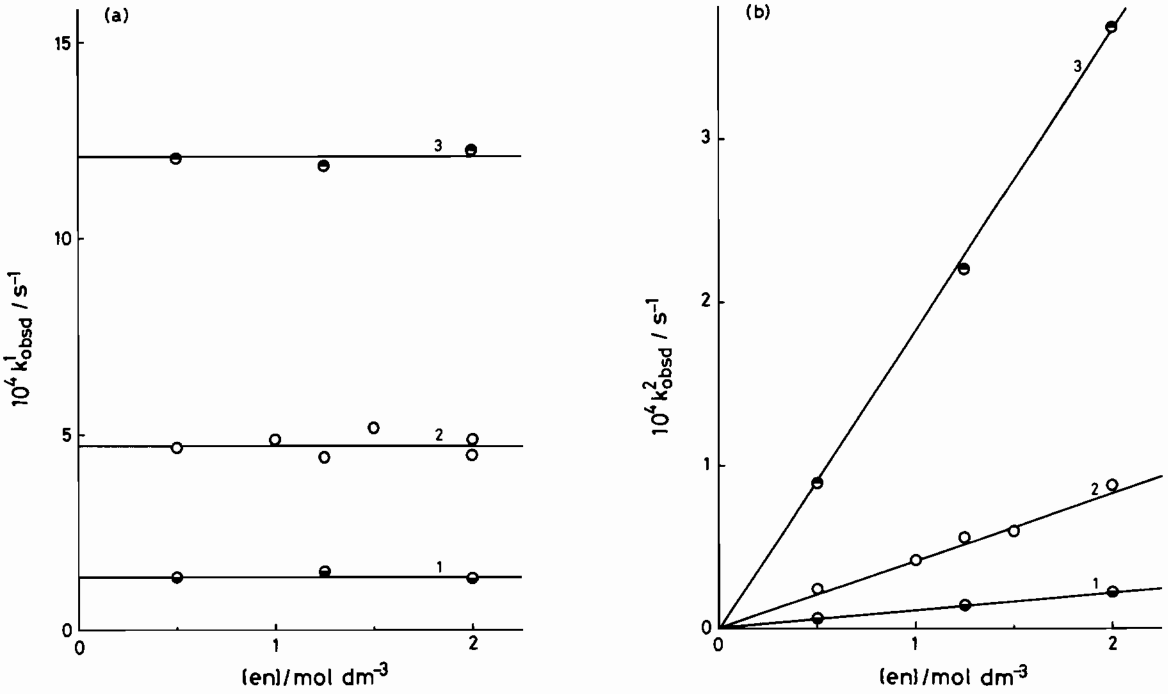

Fig. 3. Relation between $k_{obsd}^{1(or2)}$ and [en]. (a), k^1_{obsd} and (b), k^2_{obsd}. [[Co(CO$_3$)(en)$_2$]$^+$], 1.00 × 10^{-2} mol dm^{-3}; [OH$^-$], 3.63 × 10^{-3} mol dm^{-3}; and [Cl$^-$], 1.0 mol dm^{-3}. Temp./°C: 1, 45.2; 2, 55.4; and 3, 65.4.

These spectrochemical and kinetic results indicate that in the first step [Ca(CO$_3$)(en)$_2$]$^+$ undergoes the base hydrolysis and also aquation, followed by a rapid deprotonation of the coordinated water to give, in a parallel way, the intermediate complex (presumably [Co(OCO$_2$)(OH)(en)$_2$], where OCO$_2$$^{2-}$ speci-

TABLE I. Kinetic Parameters.

Pathway	Electronic absorption spectral method			Circular dichroism spectral method		
	Rate constant	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})	Rate constant	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})
Aquation	$(4.30 \pm 0.21) \times 10^{-4}$ [a]	99.0 ± 0.6	−6.5 ± 3.7	$(1.63 \pm 0.08) \times 10^{-4}$ [a]	102 ± 1	−6.8 ± 6.1
Base hydrolysis	$(1.11 \pm 0.06) \times 10^{-2}$ [b]	45.2 ± 0.5	−145 ± 3	$(0.46 \pm 0.02) \times 10^{-2}$ [b]	51.5 ± 1.0	−134 ± 6
Anation	$(4.26 \pm 0.21) \times 10^{-5}$ [c]	120 ± 2	35.2 ± 12.2			

[a] $k^1_{H_2O}/s^{-1}$. [b] $k^1_{OH}/mol^{-1}\ dm^3\ s^{-1}$. [c] $k^2_{en}/mol^{-1}\ dm^3\ s^{-1}$. $[Cl^-]$, 1.0 mol dm^{-3}. 55.4 °C.

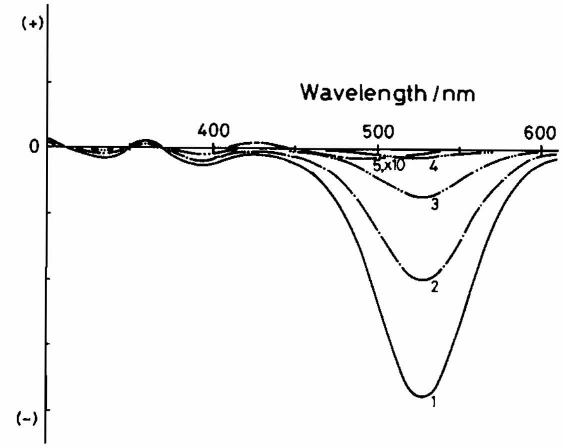

Fig. 4. Circular dichroism spectral change with time of Δ-$(-)_{589}$-$[Co(CO_3)(en)_2]^+$. [Δ-$(-)_{589}$-$[Co(CO_3)(en)_2]^+$], 1.00 × 10^{-2} mol dm^{-3}; [en], 2.00 mol dm^{-3}; $[OH^-]$, 3.55 × 10^{-3} mol dm^{-3}; and $[Cl^-]$, 1.0 mol dm^{-3}. 55.4 °C. Time/min.: 1, 0; 2, 40; 3, 100; 4, 210; and 5, 480.

fies tentatively a unidentate carbonate ligand), to which ethylenediamine coordinates in the second step to give $[Co(en)_3]^{3+}$.

Kinetic parameters of these reaction pathways are summarized in Table I.

Kinetics of the Optically Active Isomers

Figure 4 shows CD spectral changes in the d–d transition region of Δ-$(-)_{589}$-$[Co(CO_3)(en)_2]^+$ with time, under the same conditions as those adopted for the absorption spectral studies. The CD intensity decreased with time, giving isodichroic points at 370, 350 and 305 nm, during which no changes in the spectral patterns were noticed. The half-life of this stereochemical step was of the same magnitude as that of the first step in the reaction of the racemate.

The final CD spectrum, however, differed slightly from the base line; it was apparently characteristic of Δ-$(-)_{589}$-$[Co(en)_3]^{3+}$. The same stereoselective behavior was also noticed when Λ-$(+)_{589}$-$[Co(CO_3)(en)_2]^+$ was used as a starting complex.

These CD spectral features imply that the first rate-determining step accompanies principally the racemization into the intermediate complex, with some stereoselectivity on the configuration.

In the case where the starting, optically active isomer changes to the enantiomers of the intermediate complex, the kinetic process can be schematically expressed as follows.

$$S_{\Delta(\text{or}\,\Lambda)} \xrightarrow{k_{\Delta(\text{or}\,\Lambda)}} I_{\Delta} + I_{\Lambda}$$

Hence the rate constant, $k_{\Delta(\text{or}\,\Lambda)}$, for the reaction of the Δ (or Λ) isomer can be given by eqn. (3):

$$\ln\{(\Delta E_0 - \Delta E_\infty)/(\Delta E_t - \Delta E_\infty)\} = k_{\Delta(\text{or}\,\Lambda)} \times t \qquad (3)$$

where ΔE_0, ΔE_t, and ΔE_∞ are total CD intensities at the initial state, at time t, and at equilibrium, respectively (*cf.* Appendix).

A linear relation was found for the ln $(\Delta E_t - \Delta E_\infty)$ *vs.* t plots, from which the observed rate constant, $k_{obsd,\Delta}$, was calculated for the Δ isomer.

Figures 5 and 6 show hydroxide ion and ethylenediamine concentration dependences of the observed rate constants. This stereochemical kinetic process depends solely on the hydroxide ion concentration, which coincides well with the first step in the racemate.

$$k^1_{obsd,\Delta} = k^1_{H_2O,\Delta} + k^1_{OH,\Delta}[OH^-] \qquad (4)$$

Hence it is concluded that a stereochemical change is accompanied in the base hydrolysis and aquation step.

Kinetic parameters of these reaction pathways are summarized in Table I.

Discussion

The present investigation demonstrates that the substitution reaction of the coordinated carbonate ligand in $[Co(CO_3)(en)_2]^+$, with ethylenediamine, proceeds successively with two rate-determining steps; the former essentially characteristic of the base-

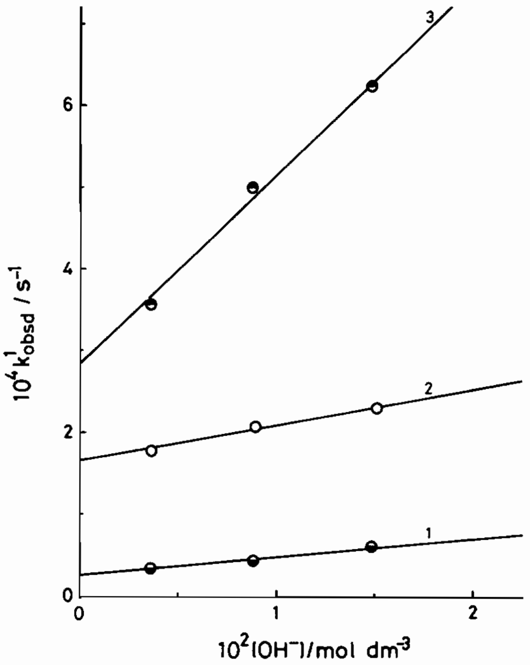

Fig. 5. Relation between k^1_{obsd} and [OH$^-$] for the optically active isomer. [Δ-(−)$_{589}$-[Co(CO$_3$)(en)$_2$]$^+$], 1.00 × 10^{-2} mol dm^{-3}; [en], 2.00 mol dm^{-3}; and [Cl$^-$], 1.0 mol dm^{-3}. Temp./°C: 1, 45.2; 2, 55.4; and 3, 65.4.

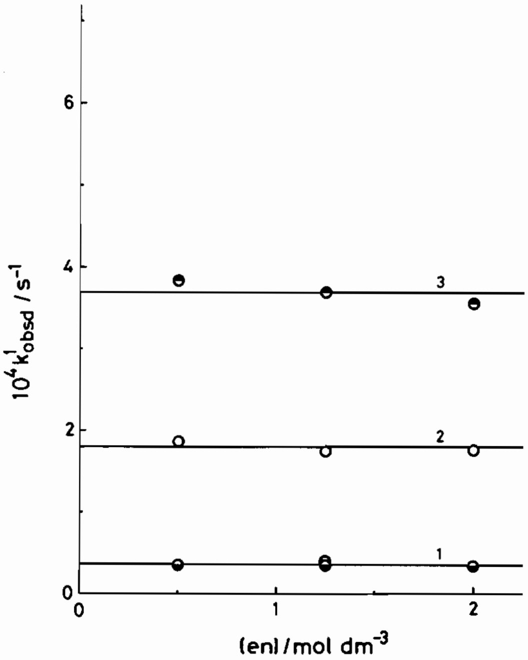

Fig. 6. Relation between k^1_{obsd} and [en] for the optically active isomer. [Δ-(−)$_{589}$-[Co(CO$_3$)(en)$_2$]$^+$, 1.00 × 10^{-2} mol dm^{-3}; [OH$^-$], 3.55 × 10^{-3} mol dm^{-3}; and [Cl$^-$], 1.0 mol dm^{-3}. Temp./°C: 1, 45.2; 2, 55.4; and 3, 65.4.

catalyzed hydrolysis accompanying the racemization for the optically active isomer [8], and the latter the anation reactions [9]. Furthermore, our spectrochemical and kinetic results suggest that the intermediate complex between these two rate-determining steps is a racemate in which the carbonate group coordinates as a unidentate ligand in the *cis* position to the hydroxide group, *i.e.*, *cis*(*O*)-[Co(OCO$_2$)(OH)(en)$_2$], because it gives no splitting pattern in the first d–d transition band ($^1A_{1g}(O_h)$–$^1T_{1g}(O_h)$) [10].

There is only one study, undertaken by Francis and Jordan [11] and concerning the base-catalyzed hydrolysis reaction of [Co(CO$_3$)(en)$_2$]$^+$, which deserves comparison with the first rate-determining step of the present investigation. The authors obtained the following kinetic parameters, $k_{obsd} = k_{H_2O} + k_{OH}[OH^-]$; k_{H_2O} = (4.31 ± 0.87) × 10^{-4} s^{-1}, $\Delta H^{\ddagger}$ = 89.5(72.4 ~ 97.5) kJ mol^{-1}, and $\Delta S^{\ddagger}$ = −27.6(−85.8 ~ −1.3) J mol^{-1} K^{-1}; k_{OH} = (2.74 ± 0.17) × 10^{-2} mol^{-1} dm^3 s^{-1}, $\Delta H^{\ddagger}$ =92.0 (87.0 ~ 97.5) kJ mol^{-1}, and $\Delta S^{\ddagger}$ = 15.1(−2.1 ~ +33.3) J mol^{-1} K^{-1} (1.0 mol dm^{-3} (NaClO$_4$), 44 °C), and concluded that the chelate ring opening of the coordinated carbonate ligand was the rate-determining step with C–O bond breaking for the aquation pathway. However, Co–O bond breaking for the base hydrolysis pathway was found to give a rather stable intermediate complex, [Co(OCO$_2$)(OH)(en)$_2$], which rapidly changed to [Co(OH)$_2$(en)$_2$]$^+$ in the final state. As for the aquation pathway, the following kinetic parameters merit comparison (k_{H_2O} = 1.2 × 10^{-4} s^{-1}, $\Delta H^{\ddagger}$ = (75 ± 13) kJ mol^{-1}, and $\Delta S^{\ddagger}$ = (−63 ± 38) J mol^{-1} K^{-1} (0.1 ~ 0.3 mol dm^{-3} (——), 25 °C), which had been obtained by the acid-catalyzed aquation study [12]. Conversion of the above rate constants to those at 55 °C and their comparison with the rate constants found by the present investigation reveals a good agreement with one another when differences in the solvent medium (especially co-existence of large excess of ethylenediamine over the cobalt(III) complex in the present investigation) are taken into consideration. Slight differences in the magnitudes of the thermodynamic parameters found in previous studies and those found in the present investigation suggest that the mechanism of the base hydrolysis pathway in the present reaction system deviates from a rigorous dissociative one, and has somewhat dissociative interchange characteristics. Thus it is stated that the first base-catalyzed hydrolysis step in the present ligand substitution reaction is limited by the dissociative carbonate chelate ring opening.

There are three possible geometrical configurations in the carbonate chelate ring opened five coordinate transitional species; a square planar configuration with (*N*)$_3$(*O*) basal plane and *N* donor atom at the apical position (**I**), a trigonal bipyramidal configuration with $(N)_3$ trigonal basal plane and O and N donor atoms at the apical positions opposite to each other (**II**), and a trigonal bipyramidal one with $(N)_2(O)$ basal plane and two N donor atoms at the apical positions (**III**). The species **I** brings about in the successive step solely configurational retention, the species **II** solely racemization, and the species **III** both configurational retention and conversion to the *trans*-(*O*) isomer, which can be ruled out in the present investigation. Our kinetic parameters for the racemate and the optically active isomer and the CD spectral evidences in the first kinetic step can be reasonably interpreted in terms of a mechanism in which the transitional species **I** converts to the species **II** followed by its change to $[Co(OCO_2)(OH)(en)_2]$. This deduction comes from the facts that $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ determined by the absorption spectral study are in fairly good agreement with those obtained by the CD spectral study, whereas k^1_{OH} and $k^1_{H_2O}$ obtained by the latter study are somewhat smaller than those obtained by the former study. Along with this principal process, however, direct change of the species **I** to the intermediate complex as an auxiliary process is also practical because configurational selectivity was noticed, to some extent, by the CD spectral study.

It is uncertain whether a water molecule coordinates directly to the ring opened, transitional species in alkaline aqueous solution of the order of 10^{-2} mol dm^{-3} buffered hydroxide ion concentration. By considering the basicity of the coordinated water molecules [13] and the dissociative characteristics of the aquation pathway, three routes may be possible; coordination of a water molecule to the ring opened, transitional species followed by a rapid liberation of a proton from it (**I′**), interaction of the ring opened, transitional species with a water molecule to form $[Co(OCO_2H)(OH)(en)_2]^+$, from which a proton is rapidly liberated (**II′**), and preliminary dissociation of a water molecule in the vicinity of the primary coordination sphere of the cobalt(III) ion to give OH^-, which then coordinates to the ring opened, transitional species (**III′**). In the aqueous solution specified above, where the carbonate ion is fully deprotonated, the concentration ratio $[OH^-]/[H_2O]$ does not exceed 2×10^{-4} even under the highest estimation. Furthermore, the ligand field strength of H_2O is higher than that of OH^- for the cobalt(III) ion [14]. Hence it may be safely stated that the route **I′** is the most plausible for the present ligand substitution reaction.

Contrary to the first kinetic step, there have been no studies, until the present, related to the second anation step. The independence in k^2_{obsd} of the hydroxide ion concentration, but the dependence on the ethylenediamine concentration by the relation, $k^2_{obsd} = k^2_{en}[en]$, and also the significance of the kinetic parameters related to k^2_{en}, reveal that the second kinetic step proceeds again with the dissociative characteristics and with no conjugate base formation for the second transitional species. Further, the reaction rate is limited by the coordination of ethylenediamine to form either $[Co(OCO_2)(en\text{-}N)(en)_2]^+$ or $[Co(OH)(en\text{-}N)(en)_2]^{2+}$, which is followed by a rapid liberation of carbonate or hydroxide group to complete chelate ring formation of the unidentate ethylenediamine (en-N) to $[Co(en)_3]^{3+}$.

The rate of hydroxide ion exchange in *cis*-(*O*)-$[Co(OH)_2(en)_2]^+$ has been determined to be $k^{-OH}_{OH} = 3 \times 10^{-5}$ s^{-1} with $\Delta H^{\ddagger} = 115$ kJ mol^{-1} and $\Delta S^{\ddagger} = 54.4$ J mol^{-1} K^{-1} (0.3 mol dm^{-3} (NaOH) + 0.5 mol dm^{-3} ($NaClO_4$), 25 ℃) [15]. This rate constant is larger than that of the unidentate carbonate ligand elimination of $[Co(OCO_2)(OH)(tren)]$ to give $[Co(OH)_2(tren)]^+$ of $k^{-OCO_2}_{OH} = 8.2 \times 10^{-6}$ mol^{-1} dm^3 s^{-1} with $\Delta H^{\ddagger} = 103$ (corrected value, 113) kJ mol^{-1} and $\Delta S^{\ddagger} = -4.2$ [16] (corrected value, 39.3 [17]) J mol^{-1} K^{-1} (1.0 mol dm^{-3} ($NaClO_4$), 25 ℃) and that of $k^{-OCO_2}_{OH} = 3.26 \times 10^{-5}$ mol^{-1} dm^3 s^{-1} with $\Delta H^{\ddagger} = 116$ kJ mol^{-1} and $\Delta S^{\ddagger} = 45.6$ J mol^{-1} K^{-1} (1.0 mol dm^{-3} ($NaClO_4$), 35.1 ℃) [17], even when differences in chelate ring structure and temperature are considered (tren, 2,2′,2″-triaminotriethylamine). Hence, we may state that the hydroxo group dissociates preliminarily before coordination of the unidentate ethylenediamine as the second rate-determining step, followed by a rapid liberation of the carbonate group [11] and the chelate ring closure to give $[Co(en)_3]^{3+}$.

In conclusion, the substitution reaction of the coordinated carbonate ligand in $[Co(CO_3)(en)_2]^+$ under the pseudo-first-order kinetic condition with respect to ethylenediamine in alkaline aqueous solution, proceeds successively as follows; $[Co(CO_3)(en)_2]^+$ changes, in the first kinetic step by the base-catalyzed hydrolysis reaction mechanism with the dissociative characteristics, to the intermediate *cis*-(*O*)-$[Co(OCO_2)(OH)(en)_2]$ complex, which then changes in the second kinetic step by unidentate coordination of ethylenediamine with the dissociative characteristics to the second intermediate $[Co(OCO_2)(en\text{-}N)(en)_2]^+$ complex, followed by a rapid chelate ring closure to form $[Co(en)_3]^{3+}$. Racemization takes place principally in the base-catalyzed hydrolysis step for the optically active isomer, but stereoselectivity is kept to some extent during the ligand substitution reaction processes.

References

1 For example: C. H. Langford and H. B. Gray, 'Ligand Substitution Processes', Benjamin, New York, 1965.
F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions, 2nd edn.' Chaps. 3 and 4, Wiley, New York, 1967.

R. G. Wilkins, 'The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes', Chaps. 4, 7 and 8, Allyn & Bacon, Boston, 1974.

2 K. Hayashi, K. Okamoto, J. Hidaka and H. Einaga, *J. Chem. Soc., Dalton Trans.*, 1377 (1982).

3 K. Hayashi, T. Ohsawa, K. Okamoto, J. Hidaka and H. Einaga, *J. Coord. Chem., 12,* 243 (1983).

4 H. Iwasaki, K. Okamoto, J. Hidaka and H. Einaga, *J. Coord. Chem., 12,* 219 (1983).

5 P. Pfeiffer and O. Angern, *Chem. Ber., 60,* 308 (1927).

6 F. P. Dwyer, I. K. Reid and F. L. Garvan, *J. Am. Chem. Soc., 83,* 1285 (1961).

7 J. B. Work, *Inorg. Synth., 2,* 221 (1946).

8 J. S. Holden and G. M. Harris, *J. Am. Chem. Soc., 77,* 1934 (1955), obtained racemization rate constant of Δ-$(-)_{589}$-$[Co(CO_3)(en)_2]^+$ to be 7.8×10^{-5} s^{-1} (0.0033 mol dm^{-3} $CO_3{}^{2-}$, pH 9.15, 56.1 ℃), which is considerably smaller than the rate constant from our CD data. Hence the racemization of the starting complex in itself can be ruled out.

9 'Anation' has been used in the substitution of coordinated water molecule in the aquametal complexes, but R. van Eldik and G. M. Harris, *Inorg. Chem., 19,* 3684 (1980), recently extended the term to include the substitution of the coordinated hydroxo group. The present paper is based on this extended notation.

10 H. Yamatera, *Bull. Chem. Soc. Jpn., 31,* 95 (1958).

11 D. J. Francis and R. B. Jordan, *J. Am. Chem. Soc., 91,* 6626 (1969).

12 V. S. Sastri and G. M. Harris, *J. Am. Chem. Soc., 92,* 2943 (1970).

13 J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand., 6,* 1265 (1952), determined the proton dissociation constants, pK_a, of coordinated water molecules in $[Co(H_2O)_2(en)_2]^{3+}$ to give pK_{a1} = 6.06 and pK_{a2} = 8.19 (1 mol dm^{-3} ($NaNO_3$), 25 ℃).
V. W. Cope, S. Chen and M. Z. Hoffman, *J. Am. Chem. Soc., 95,* 3116 (1973), determined pK_a of the coordinated water molecule in $[Co(OCO_2H)(H_2O)(en)_2]^{2+}$ to give pK_a = 5.7 (0.02 mol dm^{-3} (phosphate buffer), 23 ~ 25 ℃). These data mean that the coordinated water molecule of the intermediate complex, $[Co(OCO_2)(H_2O)(en)_2]^+$, dissociates a proton easily in the alkaline solution to produce $[Co(OCO_2)(OH)(en)_2]$.

14 For example: F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', 2nd edn., Chap. 26, Wiley, New York, 1966.

15 W. Kruse and H. Taube, *J. Am. Chem. Soc., 83,* 1280 (1961).

16 T. P. Dasgupta and G. M. Harris, *Inorg. Chem., 17,* 3123 (1978).

17 R. W. Hay and A. K. Basak, *Inorg. Chim. Acta, 71,* 73 (1983).

Appendix

Following rate equation, initial and boundary conditions, materials balance, and CD intensity relations can be given, *e.g.*, for the Δ isomer as the starting complex, based on the scheme in the text.

$$-\mathrm{d}[S_\Delta]_t/\mathrm{d}t = k_\Delta[S_\Delta]_t \qquad \text{(A-1)}$$

$$t = 0;\ [S_\Delta]_t = [S_\Delta]_0,\ [I_\Delta]_t = [I_\Lambda]_t = 0 \qquad \text{(A-2)}$$

$$t = \infty;\ [S_\Delta]_t = 0,\ [I_\Delta]_t = [I_\Delta]_\infty,\ [I_\Lambda]_t = [I_\Lambda]_\infty \qquad \text{(A-3)}$$

$$[S_\Delta]_0 = [S_\Delta]_t + [I_\Delta]_t + [I_\Lambda]_t = [I_\Delta]_\infty + [I_\Lambda]_\infty \qquad \text{(A-4)}$$

$$\Delta E_t = \Delta\epsilon_{S\Delta}[S_\Delta]_t + \Delta\epsilon_{I\Delta}[I_\Delta]_t + \Delta\epsilon_{I\Lambda}[I_\Lambda]_t \qquad \text{(A-5)}$$

$$\Delta E_\infty = \Delta\epsilon_{I\Delta}[I_\Delta]_\infty + \Delta\epsilon_{I\Lambda}[I_\Lambda]_\infty \qquad \text{(A-6)}$$

$$\Delta\epsilon_{I\Delta} = -\Delta\epsilon_{I\Lambda} \qquad \text{(A-7)}$$

From eqns. (A-5) ~ (A-7), eqn. (A-8) can be derived.

$$\Delta E_t - \Delta E_\infty = \Delta\epsilon_{S\Delta}[S_\Delta]_t + \Delta\epsilon_{I\Delta}\{([I_\Delta]_t - [I_\Delta]_\propto) - ([I_\Lambda]_t - [I_\Lambda]_\propto)\} \qquad \text{(A-8)}$$

When the deviation from the completely racemized state of the intermediate complex is sufficiently small, as in the present investigation, then the term $[I_\Delta]_t - [I_\Delta]_\infty$ can be equated to $[I_\Lambda]_t - [I_\Lambda]_\infty$ in a good approximation for the kinetic treatment. Hence eqn. (A-8′) can be obtained.

$$[S_\Delta]_t = (\Delta E_t - \Delta E_\infty)/\Delta\epsilon_{S\Delta} \qquad \text{(A-8′)}$$

Inserting eqn. (A-8′) into eqn. (A-1), solving the resulting rate equation under the initial and boundary conditions and rearranging the expression thus obtained, gives us eqn. (3).