Contribution from the Department of Chemistry,
University of the West Indies, Mona, Kingston 7, Jamaica

# Dinuclear Complexes of Transition Metals Containing Carbonate Ligands. 7.[1] Kinetics and Mechanism of Formation of the (μ-Carbonato)bis(μ-hydroxo)bis(triamminecobalt(III)) Ion in Weakly Basic Aqueous Carbonate Solution

Garfield G. Sadler and Tara P. Dasgupta*

*Received October 26, 1986*

The kinetics of formation of the title complex cation from the tris(μ-hydroxo)bis(triamminecobalt(III)) ion in aqueous buffered carbonate solution have been studied spectrophotometrically at 295 nm over the ranges $8.08 \leq pH \leq 9.31$, $20 \leq T \leq 34.8$ °C, and $7 \leq [CO_3{}^{2-}] \leq 23$ mM at an ionic strength of 0.1 M (LiClO$_4$). On the basis of the kinetic evidence, a mechanism is proposed in which $[(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3]^{3+}$ undergoes a hydroxide bridge cleavage to form a bis(hydroxo) intermediate, which then reacts with aqueous carbon dioxide. The rate of carbon dioxide uptake at 25 °C is found to be $4.31 \pm 1.00$ M$^{-1}$ s$^{-1}$ with $\Delta H^* = 11.1 \pm 1.1$ kcal mol$^{-1}$ and $\Delta S^* = -15.1 \pm 2.4$ cal deg$^{-1}$ mol$^{-1}$. The reaction has also been studied without any added carbonate over the ranges $8.2 \leq pH \leq 10.2$ and $30 \leq T \leq 44$ °C. The results have been interpreted in terms of a mechanism consisting of two parallel bridge cleavage paths—one being spontaneous and the other involving deprotonation equilibrium followed by water attack. At 30 °C and $I = 0.5$ M the kinetic parameters $k_0$ and $k_1K$ are $(6.3 \pm 0.6) \times 10^{-4}$ s$^{-1}$ and $58.4 \pm 0.5$ M$^{-1}$ s$^{-1}$, for which the activation parameters are $\Delta H_0{}^* = 28.4 \pm 0.7$ kcal mol$^{-1}$, $\Delta S_0{}^* = 20.2 \pm 2.5$ cal deg$^{-1}$ mol$^{-1}$ and $\Delta H_1{}^* = 14.9 \pm 2.6$ kcal mol$^{-1}$, $\Delta S_1{}^* -1.1 \pm 8.8$ cal deg$^{-1}$ mol$^{-1}$.

## Introduction

It has been clearly established[1-4] that the complex ion tris(μ-hydroxo)bis(triamminecobalt(III)) (triol) reacts in aqueous acidic solution to form the bis(μ-hydroxo)bis(aquatriamminecobalt(III)) ion (I). The X-ray crystallographic study[5] of I showed that the aqua ligands are in a trans configuration rather than the previously assumed cis configuration. The kinetic study of the formation of I was reinvestigated[6] in order to assign the necessary isomerization step. Preparation of several complexes in which one of the hydroxide groups of triol has been substituted by another bridging group has also been reported.[7,8] A large number of these complexes contain bridging carboxylate groups[9-12] as they are of particular interest for studies of reactions involving electron transfer through organic structural units.

Our continuing interest in the reactivity of bridging hydroxide toward aqueous CO$_2$ led to the isolation[13] of the (μ-carbonato)bis(μ-hydroxo)bis(triamminecobalt(III)) ion (II). We have reported earlier[13] the preparation and X-ray diffraction study of II, which showed that the ligand arrangement about the cobalt(III) centers in II is an edge-shared bis(octahedron) with an axial–axial connection via the bridging carbonate ligand.

We have also been able to isolate[1] several other binuclear cobalt(III) complexes containing a bridging carbonate by the reaction of a suitable μ-hydroxo complex with carbonate in aqueous solution. We now report the detailed kinetic study of the formation of II from triol in aqueous carbonate solution.

## Experimental Section

**Preparation of Complexes. Preparation of the Perchlorate Dihydrate of triol.** This compound was prepared by starting from trinitrotri-

amminecobalt(III) following the method of Linhard and Siebert.[2] The electronic spectrum is in excellent agreement with that reported in the literature.[14]

**Preparation of (μ-Carbonato)bis(μ-hydroxo)bis(triamminecobalt(III)) Perchlorate.** This compound was prepared as described in our earlier publication.[1] The purity was checked by microanalysis.[15] Anal. Calcd for Co$_2$N$_6$H$_{20}$O$_{13}$CCl$_2$: C, 2.34; H, 3.90; N, 16.38. Found: C, 2.25; H, 3.90; N, 16.25. The UV–visible spectrum of the compound also compares very well with that reported previously.[16] The infrared spectrum of the complex confirms the presence of bridging carbonate.[17]

**Materials.** All chemicals used were of reagent grade. Deionized water, obtained by passing the distilled water through the Milli-Q reagent-grade water system (Millipore Co., Bedford, MA), was used for all the kinetic runs. The lithium perchlorate solution was standardized by an ion-exchange method using Dowex 50W-X8 (50 mesh, H$^+$ form) ion-exchange resin.

**Spectra.** The visible and ultraviolet spectra were recorded on either by Pye Unicam Model SP8-100 or a Varian Cary spectrophotometer. The infrared spectra of all the complexes were recorded with a Pye Unicam SP-300 spectrophotometer by employing the KBr-disk technique.

**pH Measurements.** An Orion Model 701 digital pH meter fitted with a Markson combination electrode and a Beckman 3500 digital pH meter fitted with a Beckman combination electrode were used to measure pH. Calibration was achieved by standard buffer solutions, and pH measurements were made in a water-jacketed cell that was thermostated at the desired temperature. The hydroxide ion concentrations at various temperatures were calculated from pH values by using the values of p$K_w$ at various temperatures and at 0.1 M ionic strength obtained from the literature.[18]

**Kinetic Measurements.** The reaction of triol in aqueous carbonate was studied by recording the increase in absorbance with time at 295 nm, where there is an appreciable change[19] in absorbance between triol and the complex ion II.

The required hydrogen ion concentration was achieved by boric acid–sodium hydroxide buffer. The ionic strength was adjusted to 0.1 M with standard lithium perchlorate solution. The concentration of triol was kept at 0.5 mM in all the experiments.

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(9) Scott, K. L.; Wieghardt, K.; Sykes, A. G. *Inorg. Chem.* **1973,** *12,* 659.
(10) Wieghardt, K. *J. Chem. Soc., Dalton Trans.* **1974,** 2548.
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(13) Churchill, M. R.; Lashewycz, R. A.; Dasgupta, T. P.; Koshy, K. *Inorg. Chem.* **1981,** *20,* 376.

(14) The extinction coefficients of triol are 137, 265, and 1798 M$^{-1}$ cm$^{-1}$ at 256, 364, and 296 nm, respectively (lit.[2] 135, 263, and 1778 M$^{-1}$ cm$^{-1}$ at these wavelengths).
(15) Microanalyses were done by Dr. E. Pascher, Mikroanalytisches Labor Pascher, An der Pulvermuhle 3, D-5480 Remagen 8, West Germany.
(16) The extinction coefficient of the μ-carbonato complex is 122 M$^{-1}$ cm$^{-1}$ at 525 nm. Exactly the same value was reported previously.[1]
(17) The stretching frequencies for the bridging carbonate group are 1352 and 1495 cm$^{-1}$ (see ref 1).
(18) Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolytic Solutions,* 3rd ed.; Van Nostrand-Reinhold: New York, 1958; p 654.
(19) The extinction coefficient of triol at 295 nm is 1798 M$^{-1}$ cm$^{-1}$ whereas that of the corresponding μ-carbonato complex is 3410 M$^{-1}$ cm$^{-1}$.

**Table I.** Pseudo-First-Order Rate Constants and Rate Parameters for the Base Hydrolysis of triol[a] ([complex] = $5 \times 10^{-4}$ M; $I$ = 0.1 M (LiClO$_4$))

| 30.3 °C | | | 34.0 °C | | | 38.5 °C | | | 44.0 °C | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| pH | $10^5[OH]$/M | $10^3 k_{obsd}$/s$^{-1}$ | pH | $10^5[OH]$/M | $10^3 k_{obsd}$/s$^{-1}$ | pH | $10^5[OH]$/M | $10^3 k_{obsd}$/s$^{-1}$ | pH | $10^5[OH]$/M | $10^3 k_{obsd}$/s$^{-1}$ |
| 9.15 | 2.14 | 1.79 | 9.01 | 2.09 | 3.32 | 8.89 | 2.09 | 5.41 | 8.77 | 2.34 | 9.63 |
| 9.30 | 3.02 | 2.30 | 9.28 | 3.90 | 4.87 | 9.19 | 4.17 | 7.41 | 8.95 | 3.55 | 11.03 |
| 9.51 | 4.90 | 3.64 | 9.44 | 5.62 | 6.73 | 9.35 | 6.03 | 10.08 | 9.08 | 4.79 | 14.05 |
| 9.61 | 6.17 | 4.13 | 9.61 | 8.32 | 9.52 | 9.58 | 10.23 | 14.59 | 9.35 | 8.91 | 21.81 |
| 9.63 | 6.46 | 4.45 | 9.74 | 11.22 | 12.50 | 9.79 | 16.60 | 23.64 | 9.55 | 14.13 | 31.32 |
| 9.74 | 8.32 | 5.57 | 9.88 | 15.49 | 16.13 | 9.95 | 23.99 | 33.50 | 9.65 | 17.78 | 37.79 |
| 9.93 | 12.88 | 8.19 | 9.90 | 16.22 | 16.31 | | | | 9.79 | 24.55 | 51.07 |
| 10.23 | 25.70 | 15.58 | | | | | | | | | |
| $10^3 k_0$/s$^{-1}$ | 0.63 ± 0.06 | | | 1.05 ± 0.16 | | | 2.15 ± 0.13 | | | 4.94 ± 0.25 | |
| $k_1 K/M^{-1}$ s$^{-1}$ | 58.4 ± 0.5 | | | 102 ± 2 | | | 129 ± 2 | | | 188 ± 2 | |

[a] Average percentage error limit of $k_{obsd}$ at all temperatures is ±2%. $\Delta H_0^*$ = 28.4 ± 0.7 kcal mol$^{-1}$; $\Delta S_0^*$ = 20.2 ± 2.5 cal deg$^{-1}$ mol$^{-1}$; $\Delta H_1^*$ = 14.9 ± 2.6 kcal mol$^{-1}$; $\Delta S_1^*$ = 1.1 ± 8.8 cal deg$^{-1}$ mol$^{-1}$.

The kinetic runs for the base hydrolysis were also followed spectrophotometrically at 295 nm[20] under the same conditions as the reaction in aqueous carbonate.

All experiments were done under pseudo-first-order conditions, and the rate constants along with the standard deviations were obtained from the slope of ln $(A_\infty - A_t)$ vs. time plots by using a standard least-squares computer program. For the kinetic runs in which curvature in the ln $(A_\infty - A_t)$ vs. time plot was observed, rate constants were obtained by separation of the biphasic plot into its components as outlined before.[21-23]

**Results and Discussion**

A family of UV–visible spectra collected during the reaction of triol in 0.01 M NaHCO$_3$ solution shows only slight changes in absorbances in the visible region, but in the UV region the 295-nm peak slowly disappears as the absorbance of the product increases continuously with decreasing wavelength. The final spectrum corresponds to that of II. Since a solution of NaHCO$_3$ is weakly basic, it was first necessary to investigate the behavior of triol in basic solution without any added carbonate. The most significant spectral changes for this solution also occur in the UV region. The product of the reaction is characterized as the bis-($\mu$-hydroxo)bis(hydroxotriamminecobalt(III)) ion on the basis of its complete conversion to triol on lowering the pH of the solution to about 5–6.

The pseudo-first-order rate constants for the hydrolysis of triol over the respective acidity and temperature ranges of 8.08 ≤ pH ≤ 10.2 and 20 ≤ $T$ ≤ 44 °C are presented in Table I. The study was limited to the pH range indicated as at higher pHs the rate of decomposition to cobalt(II) is competitive with the cleavage of the second hydroxide bridge. This competing reaction also did not allow accurate determination of the absorbance of the product, and hence the rate constants were obtained by the Guggenheim method.[24]

The kinetic data in Table I for the base hydrolysis of triol can be interpreted in terms of Scheme I. This mechanism leads to the rate law
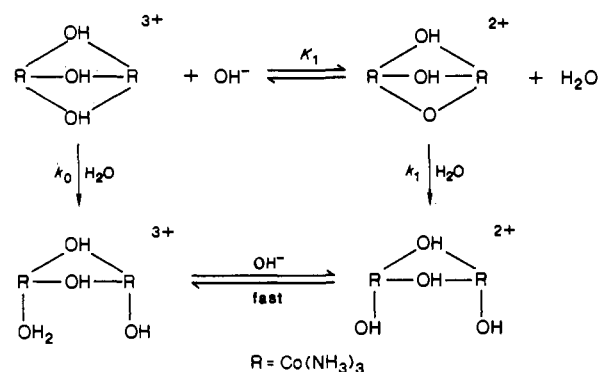
$$k_{obsd} = \frac{k_0 + k_1 K_1 [OH^-]}{1 + K_1 [OH^-]} \quad (1)$$

At low values of [OH$^-$], $K_1$[OH$^-$] ≪ 1, and then eq 1 will take the form

$$k_{obsd} = k_0 + k_1 K_1 [OH^-] \quad (2)$$

The $K_0$ values and the composite $k_1 K_1$ values were obtained from the least-squares treatment of the data in Table I, and these values along with the activation parameters are also displayed in Table I.

(20) The extinction coefficient of the product of base hydrolysis, the bis($\mu$-hydroxo) species, is approximately 2640 M$^{-1}$ cm$^{-1}$ at 295 nm. The product gradually decomposes in basic solution to the Co(II) species.
(21) Koshy, K.; Dasgupta, T. P. *J. Chem. Soc., Dalton Trans.* **1984**, 2781.
(22) Swinbourne, E. S. *Analysis of Kinetic Data*; Thomas Nelson: Toronto, Ontario, Canada, 1971; p 89.
(23) Wilkins, R. G. *The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes*; Allyn and Bacon: Boston, 1974; p 23.
(24) Reference 22, p 78.

**Scheme I**



$R = Co(NH_3)_3$

The mechanism proposed above for the base hydrolysis of triol is similar to the one proposed previously[21,25] for the decomposition of bis($\mu$-hydroxo)bis[bis(ethylenediaminecobalt(III))] ion (III). The spontaneous bridge cleavage of the complex ion III is 3.78 × 10$^{-5}$ s$^{-1}$ compared to 2.6 × 10$^{-6}$ s$^{-1}$ for triol, whereas the value of $k_1 K_1$ for the complex ion III is 180 M$^{-1}$ s$^{-1}$ compared to 41 M$^{-1}$ s$^{-1}$ for triol. These last values clearly indicate that the hydroxo group in the tribridged complex is less acidic than in the dibridged complex. This is exactly the reason the hydroxo bridge cleavage in triol occurs much more rapidly in acidic solution than in the complex ion III.[1,9]

It should be pointed out here that the cleavage of the hydroxide bridge via the D$_{cB}$ mechanism[26] would also lead to the same form of expression as in eq 1. In the absence of the $K$ value it would be difficult to distinguish between the two mechanisms mentioned above. For the D$_{cB}$ mechanism, one would expect the deprotonation constant, $K_1$, to be very small, which will make the concentration of the conjugate base quite small.

This will in turn make the $k_{obsd}$ vs. [OH$^-$] plot linear even at high [OH$^-$]. However, for the base hydrolysis[25] of the complex ion III, the $k_{obsd}$ values showed some curvature even at pH 10, a behavior that is very unlikely for a D$_{cB}$ mechanism. El-Awady[25] estimated 1150 ± 300 M$^{-1}$ for the deprotonation constant of the complex ion III. We expect the $k_1$ value for triol to be smaller than for the complex ion III and to be in the range 10–10$^2$. This assumption is quite reasonable, since the acidity of bridged hydroxide in triol would be much less than that in the complex ion III.

The activation parameters, $\Delta H^*$ and $\Delta S^*$, are also obtained from a least-squares analysis of the linear Eyring-Polanyi[27] plots of the data in Table I, and the values are 28.4 ± 0.7 kcal mol$^{-1}$ and 20.2 ± 2.5 cal deg$^{-1}$ mol$^{-1}$ for the $k_0$ path and 14.0 ± 2.6 kcal mol$^{-1}$ and −1.1 ± 8.8 cal deg$^{-1}$ mol$^{-1}$ for the $k_1 K$ path, respectively. The corresponding values for the base hydrolysis of the complex

(25) El-Awady, A. A.; Hughes, Z. Z. *Inorg. Chem.* **1971**, *10*, 1415.
(26) Tobe, M. L. *Inorganic Reaction Mechanisms*; Thomas Nelson: Toronto, Ontario, Canada, 1972; p 95.
(27) Eyring, H. *Chem. Rev.* **1935**, *17*, 65.

**Table II.** Pseudo-First-Order Rate Constants and Rate Parameters for the Reaction of triol in Aqueous Carbonate Solution[a]

| 20.0 °C; $[CO_3]_T = 0.02$ M | | | 25.0 °C; $[CO_3]_T = 0.02$ M | | | 30.0 °C; $[CO_3]_T = 0.01$ M | | | 34.8 °C; $[CO_3]_T = 0.01$ M | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| pH | $10^6[OH^-]/M$ | $10^5 k_{obsd}/s^{-1}$ | pH | $10^6[OH^-]/M$ | $10^5 k_{obsd}/s^{-1}$ | pH | $10^6[OH^-]/M$ | $10^5 k_{obsd}/s^{-1}$ | pH | $10^6[OH^-]/M$ | $10^5 k_{obsd}/s^{-1}$ |
| 8.70 | 3.50 | 1.93 | 8.40 | 2.57 | 3.95 | 8.18 | 2.24 | 4.07 | 8.08 | 2.51 | 0.97 |
| 8.71 | 3.55 | 1.88 | 8.62 | 4.27 | 3.88 | 8.25 | 2.63 | 3.98 | 8.34 | 4.57 | 9.91 |
| 8.80 | 4.37 | 1.84 | 8.81 | 6.61 | 3.77 | 8.37 | 3.47 | 3.90 | 8.39 | 5.13 | 8.77 |
| 8.88 | 4.25 | 1.75 | 8.97 | 9.55 | 3.35 | 8.45 | 4.17 | 3.65 | 8.60 | 8.32 | 8.37 |
| 9.03 | 7.41 | 1.74 | 9.02 | 10.72 | 3.31 | 8.79 | 9.12 | 3.34 | 8.78 | 12.59 | 7.44 |
| 9.20 | 10.96 | 1.44 | 9.11 | 13.18 | 3.19 | 9.01 | 15.14 | 3.00 | 8.98 | 19.95 | 6.52 |
| | | | 9.31 | 20.89 | 2.88 | | | | 9.14 | 28.84 | 5.18 |

| | | | | |
|---|---|---|---|---|
| $k_2/M^{-1} s^{-1}$ | 2.71 ± 0.51 | 4.31 ± 1.30 | 5.46 ± 1.09 | 7.39 ± 0.92 |
| $10^{-4}K_2/M^{-1}$ | 1.74 ± 0.05 | 2.22 ± 0.77 | 2.54 ± 0.84 | 3.45 ± 0.40 |

[a] Average percentage error limit of $k_{obsd}$ at all temperatures is ±2%. $\Delta H_2^* = 11.1 \pm 1.0$ kcal mol$^{-1}$; $\Delta S_2^* = 18.6 \pm 3.8$ cal deg$^{-1}$ mol$^{-1}$; $\Delta H_2^° = 8.6 \pm 0.9$ kcal mol$^{-1}$; $\Delta S_2^° = 49 \pm 3$ cal deg$^{-1}$ mol$^{-1}$.

**Table III.** Observed Rate Constants for the Reaction of Triol in Aqueous Carbonate Solution ([complex] = $2.5 \times 10^{-4}$ M; pH 8.38; Temperature 30 °C; $I = 0.1$ M (LiClO$_4$))

| $10^3[CO_3]_T/M$ | $10^5 k_{obsd}/s^{-1}$ | $10^3[CO_3]_T/M$ | $10^5 k_{obsd}/s^{-1}$ |
|---|---|---|---|
| 7.14 | 3.15 ± 0.02 | 13.1 | 4.83 ± 0.02 |
| 8.33 | 3.41 ± 0.04 | 14.3 | 5.51 ± 0.02 |
| 9.52 | 3.66 ± 0.03 | 16.7 | 6.68 ± 0.03 |
| 11.9 | 4.56 ± 0.02 | 22.6 | 8.45 ± 0.05 |

ion III are available; the $\Delta H^*$ and $\Delta S^*$ values for the $k_0$ path from the acid hydrolysis data of the complex ion III are available. The $\Delta H^*$ and $\Delta S^*$ values are 29.9 kcal mol$^{-1}$ and 5.7 cal deg$^{-1}$ mol$^{-1}$, respectively. It is interesting to note that the $\Delta H^*$ values for the $k_0$ paths for both triol and the complex ion III are very close, indicating the possibility of a similar type of mechanism operating for both systems. The difference in $\Delta S^*$ values for these two complexes is perhaps understandable in terms of the greater difficulty in forming a structured transition state in the case of triol. Since the $k_1 K_1$ path is a composite one, detailed discussion of the activation parameters will not be pursued.

The pseudo-first-order rate constants for the formation of the complex ion II were determined at a fixed total carbonate concentration of either 0.01 or 0.02 M and over the pH range of 8.08 ≤ pH ≤ 9.31 by following the increase in absorbance$^{-19}$ with time at 295 nm. A slight curvature in the plot of ln $(A_t - A_\infty)$ vs. time was observed over the lower pH range. The extent of curvature decreases with increasing pH. This behavior is characteristic of systems undergoing irreversible consecutive reactions. Separations of the biphasic plots into their components were done for the first step are in close agreement with the rate constants obtained in the base hydrolysis study. The rate constants obtained from the linear portion of the ln $(A_\infty - A_t)$ vs. time plots at four different temperatures are listed in Table II. Some kinetic runs were performed at a fixed [H$^+$] (pH 8.38) and temperature (30 °C) by varying the total carbonate concentration.

The results are presented in Table III. The equilibrium concentrations of CO$_2$, HCO$_3^-$, and CO$_3^{2-}$ have been calculated for each kinetic run from the experimentally determined p$K$ values of carbonic acid.[28] From the calculation it is clear that over the pH range in which the formation of the $\mu$-carbonato complex was studied, [CO$_2$] decreases and [CO$_3^{2-}$] increases appreciably while [HCO$_3^-$] decreases marginally with increasing pH. It should be noted here that the equilibrium rates between CO$_2$, HCO$_3^-$, and CO$_3^{2-}$, are not instantaneous in aqueous solution$^{29,30}$ and, hence, it is sometimes necessary to add micromolar quantities of the enzyme carbonic anhydrase$^{28}$ to kinetic runs of relatively fast reactions to ensure that the equilibrium is rapidly established and maintained. In our study, however, the results obtained from runs in which carbonic anhydrase was added were indistinguishable

**Scheme II**
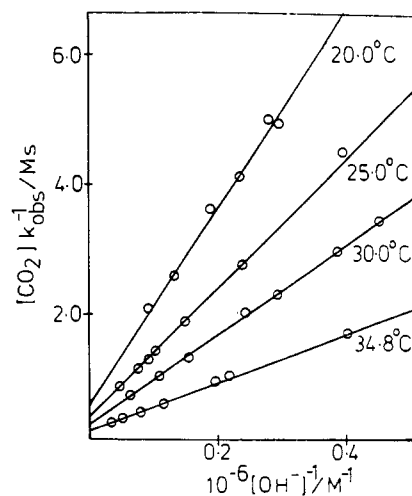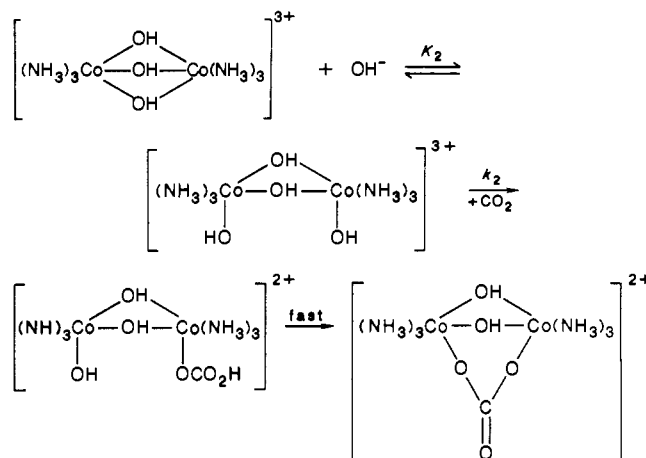
**Figure 1.** Plot of $[CO_2]/k_{obsd}$ vs. $[OH]^{-1}$ for the CO$_2$ uptake by triol at different temperatures.

from those obtained from experiments in which the enzyme was excluded. This was interpreted to mean that the reactions were slow enough for the equilibrium concentration of CO$_2$ to be maintained throughout. A close examination of the data presented in Table II allows us to propose the mechanism outlined in Scheme II, based on CO$_2$ as the reactive species. Justification for assigning the first step as a preequilibrium one is supported by the fact that curvature in the ln $(A_\infty - A_t)$ vs. time plot was only observed for a small percentage of the reaction time and only for those runs performed at lower pHs, where the base hydrolysis is slower. The proposed mechanism also requires that the ring closure of the hydroxo bicarbonato species III be relatively fast. This can reasonably be expected on the basis that the rate of ring closure$^{31}$

(28) The values of p$K_1$ and p$K_2$ for the carbonic acid are 6.03 and 9.8 at 25 °C and $I = 0.5$ M: Chaffee, E.; Dasgupta, T. P.; Harris, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 4169.

(29) Forster, R. E., Edsall, J. T., Otis, A. B., Roughton, F. J. W., Eds. *CO$_2$: Chemical, Biological and Physiological Aspects*; National Aernautical and Space Administration: Washington, DC, 1969; p 15.

(30) Harris, G. M.; Dasgupta, T. P. *J. Indian Chem Soc.* **1977**, *54*, 62.

(31) Dasgupta, T. P.; Harris, G. M. *J. Am. Chem. Soc.* **1975**, *97*, 1733.

**Table IV.** Rate Parameters for the $CO_2$ Uptake by Cobalt(III) Complexes

| complex ion[a] | $k/M^{-1} s^{-1}$ | $\Delta H^{*}/kcal\ mol^{-1}$ | $\Delta S^{*}/cal\ deg^{-1}\ mol^{-1}$ | ref |
|---|---|---|---|---|
| $Co(NH_3)_5OH^{2+}$ | 220 | $15.3 \pm 0.9$ | $3.6 \pm 3.0$ | 28 |
| $Co(tren)(OH_2)(OH)^{2+}$ | 44 | $14.7 \pm 0.1$ | $-1.9 \pm 0.2$ | 35 |
| $cis$-$Co(cyclam)(OH_2)(OH)^{2+}$ | 57 | $14.8 \pm 1.0$ | $0.8 \pm 3.5$ | 32 |
| $cis$-$Co(cyclam)(OH)_2{}^+$ | 196 | $15.2 \pm 0.5$ | $3.0 \pm 1.9$ | 32 |
| $trans$-$Co(cyclam)(OH_2)(OH)^{2+}$ | 37 | $28.0 \pm 0.6$ | $46.2 \pm 1.9$ | 32 |
| $trans$-$Co(cyclam)(OH)_2{}^+$ | 70 | $29.3 \pm 0.6$ | $44.6 \pm 1.9$ | 32 |
| $(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3{}^{3+}$ | 4.3 | $11.1 \pm 1.1$ | $-18.1 \pm 3.8$ | this work |

[a] Abbreviations: tren = 2,2′,2″-triaminotriethylamine; cyclam = 1,4,8,11-tetraazacyclotetradecane.

in $[Co(tren)(OH)(HCO_3)]^+$ is 0.05 s$^{-1}$ at 25 °C (tren = 2,2′,2″-triaminotriethylamine).

The rate expression derived from Scheme II takes the form

$$k_{obsd} = \frac{k_2 K_2 [OH^-][CO_2]}{1 + K_2[OH]} \qquad (3)$$

which then rearranges to

$$\frac{[CO_2]}{k_{obsd}} = \frac{1}{k_2 K_2 [OH^-]} + \frac{1}{k_2} \qquad (4)$$

Plots of $[CO_2]/k_{obsd}$ vs. $1/[OH^-]$ at four different temperatures are shown in Figure 1. The values of $k_2$ and $K_2$ obtained from a least-squares treatment of the data in Table II are also listed in Table II along with their temperature parameters. It is clear from eq 3 that, at a constant pH, a plot of $k_{obsd}$ vs. $[CO_2]$ should be linear passing through the origin. The value of $k_2$ obtained from the least-squares analysis of the data in Table III is 5.06 M$^{-1}$ s$^{-1}$, which compares favorably with the value of 5.46 M$^{-1}$ s$^{-1}$ at 30 °C obtained from the plot of Figure 1. In our earlier studies we have reported that the bridging hydroxide in dinuclear complexes has no tendency to react with $CO_2$. On that basis we have ruled out any possibility of triol reacting with $CO_2$ or $HCO_3{}^-$, although mechanistically one cannot distinguish between the reaction of $HCO_3{}^-$ with triol and the reaction of $CO_2$ with the bridge-opened species II. This is also substantiated by the fact that the formation of the $\mu$-carbonato species is considerably retarded at pH below 8, although the concentrations of both species, triol and bicarbonate ion, are appreciably high. According to our mechanism, once the hydroxide bridge is cleaved, the mode of reactions of the dinuclear bis(hydroxo) complex II is very similar to that observed with several mononuclear cobalt(III) hydroxo complexes in carbonate solution.[30] An examination of the data in Table IV shows that the rate constants for the $CO_2$ uptake of mono- and bis(hydroxo) species lie in the range 40–200 M$^{-1}$ s$^{-1}$ whereas the corresponding rate constant for triol is only 4 M$^{-1}$ s$^{-1}$. This is partly due to the fact that the ligands in the dinuclear structure offer much more stereochemical hindrance and hence a greater retarding influence on the $CO_2$-uptake process.

It is now of interest to compare the rate parameters for $CO_2$ uptake by the more extensively studied mononuclear complexes of cobalt(III) with the results of the present system. These rate parameters are summarized in Table IV. It is quite clear from the data in Table IV that for the pentaammine and all the cis complexes, the temperature parameters are identical within experimental error, with $\Delta H^* = 15$ kcal mol$^{-1}$ and $\Delta S^* \approx 0$. For these reactions it was suggested[32] that the gain in entropy due to the solvent shell disordering is compensated for by the loss of entropy accompanying the formation of the highly structured

transition state in which hydrogen bonding plays an important role. The $CO_2$-uptake reactions of the trans cyclam species exhibit very different activation parameters, for which an explanation is given in terms of the impossibility of achieving strengthened hydrogen bonding to adjacent OH ligands in the transition state. The activation parameters obtained for the reaction with the binuclear complex compare favorably with those for the pentaammine complex and the cis complexes. The slightly smaller $\Delta H^*$ value is compensated for by the more negative $\Delta S^*$ value.

The formation of $(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(CO_3)_2$ from $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(NH_3)_4]^{4+}$ represents the only other detailed study reported[33] on the formation of carbonato dinuclear cobalt(III) complexes. However, in this complex the carbonato groups are in the terminal position and on the same cobalt atom.

The mechanism for the formation of this complex has been proposed on the basis of collective evidence from kinetic and chemical reactions, in which the formation of three different ion pairs, X,OH$^-$, X,HCO$_3$, and X,CO$_3{}^{2-}$ (X = $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(NH_3)_4]^{4+}$) plays an important role. However, there is no evidence for ion pairing in the formation of the $\mu$-carbonato complex discussed above.

Finally, it is interesting to note here the difference in reactivity of a number of dinuclear cobalt(III) complexes with bridging hydroxo ligands in aqueous carbonate solution. The monobridged complex $[(NH_3)_5Co(\mu\text{-}OH)Co(NH_3)_5]^{5+}$ and the dibridged complex $[(en)_2Co(\mu\text{-}OH)(\mu\text{-}OH)Co(en)_2]^{4+}$ give exclusively mononuclear complexes, $[(NH_3)_5Co(CO_3)]^+$ and $[(en)_2Co(CO_3)]^+$, respectively,[34,35] in aqueous carbonate solution, indicating complete cleavage of all the hydroxo bridges (en = 1,2-diaminoethane). However, as discussed before, a completely unsymmetrical molecule, $(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(CO_3)_2$, is produced[31] from $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(NH_3)_4]^{4+}$ whereas $[(en)_2Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(en)_2]^{4+}$ reacts with carbonate ion in solution to form the bridged carbonato complex $[(en)_2Co(\mu\text{-}NH_2)(\mu\text{-}CO_3)Co(en)_2]^{3+}$. It is, therefore, clear that several factors, including the reactivity of bridging ligands as well as terminal ligands, influence the mode of reaction in carbonate solution.[36]

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