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Kinetics and Mechanism of Aquation and Formation Reactions of Carbonato Complexes.

14. Base-Catalyzed Carbonato Ring Opening of

Carbonato(β, β', β'' -triaminotriethylamine)cobalt(III) Perchlorate and Spontaneous Decarboxylation of Aquobicarbonato(β, β', β'' -triaminotriethylamine)cobalt(III) Ion¹

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Base hydrolysis of the title compound enables the preparation of the uncharged dechelated species $\text{Co}(\text{tren})(\text{OH})(\text{CO}_3)$. In acidic solution, the latter protonates to form $\text{Co}(\text{tren})(\text{OH}_2)(\text{HCO}_3)^{2+}$, which undergoes rapid decarboxylation ($k = 1.19 \text{ s}^{-1}$ at 25°C , $\Delta H^\ddagger = 14.3 \pm 0.4 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = -10.2 \pm 1.2 \text{ cal deg}^{-1} \text{ mol}^{-1}$) by a mechanism completely analogous to that of acid-catalyzed decarboxylation of related pentaaminecobalt(III) complex ions. The rate of base-catalyzed dechelation of the title compound is quite slow ($k = 3.6 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ at 25°C , $\Delta H^\ddagger = 17.2 \pm 1.9 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = -12 \pm 6 \text{ cal deg}^{-1} \text{ mol}^{-1}$) and is succeeded by even slower carbonate ion elimination to yield as the final product $\text{Co}(\text{tren})(\text{OH})_2^+$ ($k = 8.2 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$ at 25°C , $\Delta H^\ddagger = 24.7 \pm 1.2 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = 1.0 \pm 4.0 \text{ cal deg}^{-1} \text{ mol}^{-1}$). Comparisons with the results of related base-hydrolysis studies strongly suggest that the mechanism is one of direct dissociative substitution involving metal-oxygen fission in both steps of the carbonate release.

Introduction

Our series of studies of the decomposition reactions of chelated carbonato complexes of cobalt(III) has so far focused entirely on the proton-promoted ring-opening and decarboxylation processes, such as previously reported² for the title complex ion, $\text{Co}(\text{tren})(\text{CO}_3)^+$ ($\text{tren} \equiv \beta, \beta', \beta''$ -triaminotriethylamine). Furthermore, in these acidic systems, carbonato chelate ring opening is the rate-determining step except at high acid concentration, where the rate of ring opening can effectively catch up with^{2,3} or even substantially exceed⁴ the rate of CO_2 release. Base-catalyzed hydrolysis of chelated carbonato species is also known to occur, though at a very slow rate relative to the acid-induced process for the same complex. Furthermore, the ring-opened intermediate is known to be quite stable, in the case both of $\text{Co}(\text{tren})(\text{OH})(\text{CO}_3)$ (from the base hydrolysis of $\text{Co}(\text{tren})(\text{CO}_3)^+$)⁵ and of $\text{Co}(\text{en})_2$ -

$(\text{OH})(\text{CO}_3)$ (from $\text{Co}(\text{en})_2(\text{CO}_3)^+$, where $\text{en} \equiv$ ethylenediamine).⁵⁻⁹ So far, detailed studies of the kinetics of base hydrolysis of a chelated carbonato complex have been reported only for the $\text{Co}(\text{en})_2(\text{CO}_3)^+$ species,^{7,9} for which the two-step $\text{S}_{\text{N}}1\text{CB}$ mechanism has been proposed. These studies, however, are subject to some uncertainties of interpretation, since cis/trans isomerization can occur in the case of both the intermediate and the final products, $\text{Co}(\text{en})_2(\text{OH})(\text{CO}_3)$ and $\text{Co}(\text{en})_2(\text{OH})_2^+$, and may indeed play a significant role in the reaction mechanism. We feel, therefore, that an investigation of the kinetics of base hydrolysis of the geometrically rigid complex $\text{Co}(\text{tren})(\text{CO}_3)^+$ should enable some clarification of the nature of this type of reaction. A further motivation for this work is the fact that the reported stable intermediate, $\text{Co}(\text{tren})(\text{OH})(\text{CO}_3)$, can be used as the starting material with which to study the acid-catalyzed decarboxylation. This enables one to bypass the proton-promoted ring-opening reaction, which has usually been the only unequivocally observable process in carbonato chelate aquation studies.³

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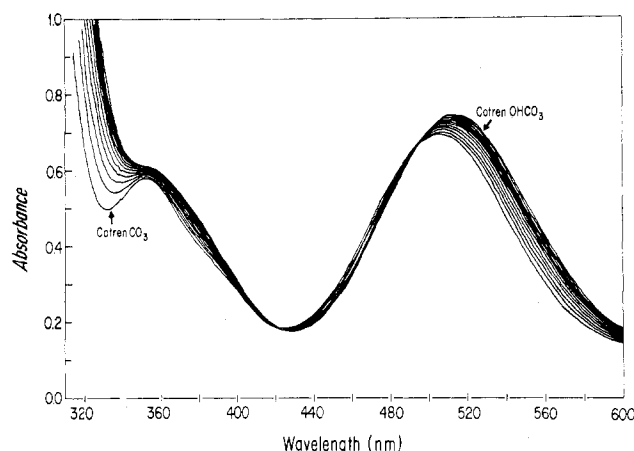


Figure 1. Spectral change during base-catalyzed ring-opening reaction of $\text{Co}(\text{tren})(\text{CO}_3)^+$ ion.

Experimental Section

Materials. Sodium hydroxide solutions were prepared by dilution of ampules of concentrated reagent (Fisher Certified reagent). Sodium perchlorate was prepared from sodium carbonate and perchloric acid and recrystallized twice before use. The sodium perchlorate solution was standardized by an ion-exchange method using Dowex 50W-X8 (50 mesh, H^+ form) ion-exchange resin. All the other reagents were of reagent grade and deionized, degassed water was used in preparing all solutions.

Preparation of Compounds. Carbonato(β, β', β'' -triaminotriethylamine)cobalt(III) perchlorate was prepared following the procedure described previously.² The purity of the compound was checked by microanalysis and by comparing its visible spectrum with that reported earlier.¹⁰ Anal. Calcd for $\text{Co}(\text{tren})(\text{CO}_3)\text{ClO}_4 \cdot \text{H}_2\text{O}$: C, 22.0; H, 5.2; N, 14.6. Found: C, 21.9; H, 5.3; N, 14.5.

Hydroxocarbonato(β, β', β'' -triaminotriethylamine)cobalt(III) ion was prepared and identified in solution as follows. A 10-mL sample of 0.2 M carbonato(β, β', β'' -triaminotriethylamine)cobalt(III) perchlorate is added to 10 mL of 1 M NaOH and the reaction is allowed to go essentially to completion. The progress of the reaction is monitored by repetitive scanning in the range 320–600 nm. Since the second step in the reaction (replacement of CO_3^{2-} by OH^-) is so much slower than base-catalyzed ring opening, a clean-cut separation is possible as shown by the persistent isobestic points at 422 and 494 nm (see Figure 1). Preliminary experiments with a mixed-bed (cation–anion) exchange column showed that the process just described converts all the $\text{Co}(\text{tren})(\text{CO}_3)^+$ complex ion to the uncharged hydroxocarbonato species without the appearance of any appreciable amount of the cationic product $\text{Co}(\text{tren})(\text{OH})_2^+$. The reaction product is therefore purified by passage through an anion-exchange resin (Dowex 1X-8, Cl^- form, 50 mesh) packed in a water-jacketed column. Ice-cold water is circulated through the column prior to the addition of the reaction mixture and also during elution. The neutral complex $\text{Co}(\text{tren})(\text{OH})(\text{CO}_3)$ is eluted by cold deionized water, while any traces of anionic impurities and of excess OH^- ion are retained on the column. The eluate is collected in a volumetric flask and kept in an ice bath to eliminate the possibility of ring closure in the weakly basic solution (pH \sim 10).

Absorption Spectra. The UV–visible absorption spectra were obtained with a Cary Model 118 recording spectrophotometer using a pair of matched 2-cm quartz cells. Our data for $\text{Co}(\text{tren})(\text{CO}_3)^+$, $\text{Co}(\text{tren})(\text{OH})_2^{3+}$, and $\text{Co}(\text{tren})(\text{OH})_2^+$ agree very well with those reported earlier.^{5,10} The spectrum of the $\text{Co}(\text{tren})(\text{OH})(\text{CO}_3)$ species was recorded at 10 °C in a borate buffer at pH 9 and shows the following features (molar absorbance in parentheses): λ_{max} 515 nm (155) and λ_{min} 425 nm (20), with a shoulder at \sim 350 nm (130).¹¹

Kinetics. Decarboxylation. The kinetics of decarboxylation of $\text{Co}(\text{tren})(\text{H}_2\text{O})(\text{HCO}_3)^{2+}$ was investigated by stopped-flow technique with a Durrum Model 110 stopped-flow spectrophotometer. The complex $\text{Co}(\text{tren})(\text{OH})(\text{CO}_3)$ in slightly basic solution (pH 10) is placed in one storage syringe, and for the higher pH runs the other storage syringe is filled with phosphate–citrate buffer¹² (0.3 M). The ionic strength of both solutions is maintained at 0.5 M with NaCl. In the lower pH runs (pH 1–3), perchloric acid is used to adjust the

Table I. Pseudo-First-Order Rate Constants for the Decarboxylation of $\text{Co}(\text{tren})(\text{OH}_2)(\text{HCO}_3)^{2+}$ ^a

pH	$k_{\text{obsd}}, \text{s}^{-1}$	pH	$k_{\text{obsd}}, \text{s}^{-1}$
1.0	0.76	5.50	0.55
2.0	0.76	5.60	0.51
2.4	0.73	5.65	0.49
3.0	0.76	5.80	0.44
4.05	0.76	5.80	0.43
4.70	0.71	5.85	0.42
5.05	0.68	5.85	0.41
5.20	0.65	5.95	0.34
5.40	0.59	6.40	0.23
5.40	0.57	6.86	0.19
5.50	0.54	6.86	0.18

^a [Complex] = 1×10^{-3} M; $T = 20$ °C; $I = 0.5$ M (NaCl).

acidity. After each series of runs, the pH of the reaction mixture is determined by means of a Radiometer Model 26 pH meter. The reaction is monitored at 510 nm where the absorbance difference between hydroxocarbonato and diaquo species is at maximum. Runs were made in the range $1 \leq \text{pH} \leq 6.8$ at 20 °C. It was found that beyond pH 6 the spectrum of the final solution is not that of pure $\text{Co}(\text{tren})(\text{OH}_2)_2^{3+}$ or $\text{Co}(\text{tren})(\text{OH}_2)(\text{OH})^{2+}$. This is because ring closure to form $\text{Co}(\text{tren})(\text{CO}_3)^+$ is competing with decarboxylation in the higher pH range.¹⁰ Other kinetic runs were carried out only in 0.1 M acid to obtain the decarboxylation rate constants over a range of temperatures. The pseudo-first-order rate constants were deduced graphically in the conventional manner from semilogarithmic plots of the data obtained from the exponential oscilloscope traces.

Base Hydrolysis. Sodium hydroxide and sodium perchlorate solutions are mixed in appropriate quantities to adjust the ionic strength to 1.0 M. After the mixture attains temperature equilibrium in the thermostat, the required weighed amount of complex is added with mixing, and a portion of the resulting solution is quickly transferred to a spectrophotometer cell. The temperature of the cell compartment is maintained constant by circulating water from the thermostat, and the increase in absorbance with time at 325 nm is followed on a Cary Model 15 or 118C spectrophotometer utilizing a time-drive chart mechanism.

Runs were made in which the hydroxide concentration was varied from 0.01 to 1.0 M in the temperature range 25–35 °C. The pseudo-first-order rate constants were calculated by the Guggenheim method¹³ and by conventional $\ln(A_\infty - A_t)$ vs. time data using A_∞ as the absorbance of $\text{Co}(\text{tren})(\text{OH})(\text{CO}_3)$ at 325 nm. Both of these methods give identical results. Additional kinetic runs at 1.0 M hydroxide ion concentration were carried out in the temperature range 35–45 °C, under which conditions the decarboxylation reaction can be observed after the completion of the ring-opening reaction. This is confirmed by the initial rapid absorbance increase at 325 nm to the maximum value indicative of total conversion to $\text{Co}(\text{tren})(\text{OH})(\text{CO}_3)$ before the absorbance starts to decrease steadily to the final value indicative of $\text{Co}(\text{tren})(\text{OH})_2^+$. The pseudo-first-order rate constants for this latter process were calculated by means of the conventional absorbance change technique already mentioned, utilizing for A_0 and A_∞ the absorbances of $\text{Co}(\text{tren})(\text{OH})(\text{CO}_3)$ and $\text{Co}(\text{tren})(\text{OH})_2^+$, respectively.

Results and Discussion

It was found that a neutral aqueous solution of $\text{Co}(\text{tren})(\text{CO}_3)^+$ is stable, with no spectral change observable over a period of at least 2 days. In the presence of sodium hydroxide, a fairly rapid change occurs with the retention of isobestic points at 422 and 494 nm and a readily identifiable shift of the spectrum from that of the chelated carbonato reactant to that of the intermediate $\text{Co}(\text{tren})(\text{OH})(\text{CO}_3)$ (see Figure 1). The latter complex is stable enough to be separated and identified by ion-exchange chromatography (see Experimental Section). However, after long standing in strongly basic solution, the spectrum changes to that of the final product $\text{Co}(\text{tren})(\text{OH})_2^+$.

The study of the acid-catalyzed decarboxylation of the nonchelated carbonato complex $\text{Co}(\text{tren})(\text{OH})(\text{CO}_3)$ yielded the observed first-order rate constants given in Table I. The

Table II. Rate Parameters for the Decarboxylation of $\text{Co}(\text{tren})(\text{OH}_2)(\text{HCO}_3)^{2+}$ ^a

$T, ^\circ\text{C}$	k_1, s^{-1}	$\Delta H^\ddagger, \text{kcal mol}^{-1}$	$\Delta S^\ddagger, \text{cal deg}^{-1} \text{mol}^{-1}$
10	0.31	}14.3 ± 0.4	}-10.2 ± 1.2
15	0.49		
20	0.76		

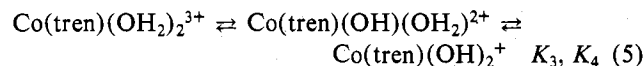
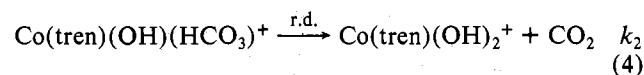
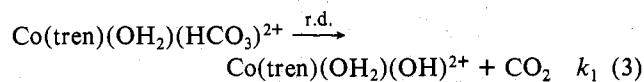
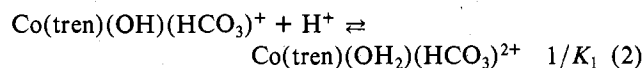
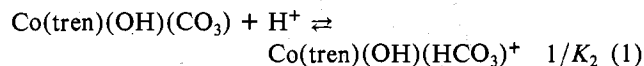
^a [Complex] = 1×10^{-3} M; $I = 0.5$ M (NaCl); $[\text{H}^+] = 0.1$ M.^b k_1 values represent the averages of at least four independent runs.

Table III. Rate Parameters for the Decarboxylation of Various Monodentate Bicarbonate Complexes of Cobalt(III) at 25 °C and Ionic Strength = 0.5 M

complex	k, s^{-1}	$\Delta H^\ddagger, \text{kcal mol}^{-1}$	$\Delta S^\ddagger, \text{cal deg}^{-1} \text{mol}^{-1}$	ref
$\text{Co}(\text{NH}_3)_5(\text{HCO}_3)^{2+}$	1.10	15.5 ± 0.4	-5.3 ± 1.3	15
<i>cis</i> - $\text{Co}(\text{en})_2(\text{NH}_3)(\text{HCO}_3)^{2+}$	0.60	16.4 ± 0.5	-4.2 ± 1.6	18
<i>trans</i> - $\text{Co}(\text{en})_2(\text{NH}_3)(\text{HCO}_3)^{2+}$	0.66	16.7 ± 0.9	-3.2 ± 3.0	18
$\text{Co}(\text{tetren})(\text{HCO}_3)^{2+}$	0.28	15.6 ± 1.9	-8.6 ± 4.4	1 ^a
$\text{Co}(\text{tren})(\text{OH}_2)(\text{HCO}_3)^{2+}$	1.19	14.3 ± 0.4	-10.2 ± 1.2	this work
<i>cis</i> - $\text{Co}(\text{en})_2(\text{OH}_2)(\text{HCO}_3)^{2+}$	0.81	14.4 ± 0.8	-10.9 ± 2.8	19
<i>trans</i> - $\text{Co}(\text{en})_2(\text{OH}_2)(\text{HCO}_3)^{2+}$	2.10	14.0 ± 1.7	-10.1 ± 6.0	19

^a tetren = tetraethylenepentamine.

data are consistent with the type of mechanism utilized previously¹⁴⁻¹⁶ to interpret the acid hydrolysis of pentaaminecarbonato species of the type $\text{M}(\text{NH}_3)_5\text{CO}_3^+$. Adapted to the present system, the reactions to be considered are



Within the pH range of this study, the major reactant species are $\text{Co}(\text{tren})(\text{OH}_2)(\text{HCO}_3)^{2+}$ and $\text{Co}(\text{tren})(\text{OH})(\text{HCO}_3)^+$, since $\text{p}K_2$ is ~ 8.7 .¹⁷ Furthermore, the rapid decrease of k_{obsd} beyond pH 5 (see Table I) indicates that the species $\text{Co}(\text{tren})(\text{OH})(\text{HCO}_3)^+$ is much more resistant to decarboxylation than is its protonated parent ($\text{p}K_1 \approx 5.3$).¹⁷ One can assume, therefore, that $k_1 \gg k_2$, so that the rate law takes the form

$$k_{\text{obsd}} = k_1[\text{H}^+]/(K_1 + [\text{H}^+]) \quad (6)$$

where the constants are as defined above. It is seen from Table I that a reliable limiting value for k_{obsd} at high acidity is $k_1 = 0.76 \text{ s}^{-1}$. Using this figure, a computerized nonlinear least-squares analysis of the data in Table I leads to a value for $\text{p}K_1$ of 5.9 ± 0.1 , in reasonable agreement with the earlier value obtained under somewhat different ionic strength conditions.¹⁷ Values for k_1 at other temperatures were obtained from runs made at pH 1 where $k_1 = k_{\text{obsd}}$ and these are listed

Table IV. Spectrophotometric Rate Data for the Base-Catalyzed Ring Opening of the $(\text{CO}_3)(\text{tren})\text{Co}^{\text{III}}$ Complex^a

[OH], M	$10^3 k_{\text{obsd}}, \text{s}^{-1}$		
	25 °C	30 °C	35 °C
0.01	0.39		
0.10	0.62	1.12	1.79
0.20	0.93	1.69	2.72
0.30	1.27	2.32	3.44
0.40	1.70	2.76	4.53
0.50	2.09	3.17	5.50
0.60	2.40	3.70	6.29
0.70	2.90	4.32	7.30
0.80	3.10	4.86	8.56
0.90		5.18	9.48
1.00	3.89	6.41	

^a [Complex ion] = 1 mM; $I = 1$ M (NaClO_4).Table V. Rate Parameters for the Base-Catalyzed Ring-Opening of $(\text{CO}_3)(\text{tren})\text{Co}^{\text{III}}$ Complex

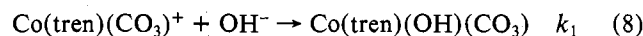
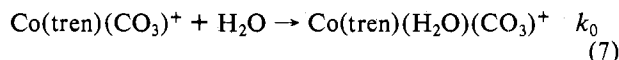
$T, ^\circ\text{C}$	$10^4 k_0, \text{s}^{-1}$	$10^3 k_1, \text{M}^{-1} \text{s}^{-1}$
25	2.63 ± 0.60	3.61 ± 0.11
30	5.55 ± 1.31	5.45 ± 0.21
35	6.99 ± 1.03	9.62 ± 0.18
	$\Delta H_0^\ddagger =$ 17.3 ± 5.1 kcal mol ⁻¹	$\Delta H_1^\ddagger =$ 17.2 ± 1.9 kcal mol ⁻¹
	$\Delta S_0^\ddagger =$ -17 ± 17 cal deg ⁻¹ mol ⁻¹	$\Delta S_1^\ddagger =$ -12 ± 6 cal deg ⁻¹ mol ⁻¹

in Table II along with the corresponding activation parameters.

It is of value at this point to compare the aquation rate constants for various monodentate carbonatocobalt(III) complexes. The relevant figures are presented in Table III. One notes that the values of k are bracketed within a factor of only 3, as expected for a series of reactions of identical mechanism, i.e., elimination of CO_2 from HCO_3^- coordinated to $\text{Co}(\text{III})$. For the pentaamine series there is a minor trend to lower k and more negative ΔS^\ddagger values as NH_3 ligands are replaced by *en*²⁰ and, finally, by tetren, with ΔH^\ddagger remaining essentially constant. A probable explanation lies in the degree of solvation of the complex ion as discussed in our preceding paper.¹

However, in comparing the aquotetraamine with the pentaamine complexes there appear to be two significant variations. First, the ΔS^\ddagger values are several units more negative for the (N_4O) series (last three in Table III) than for the (N_5) series (first four). Again, the degree of solvation provides a reasonable explanation for the ΔS^\ddagger variation, since the aquo ligand of the (N_4O) complexes probably promotes a higher degree of solvent-shell reorganization in formation of the transition state than occurs with the (N_5) species. But apparently the metal-carbonato bond energies in the (N_5) species are such that ΔH^\ddagger values for these consistently exceed the value for the (N_4O) species by about 2 kcal/mol. The net result is that the increase in ΔG^\ddagger resulting from the more negative ΔS^\ddagger values for the (N_4O) series is balanced out by the more positive ΔH^\ddagger values for the (N_5) series, so that no appreciable rate constant variations are noted.

The base-catalyzed ring opening of $\text{Co}(\text{tren})(\text{CO}_3)^+$ has been studied in alkaline solution within the concentration range $0.010 \text{ M} < [\text{OH}^-] < 1.00 \text{ M}$. The pseudo-first-order rate constants, k_{obsd} , are listed in Table IV. Plots of k_{obsd} vs. $[\text{OH}^-]$ are completely linear, and the data can be interpreted in terms of parallel rate-determining processes as follows:



This mechanism conforms to the rate law

$$k_{\text{obsd}} = k_0 + k_1[\text{OH}^-] \quad (9)$$

A least-squares analysis of the data of Table IV on this basis yields values for k_0 and k_1 , with their standard deviations, at the three temperatures, and these figures, along with the corresponding Eyring temperature parameters, appear in Table V.

Studies in our laboratory of the acid hydrolysis of $\text{Co}(\text{tren})(\text{CO}_3)^+$ have yielded the reasonably accurate value² for k_0 at 25 °C of $(1.7 \pm 0.2) \times 10^{-4} \text{ s}^{-1}$ in satisfactory agreement with the value obtained in the present base-hydrolysis study of $(2.6 \pm 0.6) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$. Some very limited flow-system data due to Scheidegger⁵ indicate a value for k_1 of about $13 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ at 20 °C and $I = 0.1 \text{ M}$ (NaClO_4), severalfold greater than the figure of $2.2 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ (extrapolated to 20 °C from data in Table V). The tenfold difference in ionic strength can however account for about a factor of 2 in the discrepancy, while the normal deviations due to variations in experimental technique no doubt determine the remainder. The base-catalyzed hydrolysis of $\text{Co}(\text{en})_2(\text{CO}_3)^+$ has been studied in several laboratories.^{7,9,21} There is some disagreement concerning the value of k_1 at high $[\text{OH}^-]$, but a figure of about $3 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C with $\Delta H^\ddagger \approx 22 \text{ kcal/mol}$ and $\Delta S^\ddagger \approx 3 \text{ cal deg}^{-1} \text{ mol}^{-1}$ is consistent with all data in the base concentration range of our study and not widely different from our figures for the $\text{Co}(\text{tren})(\text{CO}_3)^+$ complex of $k_1 = 3.6 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C, $\Delta H^\ddagger = 17.2 \pm 1.9 \text{ kcal/mol}$, and $\Delta S^\ddagger = -12 \pm 6 \text{ cal deg}^{-1} \text{ mol}^{-1}$. A further comparison is possible by use of the estimate given by Scheidegger for the ratio k_1/k_{-1} of 100 at 20 °C, i.e., the ratio of the rates of ring opening of $\text{Co}(\text{tren})(\text{CO}_3)^+$ by OH^- ion to ring closure of the hydroxo-carbonato product. We were not able to observe the ring-closure reaction in the $[\text{OH}^-]$ range of our study. However, using our extrapolated value for k_1 at 20 °C of $2.2 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, one obtains for k_{-1} a value of $2.2 \times 10^{-5} \text{ s}^{-1}$, in good agreement with the value of $2.5 \times 10^{-5} \text{ s}^{-1}$ for ring closure of $\text{Co}(\text{en})_2(\text{OH})(\text{CO}_3)$ as derived from earlier published data.⁹ There is thus a clear parallelism between the reactions of $\text{Co}(\text{tren})(\text{CO}_3)^+$ and $\text{Co}(\text{en})_2(\text{CO}_3)^+$ in basic solution, in spite of the possible isomerization reaction of first-formed *cis*- $\text{Co}(\text{en})_2(\text{OH})(\text{CO}_3)$ to the trans isomer after ring opening. Presumably this reaction is as slow as or slower than the similar reaction of $\text{Co}(\text{en})_2(\text{OH})_2^+$, for which the rate constant at 20 °C is deduced²² to be $2.9 \times 10^{-6} \text{ s}^{-1}$. Since this rate constant is only about one-tenth as great as the carbonato ring-closure rate constant, little complication due to isomerization is to be expected in the ring-opening/ring-closing kinetics of the $\text{Co}(\text{en})_2(\text{CO}_3)^+$ ion.

The site of bond fission in the hydrolytic reactions of different types of oxyanion chelates is a matter of some interest and has been studied in a number of systems by means of oxygen-18-tracer experiments. For base hydrolysis of $\text{Co}(\text{en})_2(\text{CO}_3)^+$, the ring-opening step proceeds with 100% Co-O bond cleavage.⁹ This is also undoubtedly true for the ring-opening step in acid hydrolysis of the same complex, though the subsequent CO_2 elimination involves only the O-C bond.²³ It is therefore almost certain that the ring-opening step in base hydrolysis of $\text{Co}(\text{tren})(\text{CO}_3)^+$ also proceeds with Co-O bond breakage, since the kinetics of this process is so similar to that of the $(\text{en})_2$ congener. By contrast, no Co-O bond fission occurs²⁵ in the base hydrolysis of the $\text{Co}(\text{en})_2(\text{C}_2\text{O}_4)^+$ complex. For the phosphato analogue,²⁶ the nature of the data does not enable separate identification of the two steps in base hydrolysis. However, it is found that about two-thirds of the overall phosphate ion elimination events involve Co-O cleavage and one-third O-P cleavage, while in acid solution, only Co-O fission is observed. It is generally found that the rate constants of base-catalyzed hydrolysis of cobalt(III) complexes are much greater than those of aquation. Thus, the ratio k_1/k_0 as

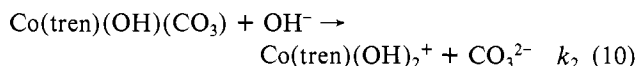
Table VI. Rate Parameters for the Base Hydrolysis of $\text{Co}(\text{tren})(\text{OH})(\text{CO}_3)^+$ ^a

$T, \text{ }^\circ\text{C}$	$10^5 k_2, \text{ M}^{-1} \text{ s}^{-1}$	$\Delta H_2^\ddagger, \text{ kcal mol}^{-1}$	$\Delta S_2^\ddagger, \text{ cal mol}^{-1} \text{ deg}^{-1}$
35	3.17	} 24.7 ± 1.2	} -0.96 ± 4.0
40	6.25		
45	13.1		

^a $[\text{Complex}] = 2 \text{ mM}$; $[\text{NaOH}] = 1 \text{ M}$.

defined above is²⁷ about 10^5 for $\text{Co}(\text{en})_2(\text{PO}_4)$ while for $\text{Co}(\text{tren})(\text{CO}_3)^+$ the corresponding ratio is only about 10 (see Table V). Clearly, there must be a considerable contrast in the reaction mechanisms of the two systems, perhaps related to a possible contribution of O-P bond cleavage to the dechelation of the phosphato ligand.

We have studied separately the base hydrolysis of the ring-opened tren species according to the reaction



and the observed second-order rate constants and derived temperature variation parameters appear in Table VI. Scheidegger's limited study⁵ of the same reaction suggests a value for k_2 which is completely inconsistent with our data. However, for the related complex $\text{Co}(\text{en})_2(\text{OH})(\text{CO}_3)$ k_2 is shown⁷ to be $\sim 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ at 47.5 °C, not very far away from our extrapolated value for the tren analogue of $\sim 2 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ (using the data of Table VI). There is also close agreement on the ΔH^\ddagger values ($\sim 24 \text{ kcal/mol}$). It is of interest that the hydroxide-for-chloride replacement reaction²⁸ of the complex *cis*- $\text{Co}(\text{en})_2(\text{OH})(\text{Cl})^{2+}$, with $k = 0.37 \text{ M}^{-1} \text{ s}^{-1}$ at 0 °C, shows vastly more base-hydrolysis reactivity than its carbonato analogue. However, the rate of solvent water exchange²⁹ with *cis*- $\text{Co}(\text{en})_2(\text{OH})_2^+$, which is presumably limited by the rate of OH^- elimination, has a value of $2.9 \times 10^{-4} \text{ s}^{-1}$ at 40 °C in 0.8 M NaOH, under which conditions our value for the pseudo-first-order rate constant of CO_3^{2-} elimination is $5.0 \times 10^{-5} \text{ s}^{-1}$, only about sixfold different. It is therefore reasonable to conclude that the rate-limiting process in base hydrolysis of $\text{Co}(\text{tren})(\text{OH})(\text{CO}_3)$ is in fact complete substitution for the CO_3^{2-} ion by OH^- , requiring Co-O bond fission for every event. As already pointed out, Co-O bond cleavage is also the likely path for the dechelation of $\text{Co}(\text{tren})(\text{CO}_3)^+$ in basic solution which is, of course, the formation reaction of $\text{Co}(\text{tren})(\text{OH})(\text{CO}_3)$. Both steps of the base-hydrolysis reaction therefore satisfy the requirements of the typical $\text{S}_{\text{N}}1\text{cB}$ dissociative mechanism of substitution.³⁰

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Registry No. $\text{Co}(\text{tren})(\text{OH})(\text{CO}_3)$, 67761-83-5; $\text{Co}(\text{tren})(\text{H}_2\text{O})(\text{HCO}_3)^{2+}$, 67761-84-6; $\text{Co}(\text{tren})(\text{CO}_3)^+$, 31240-94-5; OH^- , 14280-30-9.

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Stereoselectivity in Ion-Pair Formation. 4.¹ Stereochemical Consideration about Specific Ion Association between Optically Active (Amino acidato)bis(ethylenediamine)cobalt(III) and Tartrate Ions

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The ion association constants were determined in aqueous solution for the ion pairs consisting of optically active (phenylalaninato)bis(ethylenediamine)cobalt(III) and an L-tartrate anion, by utilizing circular dichroism measurements: $K = 4.3 \pm 0.1$ for Λ -(L-phe), $K = 4.0 \pm 0.1$ for Δ -(D-phe), $K = 2.7 \pm 0.3$ for Λ -(D-phe), and $K = 1.2 \pm 0.6$ for Δ -(L-phe). This difference in association constant was interpreted in terms of the difference in steric repulsion between the phenyl group of the complex ion and the L-tartrate anion in the ion-pair formation. Furthermore, it was noted that the difference in association constant is related to the elution order in column chromatography.

Introduction

In earlier investigations²⁻⁵ of stereoselective ion association of metal complexes, it has been reported that L-tartrate associates with the tris(ethylenediamine)cobalt(III) complex in favor of its Λ form in aqueous solution. Recently we have demonstrated by the study⁶ of X-ray analysis of Λ -[Co(en)₃]Br·L-tart·5H₂O that L-tartrate approaches [Co(en)₃]³⁺ along the direction of C₃ axis and concluded that this structural feature plays an important role in the stereoselective formation of this diastereomeric salt. In contrast to the solid state, it is difficult to detect the requisite for the stereoselectivity of L-tartrate in solution. Nevertheless, it was proposed⁷ on the basis of the above structural information that it is essential for the complex to have three sets of NH hydrogen atoms in the face perpendicular to the C₃ axis (triangular NH face) for the great stereoselective ion association with L-tartrate. This proposal is based on the consideration of the efficiency for optical resolution of *fac*- and *mer*-[Co(β -ala)₃] through column chromatography; the *fac* isomer with the triangular NH face is resolved with L-tartrate, but the *mer* isomer with no triangular NH face is not resolved.⁷ At present, however, it is not yet known how the stereoselectivity is influenced by the steric interaction. In this paper, we wish to report the investigation of the stereoselective interaction between L-tartrate and the optically active (amino acidato)bis(ethylenediamine)cobalt(III) complex, [Co(am)(en)₂]²⁺ (am = NH₂CH(R)COO⁻), which has three sets of NH hydrogen atoms in the face perpendicular to the pseudo C₃ axis and an R group related to this axis.

Experimental Section

Preparation and Resolution. Optically active phenylalanine and tartaric acids were reagent grade. The other chemicals were also reagent grade and were used without further purification. The glycinate complex was resolved into the two enantiomers. The L-

phenylalaninato complex was resolved into the two configurational isomers. The preparation of the D-phenylalaninato complex was not attempted. The complexes used here were prepared and resolved as described by Liu and Douglas.⁸

Measurements. The circular dichroism (CD) spectra were recorded on a reference solution of the complex ion (0.002 M) and on a sample solution of the complex ion (0.002 M) containing a tartrate anion (0.030 M). To obtain the association constant the CD at 445 nm was measured for the reference solution and for the sample solution containing the tartrate anion ranging in concentration from 0.010 to 0.030 M. The ionic strength (μ) was made 0.1 by the addition of an appropriate amount of sodium perchlorate. A JASCO J-40CS recording spectropolarimeter with a 2-cm cell was used. The cell was kept at 25.0 ± 0.2 °C with a Haake circulator, Model FK. The difference in the CD spectra between the sample and reference solutions was measured by using the data processor (DP) compartment operating at 0.2 nm/step of processor resolution. The D- and L-tartrate salts used here were obtained by neutralizing the corresponding tartaric acids with LiOH·H₂O. The neutralized tartaric acids showed a pH around 7, and so the hydrogen tartrate content was negligible. The CD and UV spectra do not change throughout the measurement of the CD change, and so racemization or decomposition does not take place in this system.

Cation-Anion Association Constants. The data obtained from CD measurements were analyzed by using the equation

$$C_M(C_X - C_{MX})/(\Delta CD/2) = (C_X - C_{MX})/(\Delta \epsilon_{MX} - \Delta \epsilon_M) + 1/K(\Delta \epsilon_{MX} - \Delta \epsilon_M)$$

where ΔCD refers to the difference in the CD between a sample solution and a reference solution, and $\Delta \epsilon$ refers to the molar CD of the species indicated by the subscript. The association constant, K , is obtained through the similar procedure in the previous paper¹ ([Co(en)₃]³⁺ is replaced by [Co(am)(en)₂]²⁺ in this case).

Results and Discussion

The circular dichroism (CD) spectra of Λ - and Δ -[Co(L-phe)(en)₂]²⁺, which are diastereomeric to each other, are shown in Figure 1. The CD spectra for the two complexes