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# Kinetics and Mechanism of Aquation and Formation Reactions of Carbonato Complexes. 21. Anation of Dihydroxo($\beta,\beta',\beta''$-triaminotriethylamine)cobalt(III) by Carbonate Ion in Basic Solution[1]

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The anation of $Co(tren)(OH)_2^+$ by carbonate ion was studied in the acidity range $10.5 \leq pH \leq 13$, in the temperature range 25–60 °C, and at an ionic strength of 0.5 M. The rate constant for the anation reaction at $[OH^-] > 0.025$ M is $(4.0 \pm 1.5) \times 10^{-4}\ M^{-1}\ s^{-1}$ at 50 °C, $\Delta H^* = 24.2$ kcal mol$^{-1}$, and $\Delta S^* = 1.5$ cal deg$^{-1}$ mol$^{-1}$. Rate data for the reverse reactions at 50 °C are found to be $k_{-2} = (2.8 \pm 0.3) \times 10^{-4}\ s^{-1}$, $\Delta H^* = 25.3$ kcal mol$^{-1}$, and $\Delta S^* = 3.6$ cal deg$^{-1}$ mol$^{-1}$ (ring-opening reaction of $Co(tren)CO_3^+$); $k_{-1} = (3.7 \pm 0.1) \times 10^{-4}\ s^{-1}$, $\Delta H^* = 23.0$ kcal mol$^{-1}$, and $\Delta S^* = -3.4$ cal deg$^{-1}$ mol$^{-1}$ at pH 13 (base hydrolysis of $Co(tren)(OH)(OCO_2)$). The results are discussed in reference to earlier studies on $CO_2$ uptake and base-catalyzed ring opening and hydrolysis of such complex species.

## Introduction

The earlier papers in this series reported on the kinetics and mechansm of the formation of various carbonate complexes. Such reactions in general proceed via $CO_2$ uptake by a hydroxo ligand to produce a monodentate carbonate complex,[2-6] which is in some cases[7-11] followed by a ring-closing step to produce a bidentate carbonate complex. It has generally been accepted[2-11] that the mechanism for $CO_2$ uptake does not involve the breakage of any metal–ligand bonds but that it proceeds via secondary oxygen–carbon bond formation. The investigated systems[2-11] include the metal ions Co(III), Rh(III), Cr(III), and Ir(III) and the ligands $NH_3$, en, cyclam, tren, tetren, $Cl^-$, $Br^-$, $I^-$, and $CN^-$ (en = ethylenediamine, cyclam = 1,4,8,11-tetraazacyclotetradecane, tren = $\beta,\beta',\beta''$-triaminotriethylamine, tetren = tetraethylenepentamine).

No evidence for the formation of carbonate complexes via the anation of metal aquo or metal hydroxo species by bicarbonate and carbonate ion was reported in the above-mentioned studies. Such anation reactions are expected to be significantly slower than $CO_2$ uptake, since they follow a normal substitution mechanism which is governed by the breaking of the metal–oxygen bond. Typical water-exchange rate constants for complexes of the type $M(NH_3)_5OH_2^{3+}$, M = Co(III) and Rh(III), are of the order of $1 \times 10^{-6}\ s^{-1}$ at 25 °C,[12,13] compared to stopped-flow rates of $CO_2$ uptake by $M(NH_3)_5OH^{2+}$ under such conditions. For a study of the formation of carbonate complexes via the anation by bicarbonate and carbonate ions, the experimental conditions must be such that the contribution of the $CO_2$ uptake reaction is negligible. This should be the case at pH >11, where $[CO_2] < 10^{-4}$% of the total carbonate concentration in solution.[2,3] The complex $Co(tren)(OH)_2^+$ is stable in basic medium[14] and does not undergo any cis to trans isomerization[7,15,16] such that it is an ideal complex for a study of the anation by carbonate ion.

## Experimental Section

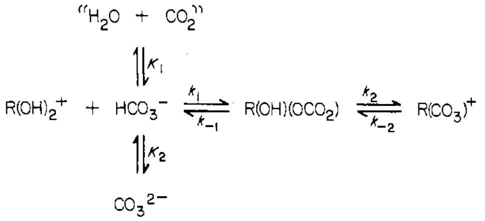
$[Co(tren)CO_3]ClO_4$ was prepared by starting from commercially available tren·3HCl (Strem Chemicals) according to the method of Scheidegger.[7,16] *cis*-$[Co(tren)(OH_2)_2](ClO_4)_3$ was prepared as described elsewhere.[7] Microanalyses were in agreement with the theoretical values. All chemicals were of reagent grade, and deionized/degassed water was used in the preparation of all solutions.

UV–visible absorption spectra were recorded on a Unicam SP 1800 spectrophotometer. The spectra of the various species involved in this study are summarized in Table I and illustrated elsewhere.[7,16] The formation of $Co(tren)CO_3^+$ was studied at an ionic strength of 0.5 M ($NaClO_4$) over the acidity and temperature ranges indicated in the Results and Discussion. The reaction was monitored at 304 nm where a large difference in absorption between $Co(tren)(OH)_2^+$ and $Co(tren)CO_3^+$ exists.

**Table I.** UV-Visible Absorption Spectra of Some (tren)Co$^{III}$ Complex Species

| complex species | $\lambda_{max}$, nm | $\epsilon_{max}$, $M^{-1}\ cm^{-1}$ | ref |
|---|---|---|---|
| $Co(tren)(OH_2)_2^{3+}$ | 504, 357 | 109, 81 | 16 |
| | 506, 357 | 110, 80 | 7 |
| | 505, 360 | 108, 79 | this work |
| $Co(tren)(OH)_2^+$ | 520, 370 | 118, 117 | 16 |
| | 520, 372 | 120, 103 | 7 |
| | 522, 374 | 118, 101 | this work |
| $Co(tren)(OH)(CO_3)$ | 520, 367 (sh) | 144, 117 | 16 |
| | 515, 350 (sh) | 155, 130 | 7 |
| $Co(tren)(CO_3)^+$ | 505, 354 | 132, 111 | 16 |
| | 506, 351 | 131, 111 | 7 |
| | 504, 354 | 130, 110 | this work |

**Scheme I**



Rate measurements were performed in the thermostated cell compartment of a Zeiss PMQ II spectrophotometer. pH measurements at pH <12 were made with a Metrohm E 500 digital pH meter of which the reference electrode was filled with saturated NaCl solution. The observed pseudo-first-order rate constants were cal-

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**Table II.** Kinetic Data for the Formation of Co(tren) Carbonate Complexes at 50 °C and pH ≥10.5[a]

| | | $10^4k_{obsd}$,[e] s$^{-1}$ | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | [total carbonate],[d] M | | | | | | |
| pH[b] | $10^3$[OH$^-$],[c] M | 0.02 | 0.04 | 0.06 | 0.08 | 0.10 | $10^4k_a$, s$^{-1}$ | $10^3k_b$, M$^{-1}$ s$^{-1}$ |
| 10.50 | 0.316 | 5.55 | 7.84 | 10.2 | 13.1 | 15.4 | 2.94 ± 0.22 | 12.5 ± 0.3 |
| 10.75 | 0.562 | 4.44 | 5.64 | 6.74 | 8.19 | 9.79 | 2.98 ± 0.19 | 6.62 ± 0.29 |
| 11.00 | 1.0 | 3.61 | 4.53 | 5.23 | 5.97 | 6.58 | 2.97 ± 0.10 | 3.69 ± 0.15 |
| 11.10 | 1.26 | 3.11 | 3.63 | 4.26 | 4.83 | 5.51 | 2.47 ± 0.05 | 3.00 ± 0.07 |
| 11.20 | 1.58 | 2.36 | 2.95 | 3.33 | 3.90 | 4.29 | 1.92 ± 0.06 | 2.40 ± 0.10 |
| 11.70 | 5.0 | 1.51 | 1.81 | 2.02 | 2.19 | 2.30 | 1.38 ± 0.07 | 0.98 ± 0.10 |
| | 27.0 | 1.81 | 2.15 | 2.05 | 2.19 | 2.28 | 1.80 ± 0.11 | 0.49 ± 0.17 |
| | 32.0 | 2.06 | 2.23 | 2.23 | 2.25 | 2.30 | 2.06 ± 0.05 | 0.25 ± 0.08 |
| | 60.0 | 2.68 | 2.80 | 2.82 | 2.90 | 2.92 | 2.65 ± 0.03 | 0.29 ± 0.05 |
| | 100.0 | 3.69 | 3.99 | 4.00 | 4.05 | 4.08 | 3.65 ± 0.14 | 0.55 ± 0.21 |

[a] [Co(III)] = 2 × 10$^{-3}$ M, wavelength = 304 nm, ionic strength = 0.5 M. [b] Measured value. [c] Calculated value. [d] Added as Na$_2$CO$_3$. [e] Average of at least two determinations.

culated in the usual way from plots of ln ($A_\infty - A_t$) vs. $t$, where $A_\infty$ and $A_t$ are the absorbances at infinity and time $t$, respectively. Such plots were linear for at least 3–4 half-lives. The reported rate constants represent the mean value of at least two kinetic runs.

## Results and Discussion

The spectra of the various complex species in solution (Table I) are in good agreement with those reported elsewhere.[7,16] These species are interrelated through the equilibria and reactions in Scheme I as outlined before[7,16] (R = Co(tren)).

The equilibrium constants $K_1$ and $K_2$ are taken as acid dissociation constants and have the following values[2] at 25 °C and 0.5 M ionic strength: p$K_1$ = 6.03, p$K_2$ = 9.8.

The constants $k_1$, $k_{-1}$, $k_2$, and $k_{-2}$ are overall composite rate constants for the formation/aquation reactions of the monodentate (ring-opened) carbonate/bicarbonate species and for the formation (ring-closing) and ring-opening reactions of Co(tren)CO$_3^+$, respectively. The magnitude of these constants will strongly depend on pH since the latter will determine the species that participate in the various reactions. For example, one would expect $k_1$ to be significantly smaller for the anation of Co(tren)(OH)$_2^+$ by carbonate ion than for CO$_2$ uptake by this complex at high pH (see Introduction).

Some experiments at pH <10.5 indicated that the reaction of Co(tren)(OH)$_2^+$ with carbonate consisted of a rapid CO$_2$ uptake step to produce Co(tren)(OH)(OCO$_2$), followed by a rate-determining ring-closing step, as reported before.[7] These two reactions can be separated very neatly since the first occurs with an increase in absorbance and the second with a decrease in absorbance at <360 nm (see data in Table I and in the figures reported in ref 7 and 16).

Some preliminary repetitive scan experiments were performed at pH 11 and 50 °C. The spectrum of Co(tren)(OH)$_2^+$ in the range 270–550 nm stays constant for several hours under such conditions. In the presence of 0.05 M Na$_2$CO$_3$, the spectrum of a 3 × 10$^{-3}$ M Co(tren)(OH)$_2^+$ solution slowly changes to that of Co(tren)CO$_3^+$. Clean isosbestic points are observed at 366, 428, and 528 nm, which are in good agreement with the values deduced from spectra reported in the literature: 363, 428, and 523 nm;[7] 359, 431, and 520 nm.[16] The infinity spectrum indicated that only partial conversion from Co(tren)(OH)$_2^+$ to Co(tren)CO$_3^+$ had occurred, which is probably due to an equilibrium situation with the reverse hydrolysis reactions.[14] No evidence for the formation of the intermediate species Co(tren)(OH)(OCO$_2$) could be observed under these conditions, which is probably due to a rapid ring-closing reaction (see further Results and Discussion). It is important to report that the first spectrum recorded in the presence of Na$_2$CO$_3$ at pH 11 differs considerably from that obtained in the absence of Na$_2$CO$_3$. This spectrum obeys the isosbestic points observed in the further reaction, and the effect can only be ascribed to the rapid formation of Co(tren)CO$_3^+$ via CO$_2$ uptake. Bubbling nitrogen through the carbonate-containing solution at pH 11 before the addition of the Co(III) complex led to a series of spectra that did not exhibit the initial fast-step phenomenon, in agreement with the above-given suggestion. As a result of this effect, nitrogen was bubbled through all test solutions prior to the addition of the Co(III) complex.

Repetitive scan experiments at pH ~12 and 50 °C illustrated that the reaction of carbonate with Co(tren)(OH)$_2^+$ resulted in the partial formation of Co(tren)(OH)(OCO$_2$). Under these conditions isosbestic points were observed at approximately 360 and 390 nm, which differ significantly from those reported above for the formation of the ring-closed carbonate complex and are in agreement with those reported elsewhere[16] for the formation of Co(tren)(OH)(OCO$_2$) from Co(tren)(OH)$_2^+$.

The formation kinetics of Co(tren) carbonate complexes was studied at 304 nm where a convenient absorbance increase is observed. The values of the pseudo-first-order rate constant ($k_{obsd}$) as a function of pH and [total carbonate] are summarized in Table II. The [total carbonate] dependence of $k_{obsd}$ over the entire pH range is such that it can be described by

$$k_{obsd} = k_a + k_b[\text{total carbonate}]$$

The values of $k_a$ and $k_b$, recorded in Table II, were calculated by means of a least-squares fit of the experimental data. In terms of the mechanism outlined in Scheme I, $k_a$ represents the reverse reactions with overall rate constants $k_{-1}$ and $k_{-2}$, whereas $k_b$ represents the forward (formation) reactions with overall rate constants $k_1$ and $k_2$.

According to this data the value of $k_b$ steadily decreases on increasing the [OH$^-$] and reaches a limiting value at [OH$^-$] > 0.025 M. Since this overall rate constant describes the formation (forward) reactions of the Co(tren) carbonate species, the observed decrease is ascribed to a change in the rate-determining step of the reaction. At the low-pH range of the data, formation of carbonate complexes may still proceed through the uptake of CO$_2$ by the hydroxy species, even though the CO$_2$ concentration may be very low, as reflected by the relatively low values of $k_b$ in this range. However, contributions made by the anation reactions of Co(tren)(OH)$_2^+$ by HCO$_3^-$ and CO$_3^{2-}$ toward the overall value of $k_1$ cannot be omitted at this stage. It follows that under such conditions

$$k_b = k_1 = k_1'f_{CO_2} + k_1''f_{HCO_3} + k_1'''f_{CO_3} = \frac{k_1'[H^+]^2 + k_1''K_1[H^+] + k_1'''K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2}$$

where $k_1'$, $k_1''$, and $k_1'''$ represent the rate constants for the formation of Co(tren)(OH)(OCO$_2$) via CO$_2$ uptake by and bicarbonate and carbonate anation of Co(tren)(OH)$_2^+$, re-

**Table III.** Temperature Dependence of $k_{\mathrm{obsd}}$ at pH 11 and 13[a]

| | | $10^4k_{\mathrm{obsd}}$, $s^{-1}$ | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | [total carbonate], M | | | | | | |
| pH | temp, °C | 0.02 | 0.04 | 0.06 | 0.08 | 0.10 | $10^4k_a$, $s^{-1}$ | $10^3k_b$, $M^{-1}$ $s^{-1}$ |
| 11.0 | 25.0 | 0.14 | 0.18 | 0.20 | 0.23 | 0.26 | 0.11 ± 0.01 | 0.15 ± 0.01 |
| | 40.0 | 0.90 | 1.14 | 1.54 | 1.80 | 1.91 | 0.65 ± 0.09 | 1.34 ± 0.14 |
| | 45.0 | 1.97 | 2.54 | 2.98 | 3.47 | 3.98 | 1.50 ± 0.03 | 2.48 ± 0.04 |
| | 50.0 | 3.61 | 4.53 | 5.23 | 5.97 | 6.58 | 2.97 ± 0.10 | 3.69 ± 0.15 |
| | 55.0 | 6.35 | 7.77 | 8.84 | 10.1 | 11.2 | 5.23 ± 0.09 | 6.05 ± 0.14 |
| | 60.0 | 14.1 | 16.9 | 18.9 | 22.4 | 23.9 | 11.7 ± 0.5 | 12.6 ± 0.7 |
| $\Delta H^{\ddagger}$, kcal $mol^{-1}$ | | | | | | | 25.3 ± 1.1 | 23.8 ± 1.0 |
| $\Delta S^{\ddagger}$, cal $deg^{-1}$ $mol^{-1}$ | | | | | | | +3.6 ± 3.4 | +4.0 ± 3.1 |
| 13.0 | 40.4 | 1.05 | 1.10 | 1.15 | 1.15 | 1.19 | 1.03 ± 0.18 | 0.16 ± 0.03 |
| | 44.9 | 2.15 | 2.29 | 2.39 | 2.46 | 2.56 | 2.07 ± 0.02 | 0.50 ± 0.04 |
| | 50.0 | 3.62 | 4.04 | 4.02 | 4.05 | 4.16 | 3.65 ± 0.14 | 0.55 ± 0.21 |
| | 54.8 | 5.73 | 5.92 | 6.15 | 6.47 | 6.55 | 5.50 ± 0.06 | 1.11 ± 0.10 |
| $\Delta H^{\ddagger}$, kcal $mol^{-1}$ | | | | | | | 23.0 ± 1.9 | 24.2 ± 6 |
| $\Delta S^{\ddagger}$, cal $deg^{-1}$ $mol^{-1}$ | | | | | | | −3.4 ± 6.1 | +1.5 ± 19 |

[a] See Table II for experimental conditions.

spectively. $f_{CO_2}$, $f_{HCO_3}$, and $f_{CO_3}$ represent the fractions of the [total carbonate] present as $CO_2$, $HCO_3^-$, and $CO_3^{2-}$, respectively, in solution. The average limiting value of $k_b$ at $[OH^-] > 0.025$ M is $(4.0 \pm 1.5) \times 10^{-4}$ $M^{-1}$ $s^{-1}$ at 50 °C and should be that for the anation of $Co(tren)(OH)_2^+$ by $CO_3^{2-}$ ion, i.e., $k_1'''$, since these are practically the only species present under these conditions.

The above expression can be rewritten in the form

$$\frac{k_b - k_1'''f_{CO_3}}{f_{HCO_3}} = k_1'' + \frac{k_1'f_{CO_2}}{f_{HCO_3}}$$

The values of $f_{CO_2}$, $f_{HCO_3}$, and $f_{CO_3}$ can be estimated from the equations given above by using the values of $K_1$ and $K_2$ quoted earlier. Since $k_1'''$ is known from the values of $k_b$ at $[OH^-] > 0.025$ M in Table II, the data for $k_b$ at pH <12 in Table II can be fitted with the above equation as shown in Figure 1. A linear-least-squares fit of the data resulted in $k_1'' = (4.7 \pm 0.1) \times 10^{-2}$ $M^{-1}$ $s^{-1}$ (anation by $HCO_3^-$) and $k_1' = (7.7 \pm 0.4) \times 10^2$ $M^{-1}$ $s^{-1}$ ($CO_2$ uptake) at 50 °C.

The values of the calculated rate constants follow the order $k_1' \gg k_1'' > k_1'''$. $CO_2$ uptake ($k_1'$) is expected to be significantly faster than the anation reactions ($k_1''$ and $k_1'''$) since it does not involve M–O bond breakage. The value obtained above for $k_1'$ is not far from the value $5.7 \times 10^2$ $M^{-1}$ $s^{-1}$, which was estimated from the activation parameters, $\Delta H^* = 32 \pm 6$ kcal $mol^{-1}$ and $\Delta S^* = +53 \pm 22$ cal $deg^{-1}$ $mol^{-1}$, reported elsewhere[7] for $CO_2$ uptake by $Co(tren)(OH)_2^+$. The error limits on the latter parameters are rather high and can account for the observed difference in the values of $k_1'$. Furthermore, the actual values of $k_1'$ and $k_1''$ will strongly depend on the values of $K_1$ and $K_2$ in the above outlined data fit, which were assumed to have the same value at 50 °C as at 25 °C. A surprising feature of the above data is the fact that $k_1'' \approx 10^2k_1'''$ at 50 °C, indicating that the anation by bicarbonate ion is significantly faster than the anation by carbonate ion.

A possible explanation for this observation is that during the anation of $Co(tren)(OH)_2^+$ by bicarbonate ion, partial proton transfer from the bicarbonate ion to one of the hydroxo ligands on the dihydroxy species occurs such that the rate-determining step closely parallels the substitution of an aquo ligand by a carbonate ion. This is expected to be significantly faster than the substitution of a hydroxy ligand by a carbonate ion, since $M–OH_2$ bond breakage is in general more favorable than M–OH bond breakage.

Both anation reactions are, however, remarkably slower than the $CO_2$ uptake reaction and should compare fairly well with other substitution reactions of the $Co(tren)(OH)_2^+$ species.

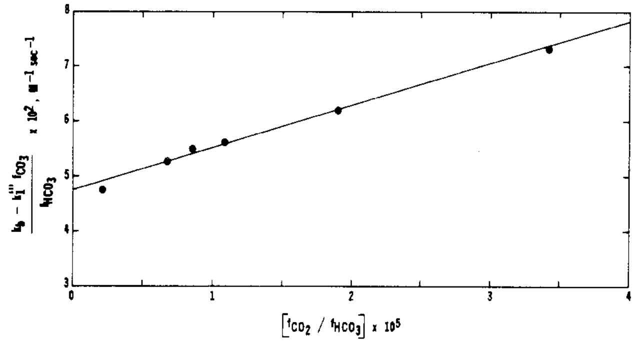

**Figure 1.** Fit of the data for $k_b$ at pH <12 in Tabe II (see Results and Discussion).

Due to a lack of such data, the only reasonable comparison can be made with the solvent water exchange data[17] of *cis*-$Co(en)_2(OH)_2^+$ which is presumably limited by the rate of $OH^-$ elimination. The latter reaction has a rate constant of $2.9 \times 10^{-4}$ $s^{-1}$ at 40 °C and 0.8 M NaOH, i.e., $3.6 \times 10^{-4}$ $M^{-1}$ $s^{-1}$, which indicates that the substitution by carbonate on the closely related tren complex[14] is governed by the release of $OH^-$.

The activation parameters reported for $k_b$ in Table III at pH 11.0 are a combination of those for $k_1'$, $k_1''$, and $k_1'''$. One can make the reasonable assumption that at 25 °C $k_b$ will largely represent the value of $k_1'$ since the anation reactions become negligibly slow under such conditions. Since $f_{CO_2} = 6.36 \times 10^{-7}$ at pH 11.0, our $k_b$ value of $(0.15 \pm 0.01) \times 10^{-3}$ $M^{-1}$ $s^{-1}$ (Table III) at 25 °C corresponds to a value of 236 ± 16 $M^{-1}$ $s^{-1}$ for $CO_2$ uptake ($k_1'$), which is indeed not far from the value 170 ± 10 $M^{-1}$ $s^{-1}$ reported before.[7] The activation parameters reported for $k_b$ in Table III at pH 13.0 are those for $k_1'''$ and are subjected to some error due to the relatively large errors in $k_b$ at high pH (see data in Table II).

Some preliminary measurements in this study (referred to earlier) illustrated that the rate of ring closure of Co(tren)(OH)($OCO_2$) ($k_2$, Scheme I) is of the order of $8 \times 10^{-3}$ $s^{-1}$ at 50 °C and pH 10.3. Under these conditions, Co(tren)(OH)($OCO_2$) should be the main monodentate carbonate species in solution.[7] This rate constant is expected to be fairly pH independent such that this reaction is significantly faster than any of the measured rate constants reported in Table II and can therefore be considered as a non-rate-determining step. A value of $1.3 \times 10^{-4}$ $s^{-1}$ at 20 °C has been reported for this

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[17] Kruse, W.; Taube, H. *J. Am. Chem. Soc.* **1961**, *83*, 1280.

particular reaction elsewhere,[16] and considering the difference in experimental conditions it is of the same order of magnitude as our value. The above arguments confirm our viewpoint that the kinetic data for the forward reaction ($k_b$ in Tables II and III) are those for the $k_1$ path in Scheme I and that the $k_2$ path is not observed kinetically.

We now turn to a discussion of the reverse processes ($k_a$, data in Tables II and III), viz., base-catalyzed ring opening ($k_{-2}$ in Scheme I) and base hydrolysis ($k_{-1}$ in Scheme I). According to the values of $k_a$ in Table II, it remains fairly constant in the range $10.5 \leq pH \leq 11.1$ with an average value of $(2.8 \pm 0.3) \times 10^{-4}$ s$^{-1}$ at 50 °C. $k_a$ is probably independent of $[OH^-]$ in the above pH range due to the relatively small values of $[OH^-]$. That means that one observes kinetically the water-catalyzed ring-opening ($k_{-2}$) or decarboxylation ($k_{-1}$) reaction. Rate data for

$$Co(tren)CO_3^+ + H_2O \xrightarrow{k_3} Co(tren)(OH)(OCO_2) + H^+$$

has been reported in two investigations. In a study of the acid-catalyzed ring-opening reaction it was found[15] that $k_3 = (1.7 \pm 0.2) \times 10^{-4}$ s$^{-1}$ at 25 °C, $\Delta H^* = 15 \pm 2$ kcal mol$^{-1}$, and $\Delta S^* = -25 \pm 5$ cal deg$^{-1}$ mol$^{-1}$. In a later study of the base-catalyzed ring-opening reaction it was reported[14] that $k_3 = (2.6 \pm 0.6) \times 10^{-4}$ s$^{-1}$ at 25 °C, $\Delta H^* = 17.3 \pm 5.1$ kcal mol$^{-1}$, and $\Delta S^* = -17 \pm 7$ cal deg$^{-1}$ mol$^{-1}$. Within experimental error limits these rate parameters for the water-catalyzed ring-opening reaction seem to be consistent. However, extrapolation to 50 °C results in values for $k_3$ of $1.6 \times 10^{-3}$ s$^{-1}$ (from data in ref 15) and $2.5 \times 10^{-3}$ s$^{-1}$ (from data in ref 14). These are significantly higher than the constant (pH independent) value of $k_a$, viz., $(2.8 \pm 0.3) \times 10^{-4}$ s$^{-1}$ at 50 °C and pH $\leq 11.1$. Under these conditions the water-catalyzed ring-opening process ($k_3$) is presumably the rate-determining reverse reaction,[16] and we cannot offer a reasonable explanation for the difference in the reported rate data. One possibility may be that the rate data for this reaction, obtained as intercepts from $k_{obsd}$ vs. $[H^+]$ plots for the acid-catalyzed ring-opening process[15] and $k_{obsd}$ vs. $[OH^-]$ plots for the base-catalyzed ring-opening process,[14] may indeed be a composite of the uncatalyzed path and the reverse ring-closure process. This would then lead to higher values than those reported for $k_a$ in Table II at pH $\leq 11.1$. More important, however, is the fact that our value for $k_a$, viz., $(2.8 \pm 0.3) \times 10^{-4}$ s$^{-1}$ at 50 °C, is in close agreement with the rate constant $8.0 \times 10^{-4}$ s$^{-1}$, extrapolated from the rate data reported elsewhere[18] for the water-catalyzed ring-opening reaction of the closely related $Co(en)_2CO_3^+$ species at 50 °C.

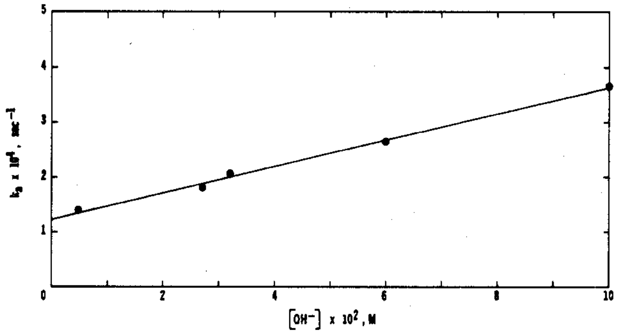

**Figure 2.** Dependence of $k_a$ on $[OH^-]$ for data at $[OH^-] \geq 5.0 \times 10^{-3}$ M in Table II (see Results and Discussion).

At higher pH a decrease in $k_a$ followed by a steady increase with increasing $[OH^-]$ is observed. A similar tendency was reported[18] for the base hydrolysis of $Co(en)_2CO_3^+$. This pattern is ascribed to the observation that at pH ~12 no ring closure of the $Co(tren)(OH)(OCO_2)$ species occurs[14,16] (see earlier Results and Discussion) such that the base hydrolysis of this species is the rate-determining reverse reaction. The discontinuity in the $k_a$ values is, therefore, due to a switch in rate-determining step for the reverse process, from a noncatalyzed ring-opening reaction to base hydrolysis of the ring-opened species. The $k_a$ data at $[OH^-] \geq 0.5 \times 10^{-2}$ M must therefore be ascribed to the overall process

$$Co(tren)(OH)(OCO_2) + OH^- \rightarrow Co(tren)(OH)_2^+ + CO_3^{2-}$$

$k_a$ at $[OH^-] \geq 0.5 \times 10^{-2}$ M shows a linear $[OH^-]$ dependence (Figure 2) according to

$$k_a = k_4 + k_5[OH^-]$$

where $k_4 = (1.23 \pm 0.05) \times 10^{-4}$ s$^{-1}$ and $k_5 = (2.4 \pm 0.1) \times 10^{-3}$ M$^{-1}$ s$^{-1}$ at 50 °C. According to this data the reverse process consists of the reactions

$$Co(tren)(OH)(OCO_2) + H_2O \xrightarrow{k_4} Co(tren)(OH)_2^+ + H^+ + CO_3^{2-}$$

$$Co(tren)(OH)(OCO_2) + OH^- \xrightarrow{k_5} Co(tren)(OH)_2^+ + CO_3^{2-}$$

The activation parameters for $k_a$ at pH 13 (Table III) are for a combination of the rate constants $k_4$ and $k_5$. The above data differ significantly from that reported earlier,[14] viz., $1.3 \times 10^{-4}$ M$^{-1}$ s$^{-1}$ at 45 °C. The latter investigators[14] report determinations in 1 M NaOH which can be extrapolated to 50 °C by using the activation parameters[19] $\Delta H^* = 27.0$ kcal mol$^{-1}$ and $\Delta S^* = +8.4$ cal deg$^{-1}$ mol$^{-1}$, leading to a value of $2.5 \times 10^{-4}$ M$^{-1}$ s$^{-1}$. The large discrepancy is probably due to the fact that no $[OH^-]$ dependence was studied by the earlier investigators[14] and the experimental condition (1 M NaOH) falls far beyond the pH range of this study. However, using the activation parameters for $k_a$ at pH 13 in Table III, we estimate a value for $k_a$ at 20 °C of $7.7 \times 10^{-6}$ s$^{-1}$, which is indeed very close to Scheidegger's value[16] of $6.4 \times 10^{-6}$ s$^{-1}$ at pH 12.4 and 20 °C.

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**Registry No.** $Co(tren)(OH_2)_2^{3+}$, 41884-78-0; $Co(tren)(OH)_2^+$, 55328-50-2; $Co(tren)(CO_3)^+$, 31240-94-5.

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

(19) These values have been recalculated from the data in Table VI of ref 14. The quoted activation parameters[14] are in error: Harris, G. M., private communication, 1979.