# Kinetics and Mechanism of Ring Opening in the Hydrolysis of Cobalt(III) Carbonato Chelates

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By appropriate choice of wavelength ($\lambda = 470-580$ nm) it is shown that decarboxylation of bidentate carbonate in a number of $[Co(L)_4(O_2CO)]^{n+}$ chelates follows consecutive first-order reactions in aqueous acidic solution ($[H^+] = 0.10-1.0$ M). Sometimes the first observed process follows the rate law $k_{fast} = k_1K[H^+]/(1 + K[H^+])$ with the subsequent slower process $k_{slow} = k_2$ being pH independent, and sometimes $k_{fast} = k_2$ with $k_{slow} = k_1K[H^+]/(1 + K[H^+])$. The limiting rate law $k_{obs} = k_1K[H^+]/(1 + K[H^+])$ is interpreted mechanistically as equilibrium protonation of the *exo*-O atom of the chelate ($K$) followed by unimolecular cleavage ($k_1$) of the Co–O bond of the bicarbonato intermediate $[Co(L)_4(O_2COH)]^{(n+1)+}$. For $(L)_4$ = $nta^{3-}$, $(gly)_2^{2-}$, and cyclen, direct spectrophotometric measurement of the acidity of the bicarbonato chelate was possible ($K_a$/M = 1.1, 0.66, 0.42, respectively). The rate law $k_{obs} = k_2$ is interpreted as unimolecular decarboxylation of *cis*-$[Co(L)_4(OH_2)(OCO_2H)]^{(n+1)+}$ to give *cis*-$[Co(L)_4(OH_2)_2]^{(n+2)+} + CO_2$. For different $(L)_4$, the following data were obtained at 25.0 °C and $I = 1.0$ ($NaClO_4$) [$(L)_4$ ($K/M^{-1}$, $k_1/s^{-1}$, $k_2/s^{-1}$)]: $nta^{3-}$ (1.19 ± 0.08, 85.0 ± 4.0, 2.0 ± 0.2); α-trien (0.71 ± 0.08, 9.7 ± 0.8, 0.62 ± 0.01); tren (0.61 ± 0.10, 4.25 ± 0.48, 0.31 ± 0.01); $(gly)_2^{2-}$ (1.37 ± 0.38, 4.1 ± 0.5; 4.1 ± 0.2); $(NH_3)_4$ (1.0 ± 0.2, 1.68 ± 0.22, 1.50 ± 0.05); β-trien (0.80 ± 0.10, 0.285 ± 0.02, 0.45 ± 0.05); cyclen (1.42 ± 0.28, $(1.02 \pm 0.10) \times 10^{-2}$, no value); N-mecylen (0.43 ± 0.04, $(7.61 \pm 0.50) \times 10^{-3}$), no value). These complexes span the range where ring opening is much faster than ($nta^{3-}$, α-trien, tren), is similar to [$(gly)_2^{2-}$, $(NH_3)_4$, β-trien], or is much slower than (cyclen, N-mecyclen) subsequent decarboxylation. For α-$[Co(trien)(O_2CO)]^{2+}$, neither $k_1$ nor $k_2$ show a significant $D_2O$ solvent isotope effect ($k_1(D_2O) = 8.67 \pm 0.38\ s^{-1}$, $k_2(D_2O) = 0.64\ s^{-1}$), but $K$ does ($K_{D_2O} = 1.82 \pm 0.18\ M^{-1}$, $K_{D_2O}/K_{H_2O} = 2.6$). The large variation in rate constant $k_1$ with changing $(L)_4$ (~$10^4$) is interpreted as differing abilities to transfer the *exo*-O proton to the *endo*-O ring oxygen in the bidentate bicarbonato intermediate $[Co(L)_4(O_2COH)]^{(n+1)+}$. It is this dechelation of $HCO_3^-$, rather than subsequent decarboxylation, that is very sensitive to the "nonparticipating" ligand. There is no evidence to suggest a spontaneous pathway for hydrolysis the above carbonato chelates.

## Introduction

Perhaps the most important unanswered question concerning the acid catalyzed hydrolysis of carbonato chelates of the type $[Co(L)_4O_2CO]^{n+}$ (eq 1) is why the observed rates of reaction

$$[Co(L)_4(O_2CO)]^{n+} + 2H^+ + H_2O \rightarrow [Co(L)_4(OH_2)_2]^{(n+2)+} + CO_2 \quad (1)$$

vary so widely with variation in $(L)_4$. Reported reaction rates[1] span a range of at least $10^7$, with α-$[Co(edda)(O_2CO)]^-$,[2] having a half-life of ~6 ms in 1 M $H^+$ while $[Co(py)_4(O_2CO)]^+$,[3] has a half-life of ~1 day under the same conditions. The only other known reaction of Co(III) complexes to show such a wide reactivity range is the $OH^-$-catalyzed hydrolysis of monodentate X from $[Co(L)_5X]^{n+}$ (e.g. X = Cl), but in this case it is the $OH^-$-catalyzed pre-deprotonation of a coordinated amine residue which is largely responsible, rather than a massive change in Co–X bond strength due to L variation.[4] Can a similar property involving preprotonation of chelated $CO_3^{2-}$ be responsible here? It is known[1] that under most conditions the rate-determining step in the hydrolysis of these carbonato chelates is ring opening (eq 2). Subsequent decarboxylation of the monodentate (eq 3)

$$[Co(L)_4(O_2CO)]^{n+} + H^+ + H_2O \xrightarrow{k_{obs}(1)} [Co(L)_4(OH_2)(OCO_2H)]^{(n+1)+} \quad (2)$$

$$[Co(L)_4(OH_2)(OCO_2H)]^{(n+1)+} + H^+ \xrightarrow{k_{obs}(2)} [Co(L)_4(OH_2)_2]^{(n+2)+} + CO_2 \quad (3)$$

is generally fast, although this is not always so. The ring opening reaction has also been accredited a "spontaneous" pathway in addition to the acid-catalyzed component (eq 4),

$$k_{obs}(1) = k_o + k'[H^+] \quad (4)$$

although this ($k_o$) has always been recognized as of minor importance.[2,5–10] Furthermore, it is now believed that protonation preceeds ring opening,[1] so the currently accepted mechanism for the acid-catalyzed reaction is that given by Scheme 1 (i.e. $k' = k_1K$). However there have been a number of difficulties associated with obtaining and treating the experimental rate data, and these have led to errors in interpretation of mechanistic rate and equilibrium constants.

For some complexes[2,7,9,11] the observed pseudo-first-order rate constant ($k_{obs}$, eq 4) has been found to tend toward a limiting

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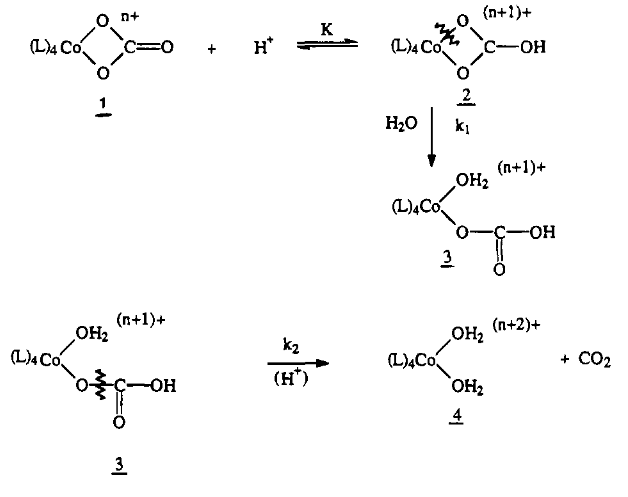
**Scheme 1.** Pathway for Stepwise Protonation, Chelate Ring Opening, and Subsequent Decarboxylation



value at high $[H^+]$ (up to 2.0 M), and this behavior has been attributed to a change in rate-determining step from chelate ring opening at lower acidicities (eq 2, $k_{obs}(1) = k_1K[H^+]$) to hydrolysis of the mondentate bicarbonato intermediate (eq 3, $k_{obs}(2) = k_2$) at higher acidities. However, when the rate of chelate ring opening becomes commensurate with, or faster than, that for hydrolysis of the monodentate, the reaction should no longer follow simple pseudo-first-order kinetics. At some acidity condition it must exhibit the features of a consecutive first-order process and display biphasic kinetics. If data obtained for such a reaction is treated as though arising from a single exponential, as has been the case with $[Co(en)_2(O_2CO)]^+$,[13] $[Co(nta)(O_2CO)]^{2-}$,[9] and α- and β-$[Co(edda)(O_2CO)]^-$,[2] the result can only be the accumulation of incorrect data and a masking of the intimate details of the reaction. Only with $[Co(tren)O_2CO]^+$ [7] was a biphasic kinetic process observed in these early investigations, but very recently in a re-examination of the hydrolysis of $[Co(en)_2(O_2CO)]^+$ over the acidity range 0.1–1.0 M we have shown that this reaction is also biphasic, with ring opening ($k_1$) and hydrolysis of the mondentate bicarbonato intermediate ($k_2$) being seen as consecutive first-order processes at 477 nm ($k_1 = 0.85$ s$^{-1}$, $k_2 = 0.93$ s$^{-1}$, 25 °C, $I = 1.0$ M).[12] This particular study also disclosed for the first time the extent of preprotonation, with $K_a$ ($=1/K$, Scheme 1) for the intermediate bicarbonato chelate having a value of 1.0 ± 0.1 M$^{-1}$. This result is in sharp contrast to previous estimates of the acidity of this species ($K \sim 10^6$ M$^{-1}$).[1,11,13]

Such observations cast doubt on the interpretation of much of the earlier rate data, and the present work was undertaken with a view toward laying a better basis for the understanding of this important reaction. The present article reports an examination, or re-examination, of the acid-catalyzed hydrolysis of $[Co(NH_3)_4(O_2CO)]^+$, α- and β-$[Co(trien)(O_2CO)]^+$, $[Co(tren)(O_2CO)]^+$, $[Co(nta)(O_2CO)]^{2-}$, *cis*-$[Co(gly)_2(O_2CO)]^-$, $[Co(cyclen)(O_2CO)]^+$, and $[Co(N\text{-}mecyclen)(O_2CO)]^+$. These complexes afford a series which span the reactivity range where $k_1$ is much greater than $k_2$, is comparable with $k_2$, and is substantially less than $k_2$ (Scheme 1). We also include data which shows that the spontaneous reaction ($k_o$, eq 4) plays no part. Also, comparisons of the unimolecular rate constants for opening up the bicarbonate chelate with other known properties of these complexes, as well as a deuterium solvent isotope study, suggest a possible reason for the large rate differences.

## Experimental Section

**Materials.** The complexes α- and β-$[Co(trien)(O_2CO)](ClO_4)\cdot H_2O$,[14] $[Co(NH_3)_4(O_2CO)](NO_3)$,[15] $[Co(tren)(O_2CO)](ClO_4)\cdot H_2O$,[16] and $[Co(en)_2(O_2CO)]ClO_4$[17] were prepared using previously published methods. *cis*-$K[Co(gly)_2(O_2CO)]\cdot H_2O$ was prepared essentially following the method of Shibata *et al.*[18] Calcd for $K[Co(gly)_2(O_2CO)]\cdot H_2O$: C, 18.52; H, 8.64; N, 3.11. Found: C, 18.41; H, 8.43; N, 2.85. Ion exchange chromatography of this material (Sephadex QAE A-25, eluent 0.05 M NaCl) gave a single blue-purple band corresponding to elution of a 1−charged species. $[Co(cyclen)(O_2CO)](ClO_4)\cdot H_2O$ was prepared from the corresponding chloride salt[19] by dissolution in warm water and adding excess $NaClO_4$. The red-purple product was recrystallized twice from hot water (70 °C) by addition of $NaClO_4$ and recovered by filtration. It was washed thoroughly with EtOH and then $Et_2O$ and air-dried. Calcd for $[Co(cyclen)(O_2CO)](ClO_4)\cdot H_2O$: C, 26.45; H, 5.42; N, 13.70. Found: C, 26.41; H, 5.24; N, 13.84. Visible spectrum in water $\lambda_{max}$ ($\epsilon$): 520 nm (274), 365 nm (213) (lit.[20] 522 nm (279), 362 (208) for the corresponding $Cl^-$ salt).

The following two complexes have not been reported previously.

***cis*-[Co(N-mecyclen)Cl₂]Cl.** To a solution of N-mecyclen·3HCl (N-mecyclen = 1-methyl-1,4,7,10-tetraazacyclodecane) (1.68 g, 5.68 × $10^{-3}$ mol) and NaOH (0.456 g, 1.14 × $10^{-2}$ mol) in water (30 cm$^3$) was added $Co(ClO_4)_2\cdot 6H_2O$ (2.08 g, 5.68 × $10^{-3}$ mol) and immediately $NaNO_2$ (0.86 g, 1.24 × $10^{-2}$ mol). Air was bubbled vigorously through the mixture for 1 h, and water (50 cm$^3$) and HCl (11 M, 10 cm$^3$) were added. Ion exchange chromatography (Dowex 50 W × 2, H$^+$ form, eluent 0.5–2.0 M HCl) gave a single red-purple band which on rotary evaporation to dryness yielded a purple-blue solid. This was washed thoroughly with EtOH and then acetone and air-dried. Calcd for $[Co(N\text{-}mecyclen)Cl_2]Cl$: C, 30.75; H, 6.31; N, 15.94. Found: C, 30.79; H, 6.35; N, 15.75.

**[Co(N-mecyclen)(O₂CO)](ClO₄)·2H₂O.** This complex was prepared by treatment of *cis*-$[Co(N\text{-}mecyclen)Cl_2]Cl$ with $CO_2$ in aqueous $Li_2CO_3$ medium essentially as described by Collman and Schneider[19] for the corresponding preparation of $[Co(cyclen)(O_2CO)]Cl$ and was likewise initially obtained as the $Cl^-$ salt. It was converted to the $ClO_4^-$ salt by dissolution in warm water and treatment with excess $LiClO_4$. Two recrystallizations from warm water afforded the analytical sample. Calcd for $[Co(N\text{-}mecyclen)(O_2CO)](ClO_4)\cdot 2H_2O$: C, 27.25; H, 5.94; N, 12.71. Found: C, 27.34; H, 5.69; N, 12.70.

**Na₂[Co(nta)(O₂CO)]·4.5H₂O.** To a slurry of freshly prepared $Na_3[Co(CO_3)_3]\cdot 3H_2O$[21] (15.2 g, 0.042 mol) in water (18 cm$^3$) was slowly added nitrilotriacetic acid (8.02 g, 0.042 mol) with stirring, and the resultant mixture was heated at 50 °C for 10 min. After cooling, the solution pH (initially ~8.8) was adjusted to ~5.6 by the dropwise addition of $HClO_4$ (3 M), and the solution was then filtered through Celite. The product was precipitated as an oil by the slow addition of EtOH (50 cm$^3$) to the rapidly stirred filtrate and the aqueous ethanolic phase was discarded. Following reprecipitation from water (30 cm$^3$) by addition of ethanol (50 cm$^3$), the resulting blue-purple solid was triturated with acetone (3 × 100 cm$^3$) and recovered by filtration. Upon ion exchange chromatography (Sephadex QAE A-25, eluent 0.30 M NaCl) a sample of the product eluted as a single blue band corresponding to a 2−charged species. Calcd. for $Na_2[Co(nta)(O_2CO)]\cdot 4.5H_2O$: C, 19.37; H, 3.48; N, 3.23. Found: C, 19.17; H, 3.53; N, 3.26%. $\lambda_{max}$ ($\epsilon$) ($H_2O$) 568 nm (165), 388 nm (150) [Mori *et al.*[22] report $\lambda_{max}$ ($H_2O$) 564 nm (165), 388 nm (150) for $K[Co(nta)(O_2CO)]\cdot H_2O$]. $^{13}$C-NMR ($D_2O$): 184.3, 182.3 ($CO_2$); 168.1 ($CO_3$); 69.3, 67.8 ppm ($CH_2$).

Solutions of $NaClO_4$ and $HClO_4$ were prepared from A. R. grade materials and were filtered through Celite prior to kinetic measurements. Stock solutions of $HClO_4$ and $DClO_4$ were standardized by titration against NaOH to the phenolphthalein end point. The $DClO_4$ solution

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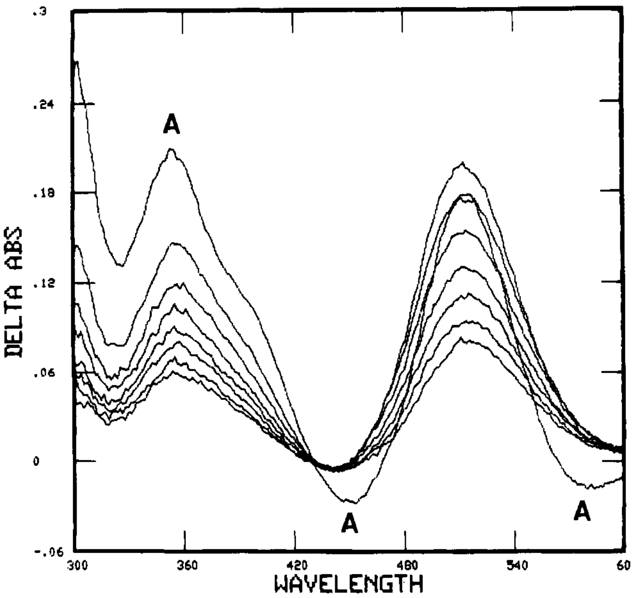

**Figure 1.** Rapid-scan difference spectra obtained on mixing α-[Co(trien)($O_2CO$)]$^+$ with $HClO_4$ and recorded over the range 300–600 nm, with $[Co]_T = 3.36 \times 10^{-3}$ M and $[H^+] = 1.00$ M. Following an initial delay of 50 ms, eight spectra were recorded over 3.000 s and are referenced to the final spectrum obtained after 6.000 s. The trace first recorded is labeled A to distinguish it from those obtained subsequently.

was prepared by addition of 70% w/w $HClO_4$ to $D_2O$ (Aldrich 99.9 atom % D) and was diluted to 2.00 M with $D_2O$.

**Kinetic Measurements.** Fast reactions ($t_{1/2} < 60$ s) were followed using a Durrum D-110 stopped-flow spectrophotometer coupled to a North Star Horizon computer utilizing OLIS software[23] for data storage and manipulation. Rapid-scan spectra were obtained using a Harrick rapid-scan monochromator in conjunction with the Durrum. The latter instrument was also used to obtain zero-time absorbances for solutions of the carbonato complexes in $HClO_4$ media. A Cary 219 uv–vis spectrophotometer was used to record visible spectra and to follow slower reactions.

Rate constants ($k_{fast}$, $k_{slow}$) appropriate to the consecutive first-order kinetic scheme $A \rightarrow B \rightarrow C$ were obtained by data-fitting absorbance–time traces using the OLIS[23] nonlinear least squares fitting routine V-DataFit. Rate constants associated with strictly first-order rate processes were evaluated from linear plots of $\ln(A_t - A_\infty)$ versus time. In all cases reactions were monitored to 97–98% of the total absorbance change.

**Spectral Determination of Acidity Constants.** $K_a$ values for [Co(gly)$_2$($O_2COH$)], [Co(cyclen)($O_2COH$)]$^{2+}$, and [Co(nta)($O_2COH$)]$^-$ were determined spectrophotometrically (553, 522, and 560 nm, respectively) following stopped-flow mixing of equal volumes of an aqueous solution of the corresponding Co(III) carbonato complex (~6 × $10^{-3}$ M) with $HClO_4$ solutions made up to the appropriate ionic strength (with $NaClO_4$) and $H^+$ concentration. Time–zero absorbance data (average of three to five values) at 25 °C were obtained by extrapolation of the observed absorbance–time traces over the first 100–300 ms of reaction. Data were recorded over the $[H^+]$ range 0–1.00 M for [Co(gly)$_2$($O_2COH$)] and [Co(nta)($O_2COH$)]$^-$ at $I = 1.0$ M and over the range 0–2.70 M for [Co(cyclen)($O_2COH$)]$^{2+}$ at $I = 2.70$ M.

## Results

**Acid-Catalyzed Hydrolysis.** Figure 1 shows a series of eight rapid-scan spectra (300–600 nm) recorded over a 3 s time period (interval between successive spectra = 0.429 s) for the reaction of α-[Co(trien)($O_2CO$)]$^+$ (3.36 × $10^{-3}$ M) in 1.0 M $HClO_4$ at 25 °C. The spectra are referenced to the final spectrum of α-[Co(trien)($OH_2$)$_2$]$^{3+}$ which was obtained after a further 3 s. Hydrolysis of the carbonato complex involves decreasing absorbances in the region 300–420 nm, whereas in the range 460–570 nm the absorbance initially increases rapidly (over ~0.5 s) and then more slowly decreases. At 477 nm both changes contribute significantly, and this wavelength was chosen for detailed data collection in the acidity range 0.1–1.0 M $H^+$. A typical absorbance–time trace obtained following stopped-flow mixing of the reactants is given by Figure 2 for the condition $[H^+] = 0.50$ M and $[Co]_T = 3.49 \times 10^{-3}$ M. Included in this figure is the absorbance–time trace calculated using the OLIS fitting routine on the basis that the observed absorbance changes arise as a consequence of two consecutive first-order reactions. An excellent fit is achieved using the rate constants $k_{fast} = 2.60$ s$^{-1}$ and $k_{slow} = 0.60$ s$^{-1}$ and associated absorbance changes $\Delta A_1 = 0.140$ (increase) and $\Delta A_2 = -0.215$ (decrease). Similar fitting of data obtained at other acidities gave the rate constants listed in Table S1 of the supplementary material and plotted vs $[H^+]$ in Figure 3. The rate constants for the slower process, $k_{slow}$, are independent of $[H^+]$ (=0.62 ± 0.01 s$^{-1}$) while $k_{fast}$ follows eq 5 Interpolation of the curve of Figure 3 suggest

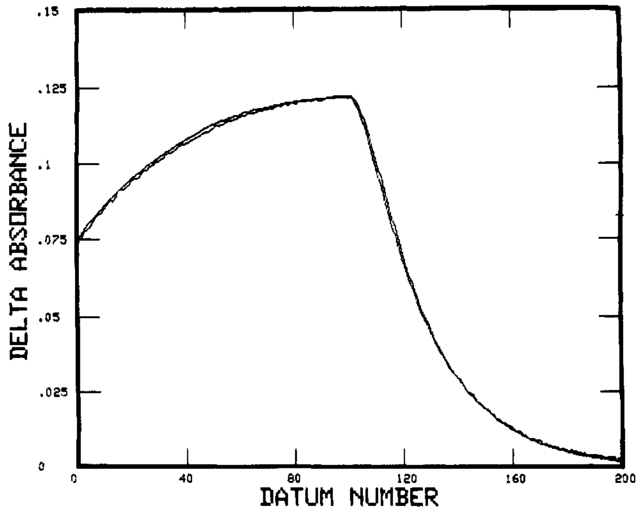

**Figure 2.** Observed and calculated absorbance–time traces (477 nm) for reaction of 3.49 × $10^{-3}$ M α-[Co(trien)($O_2CO$)]$^+$ in 0.50 M $HClO_4$ at 25 °C. The time axis is split with the first 100 data points being collected over 0.500 s, and the remaining 100 collected over the next 7.000 s. See the text for further details.

$$k_{fast} = \frac{kK[H^+]}{1 + K[H^+]} \qquad (5)$$

$k_{fast} = k_{slow} = 0.62$ s$^{-1}$ at $[H^+] = 0.10$ M, and while absorbance–time data were collected for this condition, the consecutive first-order fitting routine did not converge to a unique solution. However, inserting the rate constants $k_{fast} = k_{slow} = 0.62$ s$^{-1}$ as fixed parameters resulted in excellent agreement with the observed absorbance–time trace. Figure 3 also gives rate data collected using $D_2O$ solutions. These data also follow eq 5 with $k_{D_2O} = 8.67 \pm 0.38$ s$^{-1}$, $K_{D_2O}$ 1.82 ± 0.18 M$^{-1}$, and with $k_{slow} = 0.64 \pm 0.02$ s$^{-1}$ in 1.0 M $NaClO_4$ at 25.0 °C. Rapid-scan spectra were similarly recorded for the reaction of [Co(nta)($O_2CO$)]$^{2-}$ (3.26 × $10^{-3}$ M) in 1.0 M $HClO_4$ (Figure 4). Again two consecutive processes are evident with the first being complete within the time scale of successive scans (0.143 s) and the second being largely complete in 1 s. The large difference in the two rates is apparent from the maintenance of isosbestic points (at 416, 472, 532, and 696 nm) over the time course of the second reaction. Rate data collected at 545 and 580 nm (absorbance increase followed by decrease) are given in Table 1. These show that $k_{fast}$ again follows eq 5

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[23] OLIS, On-Line Instrument Systems Inc., Bogart, G. A. 30622-1274, U.S.A.

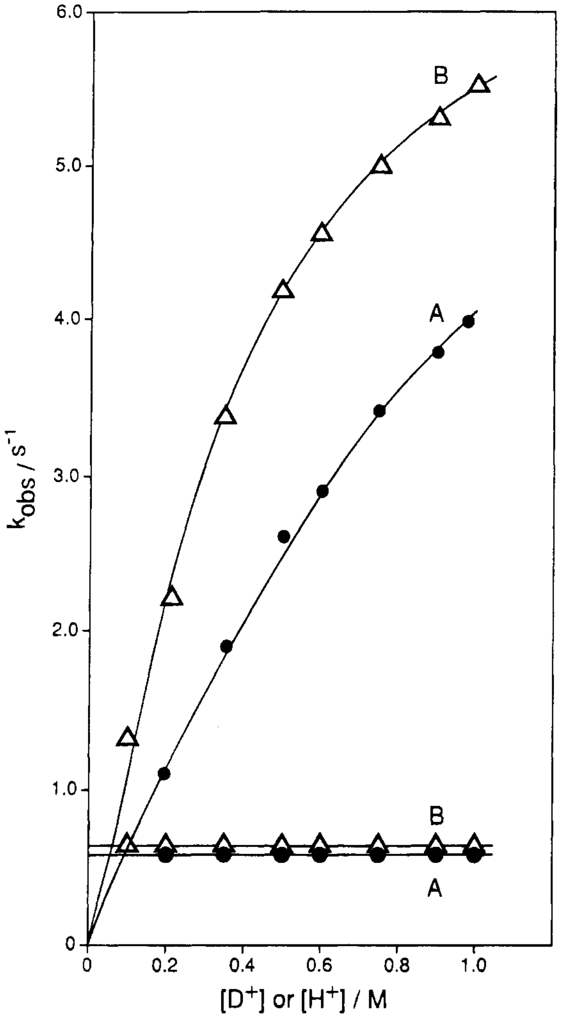


**Figure 3.** Plots of $k_{fast}$ and $k_{slow}$ versus [$H^+$] (A, closed circles) or [$D^+$] (B, open triangles) for the reaction of α-[Co(trien)($O_2CO$)]$^+$ in $H_2O$ and $D_2O$ solutions at 25 °C and $I$ = 1.0 M ($NaClO_4$). Curve fitting of $k_{fast}$ was achieved using eq 5 with $k$ = 9.7 $s^{-1}$ and $K$ = 0.71 $M^{-1}$ (for A) and $k$ = 8.67 $s^{-1}$ and K = 1.82 $M^{-1}$ (for B).

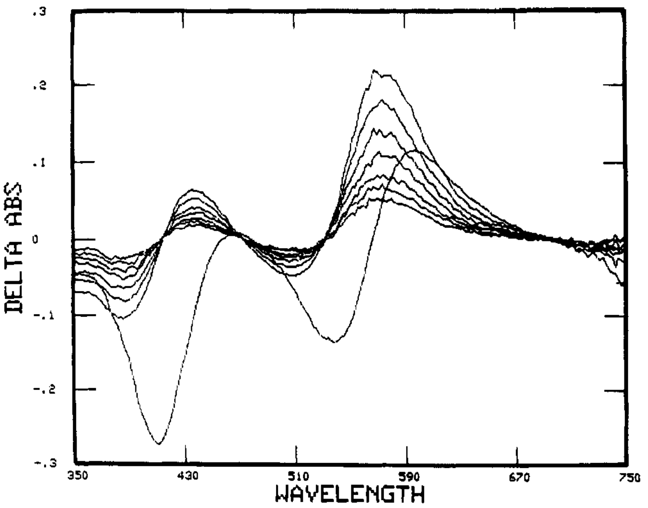


**Figure 4.** Rapid-scan difference spectra obtained on mixing [Co(nta)($O_2CO$)]$^{2-}$ with $HClO_4$ and recorded over the range 350–750 nm, with [Co]$_T$ = 3.26 × $10^{-3}$ M and [$H^+$] = 1.00 M. Following an initial delay of 5 ms, eight spectra were recorded over 1.000 s and are referenced to the final spectrum obtained after 2.000 s.

**Table 1.** Rate Constants for the Acid-Catalyzed Hydrolysis of [Co(nta)($O_2CO$)]$^2$ at 25 °C, $I$ = 1.0 M ($NaClO_4$)

| [$H^+$]/M | $k_{fast}{}^a$/$s^{-1}$ | $k_{calc}{}^c$/$s^{-1}$ | $k_{slow}{}^a$/$s^{-1}$ |
|---|---|---|---|
| 0.10 | 9.20, 9.60$^b$ | 9.06 | 2.00, 1.80$^b$ |
| 0.20 | 16.3, 17.0$^b$ | 16.7 | 2.00, 2.00$^b$ |
| 0.35 | 25.0, 24.7$^b$ | 25.0 | 2.00, 2.00$^b$ |
| 0.50 | 32.0, 32.0$^b$ | 31.7 | 1.98, 2.00$^b$ |
| 0.60 | 36.0 | 35.5 | 2.00 |
| 0.75 | 40.0 | 40.1 | 1.80 |
| 0.90 | 45.0, 44.0$^b$ | 44.0 | 1.80, 1.90$^b$ |
| 1.00 | 45.0, 46.0$^b$ | 46.2 | 1.90, 1.90$^b$ |

[a] Measured at 545 nm and [Co]$_T$ = 2.79 × $10^{-3}$ M unless otherwise stated. [b] Measured at 580 nm. [c] Values of $k_{fast}$ calculated according to eq 5 using the values of the constants given in the text.

with $k$ = 85.0 ± 4.0 $s^{-1}$ and $K$ = 1.19 ± 0.08 $M^{-1}$, while $k_{slow}$ is independent of [$H^+$] in the concentration range 0.1–1.0 M, with $k_{slow}$ = 2.0 ± 0.2 $s^{-1}$. The product spectrum (320–700 nm) was also [$H^+$]-independent: $\lambda_{max}$ ($\epsilon$) = 522 nm (204), 398 nm (195). Spectrophotometric titration of a 4.59 × $10^{-3}$ M solution established this as the diaqua complex [Co(nta)($OH_2$)$_2$] with p$K_{a(1)}$ and p$K_{a(2)}$ values of 6.52 ± 0.04 and 9.2 ± 0.1, respectively, at 25.0 °C and $I$ = 1.0 M ($NaClO_4$).

A series of rate measurements similar to those described above was carried out with the β-[Co(trien)($O_2CO$)]$^+$, [Co(tren)($O_2CO$)]$^+$, [Co($NH_3$)$_4$($O_2CO$)]$^+$, and [Co(gly)$_2$($O_2CO$)]$^-$ complex ions. However for these systems more care was needed to establish the biphasic nature of the overall reaction, and in many ways data collection and treatment followed that previously described for [Co(en)$_2$($O_2CO$)]$^+$, where rapid-scan spectra established maximum differentiation at 477 nm.[12] For reaction in 1 M $HClO_4$ rapid-scan spectra established adequate distinction (absorbance increase followed by a decrease) at 477, 470, 477, and 514 nm, respectively, and most rate data was collected at these wavelengths. At wavelengths where a continuous absorbance decrease occurred, the OLIS fitting routine usually failed to give a unique solution for $k_{fast}$ and $k_{slow}$. However, when the latter were sufficiently distinguished, the last portion of the absorbance–time trace accurately reflected $k_{slow}$. This was the case for the reactions of β-[Co(trien)($O_2CO$)]$^+$ (at 450 nm) and [Co($NH_3$)$_4$($O_2CO$)]$^+$ (at 525 nm), and supplementary data was collected at these wavelengths to confirm the values of $k_{slow}$. Rapid-scan spectra also established 447 nm as an isosbestic point for the second reaction ($k_{slow}$) of [Co(tren)($O_2CO$)]$^+$ (0.5 and 1.0 M [$H^+$]), and data collected at this wavelength followed a single exponential which gave $k_{fast}$ values directly. This was useful since $k_{fast}$ was only 3–5 times greater than $k_{slow}$ at these acidities and such measurements confirmed the values. Observed rate constants for these four complexes are given in Table S2 of the supplementary material and as plots of $k_{obs}$ vs [$H^+$] in Figure 5. While all four complexes display both [$H^+$]-dependent and [$H^+$]-independent reactions only [Co(tren)($O_2CO$)]$^+$ resembles α-[Co(trien)($O_2CO$)]$^+$ and [Co(nta)($O_2CO$)]$^{2-}$ in that the first observed process ($k_{fast}$) follows eq 5, with the second process ($k_{slow}$) being [$H^+$]-independent. For this complex, analysis of the $k_{fast}$ data according to eq 5 gave $k$ = 4.25 ± 0.48 $s^{-1}$ and $K$ = 0.61 ± 0.10 $M^{-1}$, with $k_{slow}$ = 0.31 ± 0.01 $s^{-1}$. For [Co($NH_3$)$_4$($O_2CO$)]$^+$, β-[Co(trien)($O_2CO$)]$^+$, and [Co(gly)$_2$($O_2CO$)]$^-$, the reverse order is obtained with the first observed process ($k_{fast}$) showing [$H^+$]-independent kinetics and the second ($k_{slow}$) following eq 6. Analysis of the latter data

$$k_{slow} = \frac{kK[H^+]}{1 + K[H^+]} \tag{6}$$

gave $k$ = 1.68 ± 0.22, 0.285 ± 0.020, and 4.1 ± 0.5 $s^{-1}$ and $K$ = 1.0 ± 0.2, 0.80 ± 0.10, and 1.37 ± 0.38 $M^{-1}$, respectively. The corresponding $k_{fast}$ values are 1.5 ± 0.05, 0.45 ± 0.05, and 4.1 ± 0.2 $s^{-1}$.

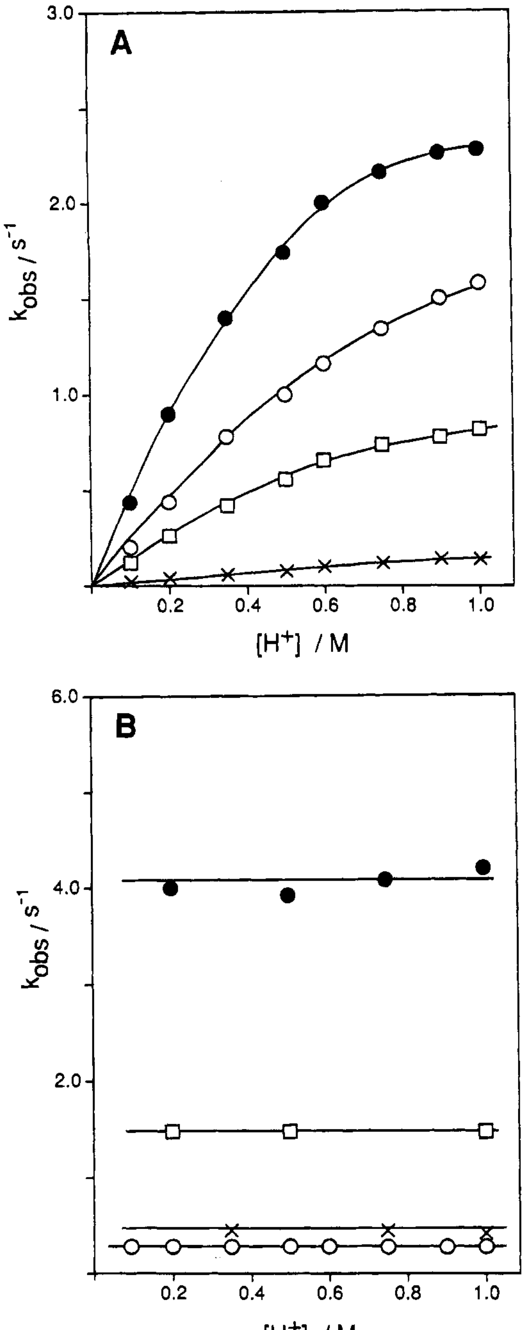


**Figure 5.** Plots of the observed [H$^+$]-dependent (A) and -independent (B) rate constants versus [H$^+$] for reaction of $[Co(gly)_2(O_2CO)]^-$ (closed circles), $[Co(tren)(O_2CO)]^+$ (open circles), $[Co(NH_3)_4(O_2CO)]^+$ (open squares) and $\beta$-$[Co(trien)(O_2CO)]^+$ (crosses) at 25 °C and $I = 1.0$ M ($NaClO_4$). Curve fitting of the [H$^+$]-dependent rates was achieved using eqs 5 or 6 as appropriate and values of the constants given in the text.

For the more robust $[Co(cyclen)(O_2CO)]^+$ and $[Co(N\text{-}mecyclen)(O_2CO)]^+$ complexes, rapid-scan spectra obtained in 1.0 M $HClO_4$ (650–350 nm) showed that each exhibited only one (slow) reaction, and from absorbance–time data (540 nm) collected at various [H$^+$] these were found to follow pseudo-first-order kinetics. These observed rate constants (Table 2) follow eq 5 with $k = (1.02 \pm 0.10) \times 10^{-2}$ and $(7.61 \pm 0.50) \times 10^{-3}$ s$^{-1}$ and $K = 1.42 \pm 0.2.28$ and $0.43 \pm 0.04$ M$^{-1}$ for the two complexes, respectively.

**Spontaneous Hydrolysis.** Absorption spectra (700–230 nm) of aqueous solutions ($2 \times 10^{-3}$ M, 0.03 M MES buffer, pH 6.3, $I = 1.0$ ($NaClO_4$), 25 °C) of $[Co(tren)(O_2CO)]^+$, $[Co(en)_2(O_2CO)]^+$, and $[Co(nta)(O_2CO)]^{2-}$ showed no change over periods of 17 days, 17 h, and 3 h, respectively. Assuming that 10% hydrolysis could have occurred and remained undetected, these times represent half-lives for hydrolysis of more than 46 days, 120 h, and 20 h, respectively. Such results contrast sharply with calculated half-times for the spontaneous reactions of 68, 96, and 3.9 min respectively based on literature rate constants.[6,7,9] Spectra of $\alpha$- and $\beta$-$[Co(trien)(O_2CO)]^+$ and $[Co(NH_3)_4(O_2CO)]^+$ recorded using the above conditions and at times corresponding to reported half-times for the spontaneous reaction of 77,[7] 1155,[7] 890 min,[5] respectively, were also found to be identical to those recorded at zero time. Thus the "spontaneous" reaction as represented by $k_o$ in eq 4 is absent.

**Table 2.** Rate Constants for the Acid-Catalyzed Hydrolysis of $[Co(cyclen)(O_2CO)]^+$ and $[Co(N\text{-}mecyclen)(O_2CO)]^+$ at 25 °C, $I = 1.0$ M ($NaClO_4$)

| | $[Co(cyclen)(O_2CO)]^+$ | | $[Co(N\text{-}mecyclen)(O_2CO)]^+$ | |
|---|---|---|---|---|
| [H$^+$]/M | $10^3k_{obs}{}^a$/s$^{-1}$ | $10^3k_{calc}{}^b$/s$^{-1}$ | $10^3k_{obs}$/s$^{-1}$ | $10^3k_{calc}{}^b$/s$^{-1}$ |
| 0.10 | 1.16 | 1.27 | 0.313 | 0.313 |
| 0.20 | 2.42 | 2.60 | 0.605 | 0.602 |
| 0.40 | 3.65 | 3.69 | 1.12 | 1.12 |
| 0.60 | 4.76 | 4.69 | 1.54 | 1.56 |
| 0.80 | 5.47 | 5.42 | 1.95 | 1.95 |
| 1.00 | 5.89 | 5.98 | 2.29 | 2.29 |

[a] Measured at 540 nm and $[Co]_T = 1.70 \times 10^{-3}$ M. [b] Calculated using equation (5) and the values of the constants given in the text.

**Spectrophotometric $K_a$ Values.** Direct spectrophotometric measurements of the acidity of the bidentate bicarbonato complexes $[Co(nta)(O_2COH)]^{1-}$, $[Co(gly)_2(O_2COH)]$, and $[Co(cyclen)(O_2COH)]^{2+}$ ($K_a = 1/K$, Scheme 1) were obtained following stopped-flow mixing of solutions of the corresponding carbonato complexes ($[Co]_T$ = constant) with $HClO_4$ solutions of varying concentration. For the highly reactive $[Co(nta)(O_2COH)]^{1-}$ and $[Co(gly)_2(O_2COH)]$ species zero-time absorbance values ($A_o$) were obtained by extrapolating the absorbance–time traces over the first few milliseconds. This was not necessary for $[Co(cyclen)(O_2COH)]^{2+}$. Only small spectral differences (<0.1 absorbance units at $\lambda_{max}$ for $3 \times 10^{-3}$ M solutions, 2 cm pathlength) were found for $\alpha$- and $\beta$-$[Co(trien)(O_2CO)]^+$, $[Co(NH_3)_4(O_2CO)]^+$, and $[Co(tren)(O_2CO)]^+$ between 1.0 M $NaClO_4$ data and that first recorded (within 15 ms) in 1.0 M $HClO_4$. No attempt was made to use this latter data.

Values of $K_a$ ($=1/K$, Scheme 1) were obtained by least squares fitting the zero-time absorbance data ($A_o$) to eq 7, where

$$\Delta A = \frac{(A_1 - A_2)\,[H^+]}{K_a + [H^+]} \qquad (7)$$

$\Delta A = A_1 - A_o$, and $A_1$ and $A_2$ correspond to the absorbances of the carbonato and bicarbonato chelates, respectively. Since the latter was never fully formed (even in 1.0 M H$^+$), $A_2$, as well as $K_a$, was treated as a variable in the analysis. Representative data are given in Figure 6 for $[Co(gly)_2(O_2CO)]^-$ as a plot of $A_o$ vs [H$^+$] with the full curve being calculated using $K_a = 0.66$ M. Similar treatment for $[Co(nta)(O_2CO)]^{2-}$ and $[Co(cyclen)(O_2CO)]^+$ gave best-fit $K_a$ values of $1.15 \pm 0.28$ ($I = 1.0$ M) and $0.42 \pm 0.06$ ($I = 2.70$ M), respectively. All values obtained in this manner are collected in Table 3.

## Discussion

The H$^+$-catalyzed ring opening reaction of carbonato chelates (Scheme 1) occurs with Co–O bond cleavage; i.e. $k_1$ represents a dechelation process. This was first demonstrated by Posey

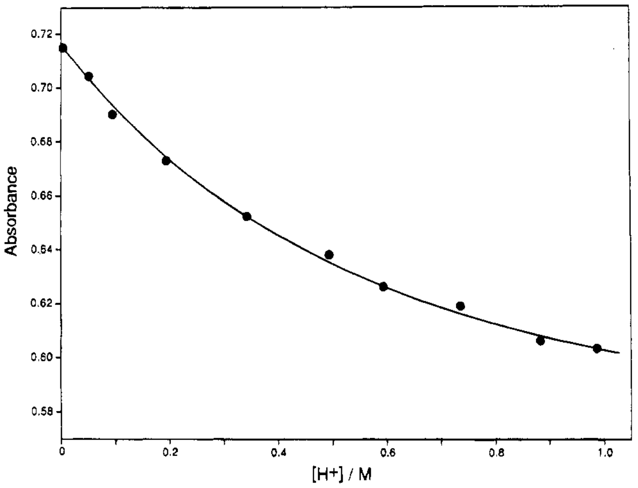
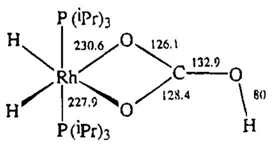


**Figure 6.** Plot of zero-time absorbance data ($A_o$) for $[Co(gly)_2(O_2CO)]^-$ ($2.99 \times 10^{-3}$ M) at 553 nm vs $[H^+]$ at 25 °C and $I = 1.0$ M ($NaClO_4$). The curve represents the least squares fit to eq 7 using $K_a = 0.66$ M and $A_2 = 0.532$ ($A_1 = 0.717$).

and Taube[24] for $[Co(NH_3)_4(O_2CO)]^+$ and subsequently by Francis and Jordan[25] for $[Co(en)_2(O_2CO)]^+$, $[Co(phen)_2(O_2CO)]^+$, and $[Co(bipy)_2(O_2CO)]^+$. Such complexes cover the medium-to-slow-reacting systems, and even though ring opening in $[Co(nta)(O_2CO)]^{2-}$ and α-$[Co(trien)(O_2CO)]^+$ is much faster, we have no reason to believe that the cleavage pattern will be any different. Subsequent loss of $CO_2$ from **3** ($k_2$, Scheme 1) on the other hand occurs by C−O bond fission, i.e., decarboxylation of bicarbonate occurs at this stage. This was established for the monodentate bicarbonato complex $[Co(NH_3)_5OCO_2H]^{2+}$ by the nonincorporation of solvent label into released $CO_2$[26] and subsequently for the chelate $[Co(NH_3)_4(O_2CO)]^+$ by the incorporation of only one solvent label into the diaqua product.[24] [This reaction involves both dechelation (eq 2) and decarboxylation (eq 3).] There is also ample evidence from the reverse carboxylation process given by eq 8 that M−OH species add rapidly to $CO_2$ without disruption of the M−O bond.[27]

$$(L)_5M{-}^{18}OH^{(n+1)+} + CO_2 \rightarrow (L)_5M{-}^{18}OCO_2H^{(n+1)+} \quad (8)$$

The currently accepted mechanism[1] for the acid-catalyzed hydrolysis of carbonato chelates is one of initial, but slight, preprotonation of the chelate in aqueous solution followed by rate-determining ring opening ($k_{obs}(1) = k_1K$, Scheme 1). The possibility of directly observing the protonated chelate has only recently been recognized,[12] although an earlier study by Springborg and Schaffer[28] might have suggested otherwise. These authors found $[Co(py)_4(O_2CO)]ClO_4{\cdot}H_2O$ to be increasingly soluble in aqueous perchlorate solutions as the $HClO_4$ content was raised, and from solubility data they suggested a protonation constant of $\sim 0.3$ $M^{-1}$ at $I = 8.0$ M. Also, since little spectral change was observed under these conditions they suggested protonation to occur at the *exo*-O atom. At higher acidities (up to 7.2 M $HClO_4$), substantial, and reversible, red shifts in the spectrum were attributed to further protonation of one of the ring oxygens. Since carbonato complexes containing pyridine ligands are very slow to hydrolyze, these observations pointed toward the possibility of crystallizing one in its protonated form. This has recently been achieved with $[Co(tepa)(O_2COH)](ClO_4)_2{\cdot}H_2O$ (tepa = tris[2-(2-pyridyl)ethyl]amine), and an X-ray study shows the 4-membered bicarbonato ring to be intact although the position of the proton remains unclear.[29,49] However the proton position is clear with the Rh(III) complex **6**, isolated



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following oxidative addition of $RhH(i\text{-}Pr)_3)_3$ to $CO_2$ in wet THF, where the structural study shows the proton to be on the *exo*-O atom.[30] We assume that the preferred protonation of carbonato chelates in aqueous solution occurs at this same site.

The $K_a$ values for a number of bicarbonato chelates have now been measured and are given in Table 3. Where comparison is possible, the directly determined spectrophotometric value agrees with that obtained kinetically (eq 5 and 6, $K_a = 1/K$). For the tetraamine systems, protonation gives an absorption decrease at $\lambda_{max}$, but for $[Co(NH_3)_4(O_2CO)]^+$, $[Co(tren)(O_2CO)]^+$, and α- and β-$[Co(trien)(O_2CO)]^+$ the decrease is very small and unreliable for a spectrophotometric $K_a$ determination. Such observations parallel those for $[Co(py)_4(O_2CO)]^{2+}$ [28,31] in 0.1−5 M $HClO_4$. However, with $[Co(nta)(O_2CO)]^{2-}$, protonation results in a reasonable absorption increase at $\lambda_{max}$, while $[Co(gly)_2(O_2CO)]^-$ shows a moderate absorption decrease (Figure 6). Clearly the sense and magnitude of the absorption change differs for the different complexes, but in no case does full protonation occur, even at $[H^+] = 1.0$ M. The acidity constant for α-$[Co(trien)(O_2COH)]^{2+}$ shows the expected solvent isotope effect,[32] $K_{D_2O}/K_{H_2O} = 2.6$, in agreement with the protonated bicarbonato chelate in $H_2O$ being a stronger acid than the deuteronated bicarbonato chelate in $D_2O$.

There is little change in $K_a$ with changing ligand (L) or charge type. Thus $[Co(nta)(O_2COH)]^-$, $[Co(gly)_2(O_2COH)]$, $[Co(NH_3)_4(O_2COH)]^{2+}$, and $[Co(en)_2(O_2COH)]^{2+}$ all have $K_a$ values of about 1.0 M. $[Co(N\text{-mecyclen})(O_2COH)]^{2+}$ is somewhat more acidic ($K_a = 2.3$ M), as is $[Co(py)_4(O_2COH)]^{2+}$ ($\sim 3.3$ M) and $[Co(tepa)(O_2COH)]^{2+}$ ($\sim 5$ M), but such differences are small and do not appear to follow any particular trend. This result is not unexpected for protonation at a site well removed from the metal center. Differences in $K_a$ are therefore not responsible for the large variation in ring opening rates.

The kinetic data which follow either eq 5 or 6 is assigned to the first mechanistic process,[33] i.e. $k = k_1$ (Scheme 1). These

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(29) Blackman, A. G.; Baxter, K. E. Unpublished results. Disorder difficulties have meant that the proton remains unlocated. The dimensions of the chelate are, however, consistent with *exo*-O atom protonation.

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(33) The $k_{fast}$, $k_{slow}$ mechanistic ambiguity (see Jackson, W. G.; Harrowfield, J. M.; Vowles, P. D. *Internatl. J. Chem. Kin.* **1977**, *9*, 535 and reference 12) meant that particular care was required when assigning $k_1$ and $k_2$. By consideration of the different $[H^+]$ dependences of $k_{fast}$ and $k_{slow}$, we assign $k_{fast}$ to $k_1$ for reaction of $[Co(nta)(O_2CO)]^{2-}$, $[Co(tren)(O_2CO)]^+$, and α-$[Co(trien)(O_2CO)]^+$ for $[H^+] > 0.10$ M, but to $k_2$ for reaction of $[Co(gly)_2(O_2CO)]^-$, $[Co(NH_3)_4(O_2CO)]^+$, and β-$[Co(trien)(O_2CO)]^+$ (and α-$[Co(trien)(O_2CO)]^+$ at $[H^+] < 0.10$ M).

**Table 3.** Acidity ($K_a$) and Rate ($k_1$) Constants for Bidentate Bicarbonato Chelates, Rate Constants for Decarboxylation of the Corresponding Aqua/Monodentate Bicarbonato Complexes ($k_2$), and Some Acid Dissociation Constants ($pK_a$) and Water Exchange Rate Constants ($k_{ex}$) for Related Aqua Species (25 °C, $I$ = 1.0 M)

| | | | | $[Co(L)_4(OH_2)_2]^{n+}$ | |
|---|---|---|---|---|---|
| complex | $K_a/M^a$ | $k_1/s^{-1}$ | $k_2/s^{-1}$ | $pK_a(1)$ | $k_{ex}/s^{-1\ e}$ |
| $[Co(nta)(O_2COH)]^{1-}$ | 0.85 (1.1) | 85.0 | 2.0 | 6.52 | |
| α-$[Co(trien)(O_2COH)]^{2+}$ | 1.4 | 9.7 | 0.62 | 5.4 | |
| | $0.55^d$ | $8.7^d$ | $0.64^d$ | | |
| $[Co(tren)(O_2COH)]^{2+}$ | 1.6 | 4.25 | 0.31 | 5.62 (p) | $3.7 \times 10^{-5}$ (p)<br>$8.5 \times 10^{-6}$ (t) |
| $[Co(gly)_2(O_2COH)]$ | 0.73 (0.66) | 4.1 | 4.1 | 6.15 | |
| $[Co(NH_3)_4(O_2COH)]^{2+}$ | 1.0 | 1.68 | 1.50 | 6.06 | |
| $[Co(en)_2(O_2COH)]^{2+\ b}$ | 0.9 (1.1) | 0.85 | 0.93 | 6.1 | $7.5 \times 10^{-6}$ |
| β-$[Co(trien)(O_2COH)]^{2+}$ | 1.25 | 0.285 | 0.45 | 5.3 | |
| $[Co(cyclen)(O_2COH)]^{2+}$ | 0.70 $(0.42)^c$ | 0.0102 | | 5.83 | $1.4 \times 10^{-4}$ |
| $[Co(N\text{-}mecyclen)(O_2COH)]^{2+}$ | 2.3 | 0.0076 | | 5.27 | $>1 \times 10^{-4}$ |

[a] Kinetically determined. Values in parentheses were determined directly from zero-time absorbance data. [b] Reference 12. [c] Determined at $I$ = 2.7 M ($NaClO_4$). [d] Values in 96–99.5% $D_2O$. [e] Most of these values have been determined, or redetermined, in our laboratory using $^{17}O$-NMR spectroscopy (unpublished).

$k_1$ values (Table 3) cover a reactivity range of $\sim 10^4$. The most rapidly reacting system, $[Co(nta)(O_2COH)]^-$, ring-opens with a half-life of ~8 ms, whereas the half-life for the $[Co(N\text{-}mecyclen)(O_2COH)]^{2+}$ reaction is ~90 s.

The spontaneous ring opening reaction[1,34] ($k_o$, eq 4) does not exist according to our measurements. α- and β-$[Co(trien)(O_2CO)]^+$, $[Co(en)_2(O_2CO)]^+$, and $[Co(tren((O_2CO)]^+$ are stable for very long periods of time at pH 6.3. Some of the other complexes show spectrophotometric changes, but these result from general decomposition rather than from specific decarboxylation (e.g. $[Co(NH_3)_4(O_2CO)]^+$). Previous authors have considered the spontaneous reaction in some detail,[5,8] but we believe that proper extrapolation of the $[H^+]$ and $[OH^-]$ dependencies to neutral pH will account for any decarboxylation under this condition.

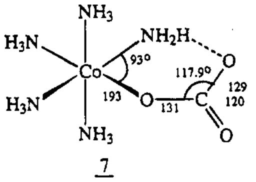
The $k_2$ values for decarboxylation of the mondentate bicarbonate complexes are remarkably constant at $\sim 1\ s^{-1}$ (Table 3). This is not unexpected for bond cleavage (C–O) remote from the metal center, and similar values have been noted for other bicarbonato complexes, e.g. $[Co(NH_3)_5(OCO_2H)]^{2+}$ ($k$ = 1.25 $s^{-1}$).[35] The reaction cannot be observed for the very slow to ring-open complexes (e.g. $[Co(cyclen)(O_2CO)]^{2+}$ and $[Co(N\text{-}mecyclen)(O_2CO)]^{2+}$), but there is no reason to believe that the rate constants will vary greatly from $\sim 1\ s^{-1}$. Previous authors have attributed differences in the observed rate ($k_1(obs) = k_1K = k_1/K_a$; Scheme 1) to (roughly in chronological order) (1) steric crowding by L restricting the attack of $H_3O^+$;[36] (2) N–H- - -O hydrogen bonding by amine L assisting protonation of the susceptible ring O atom;[6] (3) steric strain within the 4-membered ring resulting from restrictive bond angles in *trans* L–L chelates as opposed to *cis* L–L chelates;[7,8] (4) the electron donor properties of L (i.e. basicity) decreasing the residual positive charge on the Co atom, thereby leading to increased protonation of the carbonato chelate[25] and/or to a weaker C–O bond;[11] (5) solvation changes resulting from variations in overall charge on the complex[9] or from methyl substitution on L[2,8] leading to changes in basicity of L or to entropic factors; and (6) to a combination of solvation, steric, and electronic factors.[31]

Our results show that electronic factors are not responsible, at least not insofar as they affect the equilibrium protonation of the carbonato chelate ($K_a$, Table 3). It is well-known that electronic factors fall off rapidly with distance from the metal, so substantial insensitivity to varying L is to be expected for protonation at the *exo* oxygen atom. Other quantities which might be expected to relate more closely to L variation, such as the acidity or lability of coordinated water molecules in the same bonding situation also show no correlation with $k_1$. Available data for our systems are listed in Table 3, and these add to previous compilations.[2,8,25,31] Thus α-$[Co(trien)(OH_2)_2]^{3+}$ and $[Co(N\text{-}mecyclen)(OH_2)_2]^{3+}$ have similar acidities ($pK_{a(1)}$ = 5.3–5.4), yet the $k_1$ values of their bicarbonato chelates differ by $\sim 10^3$. Likewise, complexes of different charge type but of similar acidity such as $[Co(nta)(OH_2)_2]$, $[Co(gly)_2(OH_2)_2]^+$, and $[Co(en)_2(OH_2)_2]^{3+}$ result from carbonato chelates whose $k_1$ values differ by $10^2$. Kinetic parameters, such as rate constants for water exchange ($k_{ex}$) in the aqua complexes, also show no correlation. We have found that substitution processes, such as the anation reaction given by eq 9 are remarkably facile with

$$[Co(L)_4(NH_3)(OH_2)]^{3+} + Cl^- \rightarrow [Co(L)_4(NH_3)Cl]^{2+} + H_2O \quad (9)$$

$(L)_4$ = cyclen, N-mecyclen, which implies that these ligands are associated with an unusually weak Co–O bond in this situation. The stability of the corresponding bicarbonato chelates is therefore quite remarkable.

Although the carbonato chelate ring in the $[(L)_4Co(O_2CO)]^{n+}$ complexes is stable, it is under strain. The strain-free bond angle at Co would be ~90°, if the structure of monodentate **7** is taken as a guide,[37] and that at carbonyl C ~ 125°, if the theoretical



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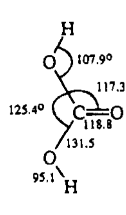

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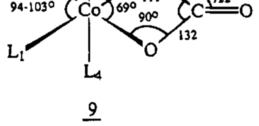

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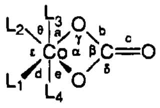
**Table 4.** Bond Lengths and Angles for Some $[CoL_4(O_2CO)]^{n\pm}$ Carbonato Chelates



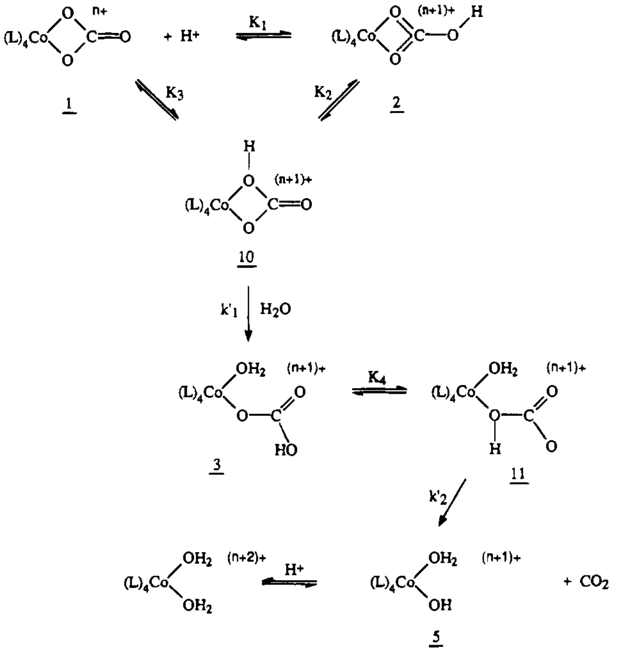
| complex | bond lengths (pm) | | | | | bond angles (deg) | | | | | | ref |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | a | b | c | d | e | α | *β* | *γ* | *δ* | *ϵ* | *θ* | |
| $[Co(NH_3)_5(OCO_2)]BrH_2O$ | 193 | 131 | 129 (H), 120 | 198 | 195(av) | 93 | 118 | | 123 | | | *a* |
| $[Co(NH_3)_4(O_2CO)]Br$ | 193 | 134 | 124 | 203 | 194 | 70.5 | 112.7 | 88.5 | 123.9 | 94 | 93 | *b* |
| $[Co(en)_2(O_2CO)]I{\cdot}2H_2O$ | 191 | 131 | 123 | 196 | 196 | 68.2 | 110 | 91 | 124 | 95 | 88 | *c* |
| $[Co(tn)_2(O_2CO)]ClO_4$ | 192 | 132 | 122 | 196 | 196 | 68.8 | 110.4 | 90.2 | | 95 | 88 | *d* |
| $[Co(tren)(O_2CO)]Cl{\cdot}3H_2O$ | 191 (t), 193 (p) | 131 | 124 | 193 | 196 | 68.5 | 111 | 90 | 124 | 98 | 88 | *e* |
| $[Co(cyclen)(O_2CO)]ClO_4{\cdot}H_2O$ | 191 | 131 | 122 | 193 | 196 | 68.4 | 110 | 90 | 126 | 103 | 87 | *f* |
| $[Co(3,8\text{-}Me_2trien))(O_2CO)]ClO_4$ | 192 | 130 | 124 | 194 | 196 | 68.6 | 112 | 89 | 123 | 98 | 86 | *g* |
| $[Co(py)_4(O_2CO)]ClO_4$ | 189 | 132 | 121 | 200 | 198 | 69.3 | 109 | 91 | 125 | 101 | 91 | *h* |
| $[Co(bipy)_2(O_2CO)]NO_3{\cdot}5H_2O$ | 189 | 131 | 124 | 193 | 192 | 69.9 | 111 | 89 | 124 | 93 | 83 | *i* |
| $[Co(phen)_2(O_2CO)]Br{\cdot}4H_2O$ | 189 | 132 | 121 | 193 | 193 | 69.0 | 110 | 89 | 122 | 96 | 84 | *i* |
| $[Co(tet\text{-}b)(O_2CO)]ClO_4$ | 191 | 129 | 125 | 198 | 202 | 68.4 | 112 | 90 | 124 | 100 | 87−93 | *j* |

[a] Freeman, H. C.; Robinson, G. *J. Chem. Soc.* **1965**, 3194 (this represents monodentate bicarbonate coordination, so α = 93° represents no significant distortion). [b] Snow, M. R. *Aust. J. Chem.* **1972**, *25*, 1307. [c] Bigoli, F.; Lanfranchi, M.; Leponati, E.; Pellinghelli, M. A. [d] Geue, R. J.; Snow, M. R. *J. Chem. Soc. A.* **1971**, 2981; *Cryst. Struct. Commun.* **1980**, *9*, 1261. [e] Schlemper, E. O.; Sen Gupta, D. K.; Dasgupta, T. P. *Acta Crystallogr.* **1983**, *C39*, 1012. [f] Loehlin, J. H.; Fleischer, E. B. *Acta Crystallogr.* **1976**, *B32*, 3063. [g] Toriumi, K.; Saito, Y. *Acta Crystallogr.* **1975**, *B31*, 1247. [h] Kaas, K.; Sorenson, A. M. *Acta Crystallogr.* **1973**, *B29*, 113. [i] Niederhoffer, E. C.; Martell, A. E.; Rudolf, P.; Chearfield, A. *Inorg. Chem.* **1982**, *21*, 3734. [j] Lu, T-H.; Chen, B-H.; Chung, C-S. *Acta Crystallogr.* **1993**, *C49*, 1912.

structure for $(HO)_2CO$, **8**, is used[38] (the 117.9° bond angle in **7** is probably distorted by H-bonding). Such strain-free values are to be compared with average bond angles of 69.0 ± 0.5° and 112 ± 2°, respectively, as given in structure **9**. However, such distortions are not influenced by the other ligand atoms or groups about the metal; the available individual bond lengths and angles listed in Table 4 lie very close to the above average values. Attempts to relieve strain are however found elsewhere in these complexes, in particular in the bond angle *trans* to the carbonato chelate (ϵ, Table 4). This angle is on average 8.5° larger ($\epsilon_{av}$ = 96.0°) than that *cis* to the carbonato ($\alpha_{av}$ = 87.5°) and chelation by *trans* L−L does not seem to affect this.[7,8] Those systems with the largest *trans* bond angle, e.g. $[Co(py)_4(O_2CO)]^+$ (ϵ = 101°), $[Co(tet\text{-}b)(O_2CO)]^+$ (100°), and $[Co(cyclen)O_2CO]^+$ (103°), are among the slowest to dechelate, even though the dimensions of the 4-membered carbonato chelate remain unaltered. Likewise the dimensions of the carbonato chelate in $K[Co((R)\text{-}Val)_2(O_2CO)]{\cdot}2H_2O$[39] (*trans* carboxylate O) and $[Co(trpy)(OH)(O_2CO)]{\cdot}4H_2O$[40] (*trans* OH) are not affected by having *trans* oxyanion donors, so we may assume that *trans* carboxylate in $[Co(nta)(O_2COH)]^{1-}$ does not directly bring about rapid dechelation ($k_1 = 85\ s^{-1}$). From such considerations we are of the view that structural effects are not primarily responsible for the large variation in dechelation rates.

We suggest that the variations in $k_1$ arise from differing degrees of protonation of the *endo* (ring) oxygen atom, either in the transition state for cleavage of the Co−O bond (a concerted mechanism with an unsymmetrical transition state[41,42] would be required) or as a pre-equilibrium (stepwise mechanism). We favor the stepwise process since we believe that breaking of the Co−O bond will be rate determining. Scheme 2 outlines this proposal. This gives $k_1 = K_2k_1'$ and allows $K_2$ to be small numerically but of wide variability depending on the basicity of the *endo*-O atom relative to the *exo*-O atom (the observed protonation constant $K = K_1 + K_3 \approx K_1$). In agreement with this proposal, $k_1$ for the α-$[Co(trien)(O_2COH)]^{2+}$ complex shows no useful solvent isotope effect ($k_1(D_2O) = 8.7\ s^{-1}$, $k_1(H_2O) = 9.7\ s^{-1}$). The constant $K_2$ should be essentially isotope-independent, and $k_1'$ represents cleavage of a very weak Co−OH(D) bond.[32] Since this latter process ($k_1'$) is overall rate-determing, the observed unimolecular ring opening rate constant $k_1$ will be isotope-independent. However, and most importantly, this mechanism requires protonation of the ring O atom of an otherwise very stable 4-membered chelate, and the variability in $k_1$ must reside in the ability of different L to influence this. Solvation, steric factors, or charge may all play a part, and in a manner which does not influence $K_1$. Likewise the decarboxylation process $k_2$ for α-$[Co(trien)(OH_2)(OCO_2H)]^{2+}$ shows no solvent isotope effect ($k_2(D_2O) = 0.62\ s^{-1}$; $k_2(H_2O) = 0.64\ s^{-1}$) and this can also be considered as a stepwise process with no

**Scheme 2.** Mechanism for Acid-Catalyzed Dechelation and Decarboxylation



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(38) Olah, G. A., *Angew. Chem. Int. Ed.* **1993**, *32*, 767.

(39) Price, M. G.; Russell, D. R. *J. Chem. Soc. Dalton Trans.* **1981**, 1067.

(40) Kucharski, E. S.; Skelton, B. W.; White, A. H., *Aust. J. Chem.* **1978**, *31*, 47.

(41) Jencks, W. P. in *Catalysis in Chemistry and Enzymology*, pp 259−273, McGraw-Hill, New York, 1969.

(42) More O'Ferrall, R. A. In *Proton Transfer Reactions* (Caldin, E., and Gold, V., eds.), pp 201−263, Wiley, New York, 1975.

H/D transfer occurring in the rate-determining elementary step, $k_2 = k_2'K_4$ (Scheme 2). A similar result was found previously with $[Co(NH_3)_5OCO_2H]^{2+}$ decarboxylation[11,43] as well as with the reverse carboxylation reaction $[Co(NH_3)_5OH]^{2+} + CO_2$.[43] Such a stepwise mechanism would require very facile CoO(H/D)$-CO_2$ bond cleavage since the equilibrium constant $K_4$ will be very small.

The mechanism for dechelation and subsequent decarboxylation has many similarities with that currently proposed for the carbonic anhydrase (CA) catalyzed dehydration of $HCO_3^-$. Recent theoretical simulations (ab initio[44] and EVB calculations[45]) as well as experimental results (crystal structures of $HCO_3^-$ binding to a Thr$^{200}$His mutant of CaII[46] and to Co(II)-substituted CAII[47]) agree that an early stage intermediate is formed containing $HCO_3^-$ *chelated* to the Zn(II) atom in a manner very similar to that given by the *endo*-O protonated intermediate **10** of Scheme 2. It is now believed that decarboxylation involves bond rotation in such a way that the protonated coordinated oxygen atom of **11** derives from the noncoordinated hydroxyl OH of **3** (i.e. O interchange occurs).[44,48] Such bond rotation and decarboxylation in the natural system is represented by $k_1'K_4k_2'$ in ours. The two essential points we wish to make from this study are (1) that decarboxylation cannot occur directly in the chelated bicarbonato species—one-ended dissociation from the metal must occur first—and (2) that the sensitivity of the ring opening rate to the coordination environment manifests itself though the stability of the essential intermediate which is protonated on the ring (*endo*) O atom rather than on the *exo*-O atom.

**Supplementary Material Available:** Table S1, giving rate data for the acid-catalyzed hydrolysis of α-$[Co(trien)O_2CO)]^+$ in $H_2O$ and $D_2O$ at 25 °C and $I = 1.0$ M ($NaClO_4$), and Table S2, giving rate data for the acid-catalyzed hydrolysis of $[Co(tren)(O_2CO)]^+$, β-$[Co(trien)(O_2CO)]^+$, $[Co(gly)_2(O_2CO)]^-$, and $[Co(NH_3)_4(O_2CO)]^+$ at 25 °C and $I = 1.0$ M ($NaClO_4$) (5 pages). Ordering information is given on any current masthead page.

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(43) Pocker, Y.; Bjornquist, D. W. *J. Amer. Chem. Soc.* **1977**, *99*, 6537.

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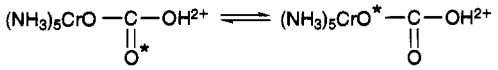
(45) Aquist, J.; Fothergill, M.; Warshel, A. *J. Am. Chem. Soc.* **1993**, *115*, 631.

(46) Xue, Y.; Vidgren, J.; Svensson, A.; Liljas, A.; Jonsson, B-H.; Lindskog, S. *Proteins: Structure, Function and Genetics*, **1993**, *15*, 80.

(47) Hakansson, K.; Wehnert, A. *J. Mol. Biol.* **1992**, *228*, 1212.

(48) In this regard it is of interest to note that Earley and Alexander (Earley, J. E.; Alexander, W., *J. Am. Chem. Soc.*, **1970**, *90*, 2294) have shown that rapid oxygen interchange occurs in the analogous, supposedly inert, Cr(III) system:



$$(NH_3)_5CrO-\underset{\underset{O^*}{\|}}{C}-OH^{2+} \rightleftharpoons (NH_3)_5CrO^*-\underset{\underset{O}{\|}}{C}-OH^{2+}$$

A similar oxygen interchange does not occur in the Co(III) system.

(49) Note added in proof: Subsequent refinement of this structure has located the proton on the *exo*-O atom.