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Kinetics and Mechanism of Aquation and Formation Reactions of Carbonato Complexes. 19. Rate of Decarboxylation of the Bis(carbonato)bis(pyridine)cobaltate(III) Complex Ion in Aqueous Pyridine Buffer Solutions[1,2]

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The kinetics of decomposition of *cis*-$K[Co(py)_2(CO_3)_2]\cdot 2H_2O$ have been investigated at various temperatures in aqueous pyridine buffer solutions. The complex decarboxylates in two successive reactions. We have examined the first step, which is described by a pseudo-first-order rate constant of the form $k_{obsd} = k_a + k_b[H^+]$. This step produces as an intermediate a relatively stable mono(carbonato) complex ion, *cis*-$Co(py)_2(CO_3)(H_2O)_2^+$. At 30 °C we find $k_a = (1.57 \pm 0.07) \times 10^{-4}$ s^{-1} and $k_b = 13.0 \pm 2$ M^{-1} s^{-1} with activation parameters for the acid dependent path of $\Delta H_b^{*} = 16.9 \pm 1.2$ kcal/mol and $\Delta S_b^{*} = 2.3 \pm 4.0$ cal/(mol K). Reaction rates for this step are accelerated in a heavy-water solvent. The results are compared with those expected for the decarboxylation of monodentate and bidentate carbonato complexes of cobalt(III). Although the stoichiometry and the kinetic data are consistent with two bidentate carbonate ligands, the possibility that the title complex contains at least one monodentate carbonate ligand is not unequivocally ruled out.

Introduction

Previous studies of decarboxylation reactions of carbonato complexes of cobalt(III) indicate that two distinct processes can occur. When the carbonate ligand is bound in a monodentate fashion, as in the $Co(NH_3)_5CO_3^+$ ion, decarboxylation in aqueous acid media is relatively fast,[4] compared with the usual rates of substitution reactions at cobalt(III) centers, and had previously been shown to occur by means of carbon–oxygen bond cleavage.[5] The acid dependence of the observed rate of decarboxylation is ascribed to a proton preequilibrium. The reaction scheme for this species ($N{\equiv}NH_3$) is as shown in eq 1 and 2. This is consistent with an experimental rate law of the form shown in eq 3a,b. The above $[H^+]$ dependence

$$[(N)_5CoOC(O)O]^+ + H^+ \overset{1/K_c}{\rightleftharpoons} [(N)_5CoOC(O)OH]^{2+} \quad (1)$$

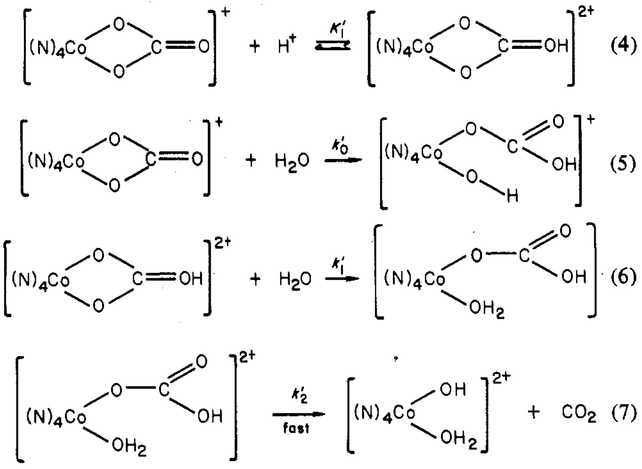
$$[(N)_5CoOC(O)OH]^{2+} \xrightarrow{k_1} (N)_5CoOH^{2+} + CO_2 \quad (2)$$

$$R = -d[Co(NH_3)_5CO_3^+]/dt = k_{obsd}[\text{total carbonato complex}] \quad (3a)$$

$$k_{obsd} = k_1[H^+]/([H^+] + K_c) \quad (3b)$$

of k_{obsd} gives a characteristic sigmoid shape when k_{obsd} is plotted vs. pH. In the systems of this type investigated to date,[6-9] the activation parameters appear to be more or less independent of changes in the ligand system or the nature of the metal center [Co(III), Rh(III), or Ir(III)]. With the exception of the *trans*-$[Co(NH_3)_4(CN)(CO_3)]$ complex,[9] the enthalpies and entropies of activation fall in the very narrow range $\Delta H^{*} = 17 \pm 1$ and $\Delta S^{*} = -1 \pm 5$ (with the uncertainties reported as standard deviations based on five values). For the cyano complex, activation parameters slightly more positive than those above are interpreted in terms of a minor role played by the trans effect of the CN^- ligand.

For a bidentate carbonate ligand, the acid-catalyzed decarboxylation involves a proton preequilibration prior to a rate-determining metal–oxygen bond rupture.[10] The observed activation parameters for this decarboxylation reaction change markedly with variations in the ligand system. In the usual situation this ring-opening step is followed by relatively rapid loss of CO_2 from the now monodentate carbonate intermediate as indicated in eq 4–7. The two-term rate law usually observed experimentally is consistent with the above mechanism. The pseudo-first-order rate constant found has the form shown in eq 8.



$$k_{obsd} = k_0' + k_1'K_1'[H^+] \quad (8)$$

The existence of the tris- and many mono(carbonato)cobalt(III) complexes has been reported.[11,12] More recently, the preparations of several mononuclear bis(carbonato)cobalt(III) complexes have been described.[13-16] Although the mode of bonding of the carbonate ligand (mono- or bidentate) in the mono(carbonato) complexes is usually unambiguous, the situation in tris complexes is not clear. The infrared spectra of the anhydrous complexes suggest fully chelated carbonate

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Table I. Spectral Data for the Complexes and Some Similar (Carbonato)- and Aquocobalt(III) Complexes That Contain the CoN_2O_4 Chromophore

complex (medium)	λ_{max} (ϵ)[a]	λ_{min} (ϵ)	λ_{max} (ϵ)	λ_{min} (ϵ)	ref
cis-$Co(py)_2(CO_3)_2^-$ (0.1 M py)	562 (156)	464 (16)	391 (197)	464 (68)	this work
(aq)	568 (178)		392 (251)		14
(1 M $NaHCO_3$)	561 (165)		388 (232)		13
$Co(py)_2(CO_3)(H_2O)_2^+$ (2 M $HClO_4$)	536 (87)	455 (18)	388 (107)	358 (81)	this work
cis-$Co(py)_2(H_2O)_4^{3+}$ (2 M $HClO_4$)	547 (45)	488 (10)			this work
$Co(en)(CO_3)_2^-$ (aq)	567 (159)		394 (164)		15
cis-$Co(NH_3)_2(CO_3)_2^-$ (satur $(NH_4)_2CO_3$)	575 (174)		395 (258)		38
(1 M $KHCO_3$)	577		393		39
$Co(en)(H_2O)_4^{3+}$ (0.05 M $HClO_4$)	510 (59)		373 (49)		15
cis-$Co(NH_3)_2(H_2O)_4^{3+}$ (1 M $HClO_4$)	540 (41)		375 (40)		28
(1 M $HClO_4$)	537 (48)		370 (46)		19

[a] All wavelengths in nanometers and extinction coefficients in M^{-1} cm^{-1} units.

ligands while those of the hydrated salts indicate at least one monodentate carbonate group.[17] The binding of carbonate ligand in bis(carbonato)diaminecobaltate(III) complexes may also be ambiguous. NMR results have been used to classify the $Co(en)(CO_3)_2^-$ ion as monomeric in D_2O solvent, with both carbonates acting as bidentate ligands.[15] However, it has been suggested that a mixture of monomeric and dimeric cobalt(III) complexes exists under the conditions of synthesis usually used for the preparation of bis(carbonato) complexes,[13] and it is claimed that acidification of these complexes yields hydroxy-bridged species.[18,19]

In our present study, we report the results for the kinetics of decarboxylation of the bis(carbonato) complex $K[Co(py)_2(CO_3)_2]\cdot 2H_2O$. The characteristic acid dependencies of the decarboxylation rate constants for the two different types of carbonate ligand systems as well as the narrow range of activation parameters observed for the decarboxylation of monodentate carbonate in various environments were expected to help in determining the mechanism of decarboxylation and the nature of the carbonate ligand coordination in the bis(carbonato) complexes. An additional motivation for the present study was to identify, during the decomposition of bis(carbonato) complexes, two distinct decarboxylation steps.

Experimental Section

Preparative Methods. The complex *cis*-$K[Co(py)_2(CO_3)_2]\cdot 2H_2O$ was prepared by the method of Davies and Hung.[13] Analytical results have been reported previously.[20] The visible absorption spectrum of the complex in 0.1 M pyridine (see Table I) is in reasonable agreement with that previously reported[13] for the same species in 1 M $NaHCO_3$. Other bis(carbonato)bis(amine)cobalt(III) complexes are expected to exhibit similar spectral parameters in the visible region, and examination of Table I reveals that a similarity does exist.

Pyridine buffers ($I = 0.5$ M, NaCl) of the desired pH were prepared from stock solutions of pyridinium chloride–sodium chloride and sodium hydroxide–sodium chloride. At lower pH's, a citrate–phosphate buffer system was used. The pH was measured with a Fisher Accumet Model 420 digital meter or a Corning Model 12 pH meter. Acidity measurements in the D_2O experiments required the addition of 0.41 unit to the pH meter reading to bring the electrode readings to the pD scale.[21] All chemicals used in the preparation of the complex and for the preparation of the pyridine buffer solutions were of reagent grade and were used without further purification. The heavy-water experiments were carried out in the usual manner except that 99.7% D_2O was used to prepare the buffer solutions.

Ion-Exchange Experiments. The characteristics of the column, relative to the movement of charged cobalt(III) complexes down the column, were evaluated by calibration with $Co(py)_4CO_3^+$, $Co(py)_3Cl(H_2O)_2^{2+}$, and $Co(py)_3(H_2O)_3^{3+}$. With 2 M $HClO_4$ as the eluent, cation–anion associations are minimized, and separations are based on the charges on the complex.[22] A small amount of the solid complex is dissolved in cold 2 M $HClO_4$. When this solution immediately is charged onto a *cold* (~−2 °C) cation-exchange column (Dowex 50W-X2, 200–400 mesh, 5 cm long with a 1.5-cm diameter) and eluted with 2 M $HClO_4$, only one band is found. The travel rate of the band on this column is similar to that of other cobalt(III) complexes with a 1+ charge. We assign the stoichiometry $Co(py)_2CO_3(H_2O)_2^+$ to this species[23] on the basis of experimental py/Co ratios (2.00 ± 0.15, based on four determinations) and the additional observation that the solution from the ion-exchange experiments slowly loses additional carbon dioxide at room temperature. This was verified by passing a stream of nitrogen through the solution and then through a saturated barium hydroxide solution. The precipitation of white $BaCO_3$ over a time span of about 1 h verified the evolution of carbon dioxide. The spectral parameters for this mono(carbonato) species are shown in Table I.

The above experiment is repeated, but now the 2 M $HClO_4$ is kept at room temperature. When this solution is charged onto a cation-exchange column after standing for about 15 min, two bands are separated. The faster moving band is identified as the above $Co(py)_2CO_3(H_2O)_2^+$ ion on the basis of the spectrum and Co/py ratio of the eluent, the characteristics of the band on the column, and the observation that the eluent slowly loses additional carbon dioxide. The second band's column behavior is characteristic of a 3+ charged species and is identified as the fully decarboxylated *cis*-$Co(py)_2(H_2O)_4^{3+}$ ion (py/Co ratio of 1.98 ± 0.13, based on four determinations). Spectra of this fully decarboxylated species[20] and some similar aquo ions are given in Table I. Due to the similar position of py and NH_3 in the spectrochemical species, the spectra of the two complexes *cis*-$Co(py)_2(H_2O)_4^{3+}$ and *cis*-$Co(NH_3)_2(H_2O)_4^{3+}$ are expected to be similar.

Analysis. Cobalt (total) in the eluates of the column chromatography experiments was determined by potentiometric titration with ferricyanide.[24] In this procedure the cobalt(II) is converted to the $Co(NH_3)_6^{2+}$ ion which provides a sufficient potential break at the end point to permit titration with a standard ferricyanide solution. Potentiometric measurements were made on a Metrohm type E436 potentiograph using a platinum electrode with a built-in reference electrode (EA 217).

Cobalt(III) also was determined potentiometrically by addition of excess iron(II) and back-titration with dichromate.[18,28] Although the end point may be detected by use of diphenylaminesulfonate as an indicator, we found it more convenient to follow the titration potentiometrically.

To analyze for pyridine, we determined the molar absorptivity of pyridine in 2 M $HClO_4$ from solutions of known pyridine concentration. A Gilmount Instrument's ultraprecision micrometer buret was used for the volumetric dilutions. Results indicate that 5488 M^{-1} cm^{-1} at 256.0 nm is a suitable molar absorptivity for pyridine in 2 M $HClO_4$. The presence of concentrations of cobalt(II) in the 10^{-3} M range were found to have no effect on the molar absorptivity of pyridine at 256

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(23) We previously assumed[20] this species to be "condensed" *cis*-$Co(py)_2(H_2O)_4^{3+}$ on the basis of the similarity of its visible spectrum to that reported for condensed amine complexes.[18,19] Such a dihydroxy-bridged dimer would possess a charge of 4+ and bind tightly to the column.

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nm in 2 M $HClO_4$ solution. This observation and the reported facile spontaneous reduction of aquo(pyridine)cobalt(III) complexes[20] permit decomposition of the complex in 2 M $HClO_4$ under mild conditions to produce free pyridine for analysis without loss.

Kinetic Measurements. A kinetic experiment was initiated by adding the solid complex to a cell that contained a buffer solution of measured pH and was at the appropriate temperature. For the slower reactions (half-lives greater than 30 min) a Cary Model 118 C or Cary Model 14 spectrophotometer was used to obtain absorption–wavelength measurements on the reacting solution at different time intervals. By such a procedure in the wavelength range of 340–650 nm, isosbestic points were located near 365, 460, and 525 nm and were invariant with pH changes in the pyridine buffer medium. At the lower temperatures these isosbestic points remained for at least 3 half-lives and are in reasonable agreement[25] with those predicted if the final product is the $Co(py)_2(CO_3)(H_2O)_2^+$ ion. Ths absorbance–time data during which the isosbestic points held were used to calculate a "best-fit" A_∞ with first-order kinetics assumed. For reactions in which the isosbestic point appeared to hold for the entire reaction, the above procedure produced an A_∞ value that was within 5% of the observed value.

For the faster reactions ($T = 50$ °C and pH $\lesssim 5$) we were unable to use the wavelength-scan procedure. Absorbance–time data were obtained at 570 nm and both a "best-fit" k_{obsd} and A_∞ were calculated from the data with first-order kinetics assumed. Since only a rough estimate could be made for the time period before which consecutive reactions complicate the data, the rate constants obtained are subject to greater uncertainty and are less accurate than those obtained for the slower reactions. For kinetic runs in pyridine buffer solutions, the conventional log $(A_t - A_\infty)$ vs. time plots were linear for at least 2 half-lives. Similar plots for reactions performed at lower pH (phosphate–citrate buffer system) indicated curvature suggestive of a series of consecutive reactions.

The decarboxylation kinetics were also investigated at several acidities above 0.1 M $[H_3O^+]$ by use of a stopped-flow spectrometer. In these experiments the complex was dissolved in a pyridine buffer ($I = 0.5$ M, NaCl) near pH 5.6. At this pH the first decarboxylation step is slow. The above solution is mixed with an appropriate HCl–NaCl solution ($I = 0.5$ M) in the stopped-flow spectrometer.

Results

Reaction Stoichiometry. An immediate color change from blue to red occurs when solid $K[Co(py)_2(CO_3)_2]\cdot 2H_2O$ or solutions of this complex in 0.01 M pyridine are added to 2 M $HClO_4$ solutions. When the solution is allowed to stand at room temperature for about 1 h, a slower color change to another shade of red is noted. At these conditions all monodentate and many bidentate (carbonato)cobalt(III) complexes rapidly decarboxylate. On the basis of the analysis of eluents from the column chromatography experiments, the reaction stoichiometry for the decarboxylation of the bis(carbonato) complex may be represented by eq 9.

$$\begin{gathered} cis\text{-}Co(py)_2(CO_3)_2^- \xrightarrow{2H_3O^+} \\ cis\text{-}Co(py)_2(CO_3)(H_2O)_2^+ + CO_2 + H_2O \xrightarrow{2H_3O^+} cis\text{-}Co(py)_2(H_2O)_4^{3+} + CO_2 + H_2O \end{gathered} \qquad (9)$$

The product of this scheme slowly undergoes further reaction to produce the reduced $Co^{2+}(aq)$ ion, and it has been shown that this latter reaction is retarded in strongly acidic solution.[20]

Table II. Observed Rate Constants (s^{-1}) for the Decarboxylation of the cis-$[Co(py)_2(CO_3)_2^-]$ Ion in Aqueous Pyridine Buffer Solutions[a]

30 °C		40 °C		50 °C	
$10^5 \times [H_3O^+]$	$10^4 k_{obsd}$[b]	$10^5 \times [H_3O^+]$	$10^3 k_{obsd}$[b]	$10^5 \times [H_3O^+]$	$10^3 k_{obsd}$[c]
5.89	9.27	5.13	2.08	8.13	7.46
2.88	5.19	2.75	1.45	7.59	8.43
1.48	3.50	1.74	1.13	5.50	4.92
0.89	2.83	0.776	0.939	4.90	7.00
0.42	2.11	0.603	0.691	4.27	5.17
		0.447	0.658	4.17	4.70
				2.40	3.64
				1.29	2.22
				1.12	3.00
				0.832	2.34
				0.776	2.02
				0.661	2.43
$10^4 k_a$, s^{-1}	1.58 ± 0.07		5.93 ± 0.52		17.1 ± 3.4
k_b, $M^{-1}\ s^{-1}$	13.0 ± 0.2		29.6 ± 2.1		78.9 ± 7.9

$\Delta H_a^\ddagger = 23 \pm 1$ kcal/mol
$\Delta S_a^\ddagger = -1 \pm 4$ cal/(mol K)
$\Delta H_b^\ddagger = 17 \pm 1$ kcal/mol
$\Delta S_b^\ddagger = 2 \pm 4$ cal/(mol K)

[a] $I = 0.5$ M (NaCl). All concentrations in molarity. [b] The k_{obsd} values shown are the average of values obtained at 390 and 570 nm during a single experiment in which wavelength was scanned at various time intervals. In all cases agreement between the two values was better than 5%. [c] Except for lowest $[H_3O^+]$, the values are obtained from absorbance vs. time curves at 570 nm only.

Table III. Observed Rate Constants (s^{-1}) for the Decarboxylation of the cis-$[Co(py)_2(CO_3)_2^-]$ Ion at 25 °C in the H_2O or D_2O Buffer Solutions[a]

$10^5 [H_3O^+]$	$10^4 k_{obsd}$[b]	$10^5 [D_3O^+]$	$10^4 k_{obsd}$[b]
4.27	2.33	1.70	4.97
4.07	2.17	1.32	2.61
3.72	2.33	0.759	2.12
3.47	1.93	0.575	1.50
2.63	1.66	0.501	1.43
1.82	1.34	0.417	1.12
1.66	1.36	0.123	1.04
1.59	1.19		
1.07	1.12		
0.692	0.751		
0.513	0.680		
0.417	0.753		
0.282	0.576		
0.178	0.479		
$10^5 k_a$, s^{-1}	5.08 ± 0.45		3.0 ± 3.5
k_b, $M^{-1}\ s^{-1}$	4.38 ± 0.19		23.5 ± 3.8

[a] $I = 0.5$ M ($NaNO_3$). All concentrations in molarity. [b] The k_{obsd} was obtained from absorbance–time data at both 560 and 390 nm. The value shown is the average of the two values.

Rates in Pyridine Buffer Solutions. The observed pseudo-first-order rate constants for the decarboxylation of the $K[Co(py)_2(CO_3)_2]\cdot 2H_2O$ complex in aqueous pyridine buffers ($I = 0.5$ M (NaCl) and pyridine buffer concentration of 0.145 ± 0.005 M) are collected in Table II. At any particular temperature, the rate constants clearly increase with increasing hydrogen ion concentration. This behavior is adequately described by a simple first-order hydrogen ion concentration dependence of the form shown in eq 10. In several additional

$$k_{obsd} = k_a + k_b[H_3O^+] \qquad (10)$$

experiments the pyridine buffer concentration was reduced by a factor of approximately 5 (buffer concentration ~0.0290 M), and the experimental rates were similar, within the limits of our experimental error, to the rates observed at the higher buffer concentrations. These experiments serve as additional

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(25) If we assume that the first product during the decomposition of the $Co(py)_2(CO_3)_2^-$ ion is the $Co(py)_2(CO_3)(H_2O)_2^+$ species, then isosbestic points near 515, 430, and 355 nm are predicted. Since the decarboxylation of the bis(carbonato) complex is acid catalyzed, it was necessary to measure spectra for the two complexes in media of widely varying pH. The spectrum of the aquo–carbonato complex was measured in cold 2 M $HClO_4$ while that of the bis(carbonato) complex was measured in 0.1 M aqueous pyridine.

support for our belief that the decomposition reaction being studied had a rate-limiting step involving decarboxylation and not the loss of ligand pyridine. This latter process has been observed to occur in aquo(pyridine)cobalt(III) complexes in acidic medium.[20,24b]

In Table III are shown additional rate constants for the decarboxylation of the $K[Co(py)_2(CO_3)_2]\cdot 2H_2O$ complex, but now the ionic strength is maintained at 0.5 M with $NaNO_3$. Results for kinetic runs in D_2O solvent are also in this table.

Rates in Other Acidity Ranges. In order to determine if k_{obsd} possessed a sigmoid $[H^+]$ dependence required by eq 3, one must obtain rate data over several pH units. Attempts were made to obtain rate data at a lower pH than that permitted by the pyridine buffer system. The decomposition of the complex was followed by recording the visible spectrum of the complex dissolved in a buffer solution appropriate to the region $2 < pH < 5$ [phosphate–citrate system, $I = 0.5$ M (NaCl)] at various time intervals. No isosbestic points were observed, and the wavelength maximum of the low-energy transition in the visible range for the spectrum of the decomposing solution first shifted to lower wavelength. At pH 3 and over a 2-h time span this initial shift was followed by additional shifts to higher and finally lower wavelengths. The ultimate cobalt-containing product of the decomposition was noted to be Co^{2+}(aq). At 570 nm the absorbance rapidly dropped, followed by several additional stages of decreasing absorbance. Plots of log $[A_t - A_\infty(Co^{2+})]$ at several wavelengths were nonlinear and suggested the occurrence of at least three successive reactions. After similar results were obtained at several other pH values in this buffer-system range, attempts to evaluate the rate constants in this pH region were abandoned.

Stopped-Flow Rates. A limited number of rate measurements at 25 °C were made at higher acidities by use of the stopped-flow spectrophotometer. The occurrence of a slower second reaction prevented accurate measurement of A_∞ values; hence A_∞ was obtained by a nonlinear best-fit procedure. First-order plots of log $(A_t - A_\infty)$, using the calculated A_∞, were linear over about 2 half-lives. The observed rate constant increases from $k_{obsd} = 0.25\ s^{-1}$ at $[H_3O^+] = 0.10$ M to 0.52 s^{-1} at $[H_3O^+] = 0.25$ M. From these two points, only a rough estimate of the acid dependence of the rate constant for the decarboxylation process at high acidity can be made. It is seen to be approximately first order in $[H_3O^+]$, and the data suggest a value of $k_b \approx 2\ M^{-1}\ s^{-1}$.

Discussion

Column chromatography and chemical analysis of acidified solutions of $K[Co(py)_2(CO_3)_2]\cdot 2H_2O$ present strong evidence for the isolation and characterization in solution of an intermediate mono(carbonato) complex of stoichiometry $Co(py)_2(CO_3)(H_2O)_2^+$. Shifts of absorption-spectrum maxima toward higher energies as the first carbonate ligand in $Co(py)_2(CO_3)_2^{2-}$ is replaced by H_2O molecules to produce $Co(py)_2(CO_3)(H_2O)_2^+$ are consistent with similar shifts observed during the decarboxylation of (carbonato)cobalt(III) complexes and with the positions of CO_3^{2-} and H_2O in the spectrochemical series.[26] In addition, the usual reduction in band-maxima intensities is observed as water molecules replace coordinated carbonate (chelated or monodentate). Loss of the second carbonate ligand to form *cis*-$Co(py)_2(H_2O)_4^{3+}$ shows the expected diminished intensities at the band maximum, but the shift toward higher wavelengths (from $\lambda_{max} = 536$ to 547 nm) is in the opposite direction as usually observed during decarboxylation to produce the aquo complex. The above comments with regard to the intensities and shifts of absorption band maxima are based on the presence of monomeric cobalt(III) centers. Modification of the interpretation might be necessary because of the high acidity of aquo(pyridine)cobalt(III) ions[27] (e.g., the presence of hydroxo rather than aquo complexes) and the possibility of the existence of dimeric species as are thought to exist in the corresponding ammine complexes.[18,19,28,29]

The experimental rate law, found for the loss of the first carbonate $[H_3O^+]$ from the *cis*-$Co(py)_2(CO_3)_2^-$ ion and shown in eq 10, is of the same form as that observed for the decarboxylation of bidentate (carbonato)cobalt(III) complexes (eq 8). However, the form of the rate law alone need not be diagnostic of the nature of the binding of the carbonate ligand, since the rate law expected for the decarboxylation of monodentate carbonato complexes (eq 3) also will reduce to one that has a linear hydrogen ion concentration but without the k_0' term, which in any case is always small by comparison to the $k_1'K_1'$ term at the higher acidities. The necessary condition, as seen in eq 3, is that $K_c \gg [H_3O^+]$. In addition, the experimental activation parameters, $\Delta H_b^\ddagger$ and $\Delta S_b^\ddagger$, shown in Table II fall precisely in the narrow range previously observed for carbon–oxygen bond cleavage in monodentate carbonato complexes. In view of these considerations and the possibility of the occurrence of carbonato hydroxy-bridged complexes of approximately the same stoichiometry, we must consider in detail our kinetic results with respect to each of the possible mechanisms (mono- or bidentate carbonate decarboxylation).

First, as mentioned above, K_c must be much greater than the maximum $[H_3O^+]$ investigated so that the observed rate constant given in eq 3 reduces to one with a linear hydrogen ion dependence. Previous studies[6-9] indicate that $pK_c \approx 6$ for monodentate pentamine–carbonato complexes and varies over about 1 pK unit. Also, our limited stopped-flow results in the high-acid range ($[H_3O^+] \geq 0.1$ M) suggest that the hydrogen ion dependence of k_{obsd} is still present, and we note no tendency for k_{obsd} to reach the maximum expected for a monodentate carbonato complex (eq 3). Indeed, the value of the specific rate constant ($k_b \approx 2\ M^{-1}\ s^{-1}$ at 25 °C) for the acid-dependent path obtained from the stopped-flow experiments is in reasonable agreement with a value of 7 $M^{-1}\ s^{-1}$ at the same temperature which is obtained by extrapolation of k_b values obtained at higher temperatures but at much lower acidities and in a different medium. If the decarboxylation process does involve a rate-determining loss of monodentate carbonate, a value of $K_c \gg 0.1$ M is implied. We consider this value unrealistically high even though features of ligand pyridine that act to increase the acidity (pK_a) of aquo(pyridine)cobalt(III) complexes relative to the corresponding amine complexes[30] could also act to increase pK_c in a monodentate complex, but presumably to a much lesser extent because of the greater distance between the protonation site and the metal center.

Second, although the activation parameters for the loss of the first carbonate ligand from *cis*-$Co(py)_2(CO_3)_2^-$ fall within the narrow range expected for monodentate decarboxylation, both the rate constants and the activation parameters for the decarboxylation of bidentate carbonato complexes vary over a wide range which includes the narrow one covered by monodentate decarboxylation. Of nearly 20 such bidentate complexes investigated, three [*cis*-$Co(en)(NH_3)_2CO_3^+$, β-

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(26) Hare, C. R. In "Spectroscopy and Structure of Metal Chelate Compounds"; Nakamoto, K., McCarthy, P. J., Eds.; Wiley: New York, 1968; p 106.

(27) Springborg, J.; Schaffer, C. E. *Acta Chem. Scand.* **1973**, *27*, 3312.

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(30) The π-acid character of ligand pyridine greatly affects the acidity of water molecules coordinated to a cobalt(III) center. At 25 °C and I = 1 M, the pK_a for *trans*-$Co(py)_4(H_2O)_2^{3+}$ ion is 1.4[27] while that for *trans*-$Co(en)_2(H_2O)_2^{3+}$ is 4.5 (Bjerrum, J.; Rasmussen, S. E. *Acta Chem. Scand.* **1952**, *6*, 1265).

$Co(trien)CO_3^+$, and β-$Co(edda)CO_3^-$] undergo acid-catalyzed decarboxylation with rate constants and activation parameters[31] quite similar to those observed in the present study.

In the overview, our kinetic results appear more consistent with the typical mechanism for the decarboxylation of chelated carbonate (eq 5–7), with $k_a = k_0'$ and $k_b = k_1'K'$, and hence we suggest that both carbonate ligands in the *cis*-$Co(py)_2(CO_3)_2^-$ anion are bidentate and that the complex is monomeric. The acceleration of the rate in D_2O solvent (see Table III) is also consistent with the bidentate decarboxylation mechanism (eq 4–7) through the ratio of $k_b^H/k_b^D = 0.19$ is somewhat lower than the ratio of $\sim$0.4 reported[10] for the decarboxylation of several carbonato–tetraamine complexes. However, it is not outside the range of expectation for the D_2O effect for a mechanism of this type.[32] It is of further interest that the rate-limiting first-order decarboxylation of the monodentate carbonato–pentaammine complex is not accelerated in D_2O solvent.[10]

Prior experience with (carbonato)(pyridine)cobalt(III) complexes suggests that the loss of the first CO_2 molecule from *cis*-$Co(py)_2(CO_3)_2^-$ is, by comparison with these, unusually rapid.[33] We attribute this to the much greater ring strain caused by the occurrence of a second chelated carbonate and two bulky pyridine molecules in the first coordination sphere. Another unexpected result is an apparent rate deceleration in the presence of nitrate ion. As shown in Table III, the rate constant k_b at 25 °C, with nitrate ion used to maintain ionic strength, is somewhat lower than the value of $\sim 7\ M^{-1}\ s^{-1}$ estimated from the kinetic data obtained in the presence of chloride ion. Although nitrate ion assisted formation of a reactive intermediate has been proposed to explain the nitrate ion catalysis of the anation of $Co(en)_2(H_2O)_2^{3+}$ by oxalate,[35] we choose, in the absence of additional studies, to assign this observation simply to nonspecific anion interaction effects. For example, an enhancement is observed[36] for the rate of water exchange in $Cr(H_2O)_6^{3+}$ when the nature of the anion used to maintain the ionic strength is changed along the series Br^-, Cl^-, ClO_4^-, and NO_3^-.

The occurrence of a transient intermediate when solid bis(carbonato)–bis(amine) complex is added to cold 1 or 2 M $HClO_4$ has been noted previously.[19,20,28,37] These species have been tentatively identified as dihydroxy-bridged dimers on the basis of their visible spectra and cation-exchange column behavior. This assignment appears to be inappropriate when the ligand is pyridine, where the presence of carbonate ligand and a species with unit charge have now been found. The reported[37] acid-catalyzed conversion of this intermediate to $Co(py)_2(H_2O)_4^{3+}$ would be consistent with the decarboxylation of our proposed mono(carbonato) complex. We also note that the claimed production of monomeric *cis*-$Co(NH_3)_2(H_2O)_4^{3+}$ from a presumed condensed intermediate on standing at room temperature and warming or rotovaping[28] would be consistent with the decarboxylation of a mono(carbonato) complex, as well as with the presumed cleavage of hydroxy bridges.

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Registry No. *cis*-$Co(py)_2(CO_3)_2^-$, 73090-53-6; $Co(py)_2(CO_3)(H_2O)_2^+$, 73104-76-4; *cis*-$Co(py)_2(H_2O)_4^{3+}$, 73136-37-5; *cis*-$K[Co(py)_2(CO_3)_2]$, 54967-61-2.

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(33) We have prepared three mono(carbonato)(pyridine)cobalt(III) complexes, *trans*-$Co(py)_4CO_3^+$,[34] $Co(py)_3CO_3(H_2O)^+$,[24] and $Co(py)_2(CO_3)(H_2O)_2^+$. All are reasonably stable in 1 M $HClO_4$ and may be eluted from a cation-exchange column with 1 M $HClO_4$. The last complex has $t_{1/2} \approx 0.5$ h at room temperature and in 1 M $HClO_4$.

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