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Rates of Decarboxylation and Reduction of the (Carbonato)diaquobis(pyridine)cobalt(III) Ion in Aqueous Perchloric Acid

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The kinetics of the complete decomposition of *cis*-$K[Co(py)_2(CO_3)_2]\cdot 2H_2O$ in aqueous perchloric acid have been investigated. Decomposition occurs via two successive decarboxylation steps and a final reduction step that produces Co^{2+}(aq) as the only cobalt-containing product. The relative rates are such that each step may be studied independently. The first step produces a stable mono(carbonato)cobalt(III) ion intermediate, *cis*-$Co(py)_2(CO_3)(H_2O)_2^+$, as the product. The rate data for the loss of CO_2 from this intermediate is described by a pseudo-first-order rate constant of the form $k_{obsd} = k_a + k_b[H_3O^+]$. Rate parameters at 25 °C and $I = 1.0$–2.0 M ($NaClO_4$, $HClO_4$) are $k_a = (7.4 \pm 0.5) \times 10^{-5}\ s^{-1}$ and $k_b = (33.5 \pm 0.6) \times 10^{-5}\ M^{-1}\ s^{-1}$ with activation parameters of $\Delta H_a^{\ddagger} = 24 \pm 4$ kcal mol^{-1}, $\Delta S_a^{\ddagger} = 3 \pm 13$ cal deg^{-1} mol^{-1}, $\Delta H_b^{\ddagger} = 19.7 \pm 1.1$ kcal mol^{-1}, and $\Delta S_b^{\ddagger} = -8.5 \pm 3.7$ cal deg^{-1} mol^{-1}. These results are compared with those for the decarboxylation of the corresponding bis(carbonato) complex and other bidentate (carbonato)cobalt(III) complexes. The *cis*-$Co(py)_2(H_2O)_4^{3+}$ ion formed following complete decarboxylation undergoes a reduction to give Co^{2+}(aq) and other products. Rate data are well described by a pseudo-first-order rate constant of the form $k_{obsd} = k_c + k_d/[H_3O^+]$. At 25 °C ($I = 1.0$–$2.0$ M), rate parameters are $k_c = (0.96 \pm 0.82) \times 10^{-6}\ s^{-1}$ and $k_d = (4.82 \pm 0.06) \times 10^{-6}\ M\ s^{-1}$, with activation parameters for the acid-dependent path of $\Delta H_d^{\ddagger} = 27.9 \pm 0.8$ kcal mol^{-1} and $\Delta S_d^{\ddagger} = 11 \pm 3$ cal mol^{-1} K^{-1}. These results are compared with previous work on the reduction of aquoamminecobalt(III) ions. The rate constant for the reduction of *cis*-$Co(py)_2(CO_3)(H_2O)_2^+$ by iodide ions is $(4.04 \pm 0.08) \times 10^{-2}\ M^{-1}\ s^{-1}$ at 25 °C and ionic strength 2.0 M. An outer-sphere mechanism is suggested by its insensitivity to variations in acid concentration.

Introduction

Decarboxylation reactions of (carbonato)cobalt(III) complexes have received considerable study.[2-5] The reactivities of different complexes have been examined with respect to variations in the nonparticipating ligands,[6,7] the binding mode of the carbonate ion,[3,4] the hydrogen ion concentration of the reaction medium,[3,4] and the nature of the metal center itself.[8-10] It has been convincingly demonstrated that the two distinct mechanisms observed depend solely on the manner in which the carbonate ligand is coordinated to a given metal center.[3,4]

Previous work on the rate of decarboxylation of monodentate carbonato complexes indicates a mechanism that does not involve the cleavage of a metal–ligand bond. Activation parameters fall in a limited range, and plots of k_{obsd} vs. pH have a characteristic sigmoidal shape.[3] Bidentate carbonato complexes decarboxylate at rates that are much more sensitive to changes in both the nature of the nonparticipating ligands and the metal center itself. This is consistent with rate-determining ring opening[4] via cleavage of a metal–oxygen bond in bidentate carbonato complexes.

The stoichiometry of the complex *cis*-$K[Co(py)_2(CO_3)_2]\cdot 2H_2O$ suggests the presence of two chelated carbonate ions. Our previous work[11] on this compound indicated that decarboxylation occurs in two distinct steps and that each step could be studied separately. We have reported the detailed kinetics of the first step.[11] The complex decomposes in aqueous perchloric acid ultimately to produce Co^{2+}(aq) as the only cobalt-containing product.[11] We now complete the kinetic study of the three-step decomposition of this complex by reporting both the rate of decarboxylation of the *cis*-$Co(py)_2(CO_3)(H_2O)_2^+$ ion, the product of the first decarboxylation step, and the rate of reduction of the *cis*-$Co(py)_2(H_2O)_4^{3+}$ ion, the product of the second decarboxylation step. This paper thus completes our description of the first reported kinetic study of the complete loss of CO_2 from a bidentate bis(carbonato) complex. The results provide an opportunity to further assess the factors that affect rates of decarboxylation and metal–oxygen bond rupture.

An additional benefit of the present study is the measurement of detailed rate data for the spontaneous reduction of the *cis*-$Co(py)_2(H_2O)_4^{3+}$ ion. The results permit a test of the proposal that *trans*-$Co(py)_4(H_2O)_2^{3+}$ and *mer*-$Co(py)_3(H_2O)_3^{3+}$ ions undergo spontaneous reduction in perchloric acid solution via a reaction scheme that involves the loss of pyridine and a final rate-determining step that is the spontaneous reduction of the *cis*-$Co(py)_2(H_2O)_4^{3+}$ ion.[12] The kinetics of direct reduction of *cis*-$Co(py)_2(CO_3)(H_2O)_2^+$ by iodide ion have also been measured.

Experimental Section

The complex *cis*-$K[Co(py)_2(CO_3)_2]\cdot 2H_2O$ was prepared as previously reported.[11,13] The purity of the compound was verified by determination of the py/Co(III) ratio and by comparison of the spectral parameters of the compound in solution with those available in the literature.[11,13] The elemental analysis for our earlier synthesis[11] was in agreement with the above stoichiometry.

A cation-exchange column (Dowex 50W-X2, 200–400 mesh, 1.5 cm in diameter, and 4 cm long; after prewashing in 1 M $HClO_4$) was used to obtain solutions of *cis*-$Co(py)_2(CO_3)(H_2O)_2^+$ ion from samples of *cis*-$K[Co(py)_2(CO_3)_2]\cdot 2H_2O$. This was accomplished by dissolving a small amount of the solid bis(carbonato) complex (50–100 mg) in 2 mL of cold 1.0 M perchloric acid. This solution was immediately charged onto a cold column (−5 °C) that had been prewashed with 1.0 M $HClO_4$. Elution with 1.0 M $HClO_4$ separated two distinct bands. The faster moving band, that previously has been identified[11] as *cis*-$Co(py)_2(CO_3)(H_2O)_2^+$, was collected at 0 °C.

Solutions of this complex at various hydrogen ion concentrations and ionic strengths of 1.0 M were prepared from the eluent by appropriately diluting with 1.0 M $NaClO_4$. A kinetic experiment was initiated by injecting these solutions into a cell thermostated at the desired temperature. For studies of the redox reaction with iodide, the cell contained a deoxygenated acidic solution of standardized, excess potassium iodide. A Cary 14 spectrophotometer was used to obtain absorbance–wavelength data at various time intervals or absorbance–time data at a fixed wavelength.

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(2) There are numerous examples. References 3 and 4 represent several of the earlier studies and ref 5 is one of the more recent.

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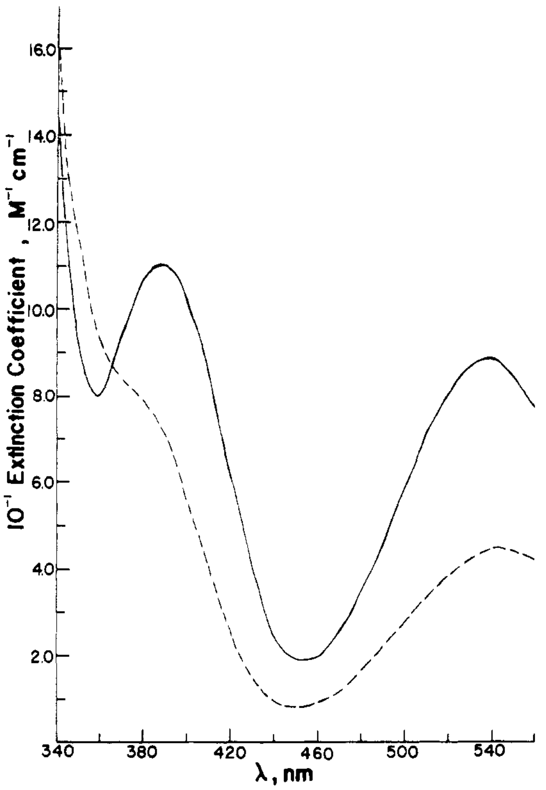

Figure 1. Visible spectra of *cis*-$Co(py)_2(CO_3)(H_2O)_2^+$ and *cis*-$Co(py)_2(H_2O)_4^{3+}$ in 2 M $HClO_4$. The solid and dashed lines represent the spectra of *cis*-$Co(py)_2(CO_3)(H_2O)_2^+$ and *cis*-$Co(py)_2(H_2O)_4^{3+}$, respectively.

Chemicals required for compound or solution preparations were of reagent grade and were used without further purification. Procedures for both cobalt(III) and pyridine analyses, as well as for the preparation of standard solutions of $NaClO_4$, have been reported previously.[11] Stock potassium iodide solutions were standardized by titration with silver nitrate. Iodine produced in the reaction of *cis*-$Co(py)_2CO_3(H_2O)_2^+$ and *cis*-$Co(py)_2(H_2O)_4^{3+}$ with iodide was determined spectrophotometrically by comparison with standard iodine/iodide solutions under identical conditions. The results were checked by titration with standard sodium thiosulfate under nitrogen (starch indicator).

Results and Discussion

Decomposition of *cis*-$(py)_2Co(CO_3)(H_2O)_2^+$ in Acid Perchlorate Solution. Kinetic Results at 14 °C. At 14 °C and over a range of acidities, absorbance–wavelength sweeps (340–650 nm) of decomposing solutions of *cis*-$Co(py)_2(CO_3)(H_2O)_2^+$ exhibited a single isosbestic point at approximately 360 nm. The position of this point is in reasonable agreement with that expected to occur at 365 nm for the loss of the carbonate ligand from *cis*-$Co(py)_2(CO_3)(H_2O)_2^+$ to form *cis*-$Co(py)_2(H_2O)_4^{3+}$ (see Figure 1). This isosbestic point held for approximately 2–3 half-lives. Although the position of the isosbestic point was invariant with changes in acid concentration, its duration was not. The eventual loss of this isosbestic point served as indication of a second reaction occurring at an appreciable rate. Absorbance vs. time data were tabulated at both 536 and 388 nm, and first-order plots of log $(A_t - A_\infty)$, where A_∞ was obtained by a best-fit procedure with the assumption of first-order kinetics, were linear over at least 3 half-lives. The observed pseudo-first-order rate constants, k_{obsd}, for the decarboxylation process at this temperature are given in Table I.

Kinetic Results at 25 and 35 °C. Attempts to conduct kinetic studies of the decarboxylation reaction at these temperatures using the same procedure employed at 14 °C were unsuccessful. The isosbestic point held for less than 1 half-life. This change in spectral characteristics of the decomposing solutions with variation in temperature is attributed to the increased importance of a reaction that follows the initial decarboxylation. The kinetic experiments conducted at 25 and 35 °C were initiated in the same manner as those at 14 °C, but absorbance–time data was collected at a constant wavelength of 535 nm.

At 25 °C the decomposing solutions were monitored until the absorbance had decreased to a value below a calculated A_∞. This A_∞ was obtained from Co(III) analyses concurrent with the kinetic experiments and by use of an experimentally determined molar absorptivity of the first product, *cis*-$Co(py)_2(H_2O)_4^{3+}$ (ϵ 48 ± 1 M^{-1} cm^{-1} at 535 nm). At 35 °C the decomposition was monitored until the absorbance attained a constant value. Calculated A_∞ values, with $Co^{2+}(aq)$ (ϵ 4.25 M^{-1} cm^{-1}) assumed as the final cobalt-containing species, were in good agreement with those A_∞ values obtained experimentally. Plots of log $[A_t - A_\infty(Co^{2+})]$ vs. time at both 25 and 35 °C indicated a slower reaction which exhibited good first-order behavior (see Figure 2). Back extrapolation of the linear portion of this curve allows the calculation of the k_{obsd} of the faster reaction based on the difference between the experimental curve and the extrapolated portion. The "curve-stripped" data for the faster reaction also resulted in good first-order plots (see Figure 3). The faster reaction was designated as the decarboxylation (see Discussion). The rate

Table I. Kinetic Data for the Decarboxylation of the *cis*-$Co(py)_2(CO_3)(H_2O)_2^+$ Ion in Aqueous Perchloric Acid Solutions[a]

14.0 °C			25.0 °C		35.0 °C	
	$10^5 \times k_{obsd}$[b,c]					
$[H_3O^+]$	536 nm	388 nm	$[H_3O^+]$	10^4k_{obsd}[b,d]	$[H_3O^+]$	10^4k_{obsd}[b,d]
1.01	8.77	8.95	1.80[e]	6.75	1.06	12.9
1.01	9.25	10.30	1.40[e]	5.38	0.990	11.3
1.01	9.15	9.02	0.998	4.30	0.850	12.5
1.01	8.93	8.85	0.998	4.23	0.792	11.0
1.00	9.78	10.22	0.998	3.80	0.640	10.0
0.795	8.57	8.95	0.798	3.50	0.594	7.87
0.795	7.80	7.37	0.599	2.65	0.396	7.58
0.505	6.12	5.82	0.599	2.82	0.396	6.80
0.505	5.67	5.37	0.500[e]	2.33	0.210	5.98
0.496	5.67	6.37	0.399	2.15	0.210	4.80
0.397	4.53	4.53	0.200	1.40	0.100[e]	3.25
0.400	3.07	3.40	0.200[e]	1.48	0.025[e]	2.15
0.400	3.98	3.85	0.100[e]	1.09		
0.200	3.00	2.67	0.067[e]	0.85		
0.200	3.68	3.23	0.025[e]	0.83		
$10^5k_a = 1.34 \pm 0.29$ s^{-1}			$10^4k_a = 0.74 \pm 0.05$ s^{-1}		$10^4k_a = 2.86 \pm 0.46$ s^{-1}	
$10^5k_b = 8.05 \pm 0.41$ M^{-1} s^{-1}			$10^4k_b = 3.35 \pm 0.06$ M^{-1} s^{-1}		$10^4k_b = 9.86 \pm 0.72$ M^{-1} s^{-1}	

$\Delta H_a^\ddagger = 24 \pm 4$ kcal mol^{-1} [f] $\Delta H_b^\ddagger = 19.7 \pm 1.1$ kcal mol^{-1} [f]
$\Delta S_a^\ddagger = 3 \pm 13$ cal deg^{-1} mol^{-1} [f] $\Delta S_b^\ddagger = 8.5 \pm 3.7$ cal deg^{-2} mol^{-1} [f]

[a] Ionic strength = 1.0 M $NaClO_4$ except where noted; all hydronium ion concentrations are given in M. [b] Units are s^{-1}. [c] For kinetic runs at 14 °C, the rate constants were calculated at both 536 and 388 nm. The k_{obsd} values were obtained from a nonlinear curve-fitting program for simple first-order kinetics with only k_{obsd}(fast) and $[A]_\infty$ as parameters. [d] The tabulated k_{obsd}(fast) values were obtained from a nonlinear curve-fitting program for consecutive reactions that used k_{obsd}(slow), k_{obsd}(fast), and initial complex concentration as parameters. Estimates of k_{obsd}(slow) and k_{obsd}(fast) were obtained graphically by curve stripping biphasic plots of ln $(A_t - A_\infty)$ vs. time.[15] Estimates of k_a and k_b are from a nonlinear least-squares fit of the data to eq 9. [e] Ionic strength = 2.0 M $NaClO_4$. [f] Calculated from a nonlinear least-squares fit of all of the data to eq 9 with temperature as an independent variable.[27]

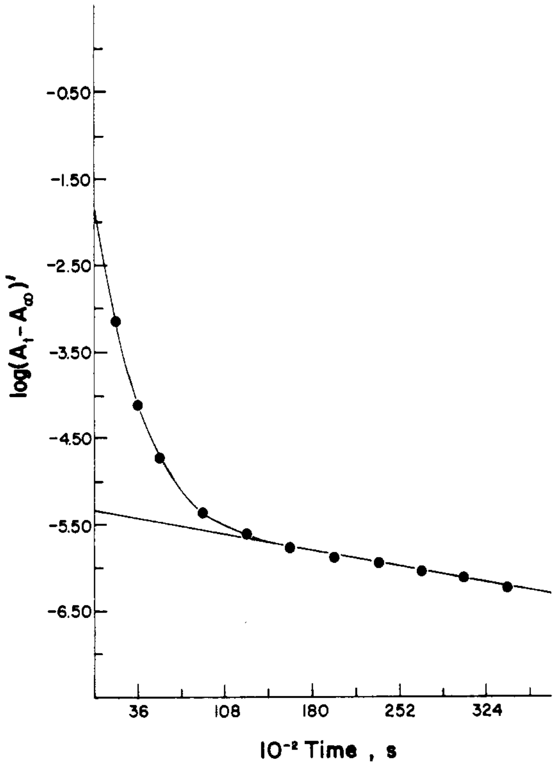

Figure 2. First-order rate plot for decomposition of the *cis*-Co-(py)$_2$(CO$_3$)(H$_2$O)$_2$$^+$ ion ([H$_3$O$^+$] = 0.8 M at 25 °C, I = 1.0 M).

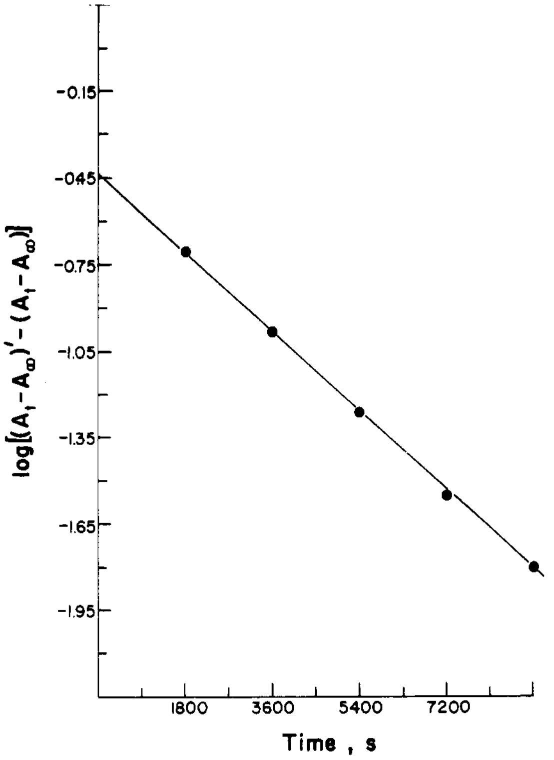

Figure 3. Difference plot for the decomposition shown in Figure 2.

constants at 25 and 35 °C for the decarboxylation (k_{obsd}) and the slower reaction (k_{obsd}, slow) are collected in Tables I and II, respectively.

Table II. Kinetic Data for the Reduction of the *cis*-Co(py)$_2$(H$_2$O)$_4$$^{3+}$ Ion in Aqueous Perchloric Acid Solutions[a]

25.0 °C		35.0 °C	
[H$_3$O$^+$]	10^5k_{obsd}(slow)[b]	[H$_3$O$^+$]	10^5k_{obsd}(slow)[b]
1.50[c]	0.50	2.00[c]	3.20
1.00[c]	0.83	1.06	3.33
0.998	0.60	0.990	3.68
0.798	0.55	0.850	4.55
0.700[c]	0.58	0.792	4.27
0.599	0.87	0.640	6.33
0.599	0.83	0.594	5.78
0.500[c]	1.05	0.396	8.57
0.399	1.38	0.396	8.25
0.200	2.68	0.210	12.6
0.200[c]	2.40	0.210	12.3
0.100[c]	4.81		
0.067[c]	7.60		
0.050[c]	9.15		
0.033[c]	15.1		
0.020[c]	19.2		
10^6k_c = 0.96 ± 0.82 s^{-1}		10^5k_c = 1.9 ± 0.32 s^{-1}	
10^6k_d = 4.82 ± 0.06 M s^{-1}		10^5k_d = 2.29 ± 0.13 M s^{-1}	
$\Delta H_c^{\ddagger}$ = 54 ± 25 kcal mol^{-1} [d]		$\Delta H_d^{\ddagger}$ = 27.9 ± 0.8 kcal mol^{-1} [d]	
$\Delta S_c^{\ddagger}$ = 91 ± 81 cal deg^{-1} mol^{-1} [d]		$\Delta S_d^{\ddagger}$ = 11 ± 3 cal deg^{-1} mol^{-1} [d]	

[a] All concentrations are M; ionic strength = 1.0 M except where noted. [b] Rate constants were obtained from a nonlinear regression treatment of data from the latter portions of the decomposition. Estimates of k_c and k_d are from a nonlinear least-squares fit of the data to eq 10. [c] Ionic strength = 2.0 M. [d] Calculated from a nonlinear least-squares fit of all of the data to eq 10 with temperature as an independent variable.[27]

The well-established[14] mechanism for ring opening and decarboxylation of numerous bidentate (carbonato)cobalt(III) complexes appears to be operative in the present system. All species are assumed to be cis, but the trans geometry cannot be ruled out for the diaquo complex. The precursor bis(carbonato) complex is definitely cis, and the similarity of the visible spectrum of Co(py)$_2$(H$_2$O)$_4$$^{3+}$ to that assigned to *cis*-Co(NH$_3$)$_2$(H$_2$O)$_4$$^{3+}$ suggests that the tetraaquo complex is cis. For the diaquo complex intermediate to be trans, two rearrangements would be required for the total decarboxylation of *cis*-Co(py)$_2$(CO)$_{32}$$^-$ to *cis*-Co(py)$_2$(H$_2$O)$_4$$^{3+}$, eq 1–6, where

$$\text{Co(O}_2\text{CO)(py)}_2\text{(H}_2\text{O)}_2^+ + \text{H}_2\text{O} \xrightarrow{k_0} \text{Co(OCO}_2\text{)(py)}_2\text{(H}_2\text{O)}_3^+ \quad (1)$$

$$\text{Co(O}_2\text{CO)(py)}_2\text{(H}_2\text{O)}_2^+ + \text{H}^+ \overset{K_1}{\rightleftharpoons} \text{Co(O}_2\text{COH)(py)}_2\text{(H}_2\text{O)}_2^{2+} \quad (2)$$

$$\text{Co(O}_2\text{COH)(py)}_2\text{(H}_2\text{O)}_2^{2+} + \text{H}_2\text{O} \xrightarrow{k_1} \text{Co(OCO}_2\text{H)(py)}_2\text{(H}_2\text{O)}_3^{2+} \quad (3)$$

$$\text{Co(OCO}_2\text{H)(py)}_2\text{(H}_2\text{O)}_3^{2+} \overset{K_2}{\rightleftharpoons} \text{Co(OCO}_2\text{)(py)}_2\text{(H}_2\text{O)}_3^+ + \text{H}^+ \quad (4)$$

$$\text{Co(OCO}_2\text{H)(py)}_2\text{(H}_2\text{O)}_3^{2+} \xrightarrow{k_2} \text{Co(py)}_2\text{(OH)(H}_2\text{O)}_3^{2+} + \text{CO}_2 \quad (5)$$

$$\text{Co(py)}_2\text{(OH)(H}_2\text{O)}_3^{2+} + \text{H}^+ \overset{K_3}{\rightleftharpoons} \text{Co(py)}_2\text{(H}_2\text{O)}_4^{3+} \quad (6)$$

equilibrium 2 involves protonation (presumed to be at the carbonyl oxygen), k_0 and k_1 govern the parallel rate-determining ring-opening mechanistic steps, and k_2 is the relatively rapid carbon–oxygen bond-breaking step. The pseudo-first-order rate constant consistent with this mechanism has the form shown in eq 7. Since experimental conditions[14] are such

$$k_{\text{obsd}} = \frac{k_0 + k_1K_1[\text{H}^+]}{1 + K_1[\text{H}^+]} \quad (7)$$

that 1 >> K_1[H$^+$], the expression 7 reduces to eq 8.

$$k_{\text{obsd}} = k_0 + k_1K_1[\text{H}^+] \quad (8)$$

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Table III. Kinetic Parameters for Acid-Catalyzed Decarboxylation of Various (Carbonato)(pyridine)cobalt(III) Ions at 25 °C

complex	I, M	10^5k_a, s^{-1}	$\Delta H_a^\ddagger$, kcal mol^{-1}	$\Delta S_a^\ddagger$, cal mol^{-1} K^{-1}	10^5k_b, s^{-1} M^{-1}	$\Delta H_b^\ddagger$, kcal mol^{-1}	$\Delta S_b^\ddagger$, cal mol^{-1} K^{-1}
^{a}Co(py)$_4$(CO$_3$)$^+$	1.0	0.132	32.3	25.9	0.0361	34	26
	5.0				0.826	23.2	−4
^{b}Co(py)$_3$(CO$_3$)(H$_2$O)$^+$	1.0				40		
^{c}Co(py)$_2$(CO$_3$)(H$_2$O)$_2$$^+$	1.0, 2.0	7.4	24	3	33.5	19.7	9
^{d}Co(py)$_2$(CO$_3$)$_2$$^-$	0.5	5.22	23	−1	590000	17	2

^{a} Data from ref 12. ^{b} A recent estimate of the half-life for the decarboxylation of this complex in 4 M HClO$_4$ (see ref 21) is in reasonable agreement with our estimate when differences in acidity and ionic strength are considered. ^{c} This work. ^{d} Data from ref 11.

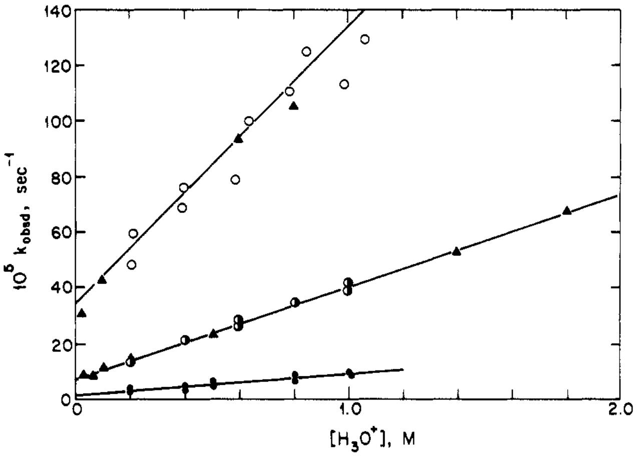

Figure 4. Acid dependence of the carboxylation of the *cis*-Co(py)$_2$CO$_3$(H$_2$O)$_2$$^+$ ion at the following temperatures: ●, 14 °C; ◑, 25 °C; ○, 35 °C and ionic strength 1.0 M (NaClO$_4$, HClO$_4$). Triangles denote data at ionic strength 2.0 M (NaClO$_4$, HClO$_4$).

Acid Dependence of the Decarboxylation Reaction. Our acid-dependence studies on the decarboxylation reaction at 14 °C clearly indicate an increase in the rate with increasing hydrogen ion concentration. This behavior is well described by a simple first-order hydrogen ion concentration dependence, eq 9, and is consistent with that expected for the decarboxylation of a bidentate carbonato complex (eq 9 with $k_a = k_0$ and $k_b = k_1K_1$). The values of k_a and k_b calculated from a linear regression treatment of the k_{obsd} vs. [H$_3$O$^+$] data at 14 °C are reported in Table I (bottom).

$$k_{obsd} = k_a + k_b[H_3O^+] \qquad (9)$$

In the acid-dependence studies conducted at both 25 and 35 °C, our inability to obtain consistent results by simply collecting data while the isosbestic point held indicated that the data were not accumulated for a sufficient length of time. The decarboxylation product, the *cis*-Co(py)$_2$(H$_2$O)$_4$$^{3+}$ ion, undergoes a subsequent reduction reaction at an appreciable rate. Assignment of the k_{obsd}(fast) to the decarboxylation and the k_{obsd}(slow) to the reduction reaction is not obvious.[15] However, in this particular system, the consecutive reactions of the overall decomposition could be designated from an examination of the order of the pseudo-first-order rate constants with respect to the hydrogen ion concentration. At 14, 25, and 35 °C, plots of k_{obsd}(fast) vs. [H$_3$O$^+$] are linear (see Figure 4). Values of k_a and k_b at 25 and 35 °C obtained from a non-linear-regression treatment of k_{obsd}(fast) are given at the bottom of Table I. These parameters are not significantly different at ionic strengths 1.0 and 2.0 M.

Attempts to glean mechanistic information from comparisons of the relative magnitudes of the decarboxylation rate constants (k_a and k_b) and of the corresponding activation parameters for various bidentate (carbonato)metal complexes have met with only limited success. For certain select series of bidentate carbonato complexes, reactivity appears to correlate with stereochemistry[16,17] or electronic structure of the "nonparticipating" ligands attached to the metal center,[18] or solvation factors related to the overall net ionic charge on the complex.[19,20] The values of the activation parameters reported here for *cis*-Co(py)$_2$(CO$_3$)(H$_2$O)$_2$$^+$ ($\Delta H_a^\ddagger$ = 24 kcal mol^{-1}, $\Delta H_b^\ddagger$ = 20 kcal mol^{-1}, $\Delta S_a^\ddagger$ = 3 cal deg^{-1} mol^{-1}, and $\Delta S_b^\ddagger$ = −9 cal deg^{-1} mol^{-1}) are not untypical. The values for the acid-catalyzed paths are virtually identical with those found[18] for Co(phen)$_2$CO$_3$$^+$ and quite similar to those of the other carbonato complexes that rank high in resistance to decarboxylation. For all complexes, the full range of values previously reported are as follows: $\Delta H_a^\ddagger$, 12–33 kcal mol^{-1}; $\Delta S_a^\ddagger$, −37 to +28 cal deg^{-1} mol^{-1}; $\Delta H_b^\ddagger$, 11–34 kcal mol^{-1}; $\Delta S_b^\ddagger$, −20 to +26 cal deg^{-1} mol^{-1}. In compiling these ranges, we have made no attempt to assess the effect of experimental uncertainties in the parameters. In addition, the interpretation of activation parameters for the acid-dependent path ($\Delta H_b^\ddagger$ and $\Delta S_b^\ddagger$) is complicated by the fact that they are composite values[14] (e.g., $\Delta H_b^\ddagger = \Delta H_1 + \Delta H^\ddagger$, see mechanism). The activation parameters for the acid-independent path ($\Delta H_a^\ddagger$ and $\Delta S_a^\ddagger$) are less precise that those for $\Delta H_b^\ddagger$ and $\Delta S_b^\ddagger$. The noted trend[9] that the acid-catalyzed ring-opening rate constant is generally several orders of magnitude greater than the spontaneous path is violated for the Co(py)$_4$CO$_3$$^+$ ion, where $k_a > k_b$ at I = 1.0 M. In the present study, the values found for k_a and k_b are of similar magnitude at 25 °C. For the total series of carbonato complexes, the factors that affect reactivity appear to be not amenable to simple correlation.

This view is reaffirmed by examination of the decarboxylation rate parameters for the series of pyridine containing (carbonato)cobalt(III) ions shown in Table III. Although the rate constants for the spontaneous path are similar at 25 °C, examination of the corresponding activation parameters indicates that the similarity is fortuitous. For the acid-catalyzed path, activation parameters vary widely and the rate constants vary over approximately 7 orders of magnitude. In view of the extreme inertness of the *cis*-Co(py)$_4$CO$_3$$^+$ ion, one might relate the lack of reactivity to the presence of coordinated pyridine.[12] This view is further supported by the relative lack of reactivity of the *cis*-Co(py)$_2$(CO$_3$)(H$_2$O)$_2$$^+$ ion when compared to other bidentate carbonato complexes. A limited half-life measurement[12] of the decarboxylation of *mer*-Co(py)$_3$(CO$_3$)(H$_2$O)$^+$ suggests a similar reactivity.

Acid Dependence of the Reduction Reaction. Plots of k_{obsd}(slow) vs. [H$_3$O$^+$] reveal significant curvature while plots

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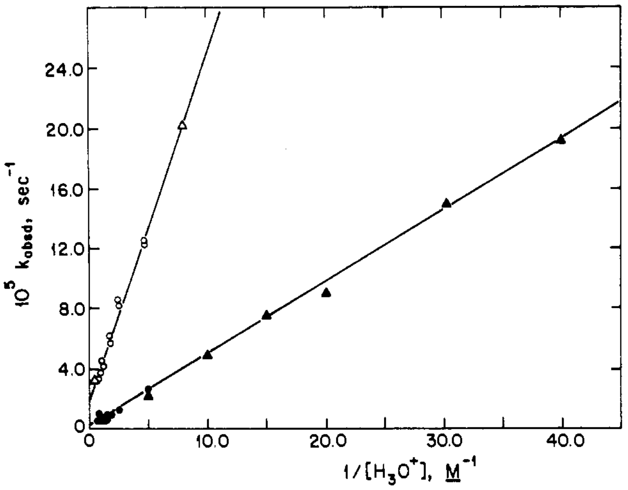

Figure 5. Acid dependence of the spontaneous reduction of *cis*-Co$(py)_2(H_2O)_4^{3+}$ at 25 (○) and 35 °C (●). Circles and triangles denote ionic strengths 1.0 and 2.0 M, respectively.

of the k_{obsd}(slow) vs. $1/[H_3O^+]$ exhibit a linear dependence (see Figure 5). This relationship is well described by eq 10

$$k_{obsd} = k_c + k_d/[H_3O^+] \qquad (10)$$

and is of the form previously observed for the thermal reduction of *trans*-$Co(py)_4(H_2O)_2^{3+}$ and various other aquoaminecobalt(III) ions.[12] Hence the mechanism proposed for the reduction step is given by eq 11–13 with rate constants

$$cis\text{-}Co(py)_2(H_2O)_4^{3+} \overset{K'}{\rightleftharpoons} cis\text{-}Co(py)_2(H_2O)_3(OH)^{2+} + H^+ \qquad (11)$$

$$cis\text{-}Co(py)_2(H_2O)_4^{3+} \xrightarrow{k'_0} Co^{2+}(aq) + \text{other products} \qquad (12)$$

$$cis\text{-}Co(py)_2(H_2O)_3(OH)^{2+} \xrightarrow{k'_1} Co^{2+}(aq) + \text{other products} \qquad (13)$$

$k_c = k'_0$ and $k_d = K'k'_1$. The values of k_c and k_d were obtained from a non-linear-regression treatment of k_{obsd}(slow) vs. $1/[H_3O^+]$ and are collected at the bottom of Table II. These parameters are not significantly different at ionic strengths 1.0 and 2.0 M.

Activation parameters for the reduction of *cis*-$Co(py)_2(H_2O)_4^{3+}$ ion calculated from the data with temperature as an independent variable[27] are included in Table II. The parameters associated with k_c are too imprecise for interpretive use; those associated with k_d ($\Delta H_d^{*} = 27.9 \pm 0.8$ kcal mol^{-1}, $\Delta S_a^{*} = 11 \pm 3$ cal deg^{-1} mol^{-1}) are of the precision normally expected for data of this type.

For the acid-dependent reduction path, the activation enthalpy ($\Delta H_d^{*} = 27.9$ kcal mol^{-1}) is considerably less than the documented values for the thermal reduction of other aquoaminecobalt(III) ions [$\Delta H^{*} = 43.9$, 36.8, and 34.3 kcal mol^{-1} for the cis complexes $Co(en)_2(H_2O)_2^{3+}$, $Co(NH_3)_2(H_2O)_4^{3+}$, and $Co(tmd)(H_2O)_2^{3+}$ (where tmd = trimethylenediamine), respectively,[22,23] at ionic strength 1.0 M]. This relative ease of reduction for the aquobis(pyridine)cobalt(III) ion may well be related to the π-acid properties of ligand pyridine.[12] This value is also significantly lower than that obtained[12] for the reduction of the *trans*-$Co(py)_4(H_2O)_2^{3+}$ ion at a higher ionic strength ($\Delta H_d^{*} = 32$ kcal mol^{-1} at $I = 5.0$ M).

The Arrhenius plot of our values of k_{obsd}(slow) at $[H_3O^+] = 1.0$ M for the spontaneous reduction of *cis*-$Co(py)_2(H_2O)_4^{3+}$ and data at similar conditions but higher temperature for the thermal reduction[12] of *trans*-$Co(py)_4(H_2O)_2^{3+}$ are superimposable. This observation suggests identical activation parameters for the two reduction reactions and strongly supports the previous proposal[12] that the mechanism for the reduction of *trans*-$Co(py)_4(H_2O)_2^{3+}$ involves the loss of two pyridine ligands before a rate-determining reduction of the *cis*-$Co(py)_2(H_2O)_4^{3+}$ ion.

Table IV. Kinetic Data for Reduction of *cis*-$Co(py)_2(CO_3)(H_2O)_2^+$ by Iodide Ions in Aqueous Perchlorate Media at 25 °C, $I = 2.0$[a]

$[H_3O^+]$	$[I^-]$	10^3k_{obsd}[b]	10^3k_e[b,c]	10^2k_f[c,d]
1.80	0.010	0.56	0.35 ± 0.03	2.04 ± 0.03
	0.020	0.72		
	0.050	1.44		
	0.100	2.36		
	0.200	4.43		
1.00	0.010	0.46	0.22 ± 0.04	2.00 ± 0.04
	0.020	0.58		
	0.050	1.18		
	0.100	2.29		
	0.200	4.20		
0.100	0.010	0.24	0.05 ± 0.02	2.02 ± 0.02
	0.020	0.47		
	0.050	1.07		
	0.100	2.06		
	0.150	3.04		
	0.200	4.11		

[a] All concentrations are given in M. [b] Given in s^{-1}. [c] Parameters obtained by linear regression fit of the data to eq 18. [d] Given in M^{-1} s^{-1}.

Total Decomposition Stoichiometry. We may summarize our results by indicating that the total decomposition of *cis*-$Co(py)_2(CO_3)_2^-$ occurs as indicated in the scheme of eq 14–16.

$$cis\text{-}Co(py)_2(CO_3)_2^- + 2H_3O^+ \xrightarrow{\text{step 1}} cis\text{-}Co(py)_2(CO_3)(H_2O)_2^+ + CO_2 + H_2O \qquad (14)$$

$$cis\text{-}Co(py)_2(CO_3)(H_2O)_2^+ + 2H_3O^+ \xrightarrow{\text{step 2}} cis\text{-}Co(py)_2(H_2O)_4^{3+} + CO_2 + H_2O \qquad (15)$$

$$cis\text{-}Co(py)_2(H_2O)_4^{3+} \xrightarrow{\text{step 3}} Co^{2+}(aq) + 2py + {}^1/_4O_2 \qquad (16)$$

Two distinct decarboxylation steps occur, and each has been subjected to detailed kinetic analysis. The results are consistent with the presence of two bidentate carbonate ligands. It is interesting to note that recent studies[24] indicate that the doubly monodentate carbonato complex *trans*-$Rh(en)_2(OCO_2)_2^-$ decarboxylate at pH <6.5 with the simultaneous loss of both carbonate ligands. This simultaneous loss may be consistent with the insensitivity of activation parameters for *monodentate* decarboxylation to changes in charge and nature of the nonparticipating ligands. Parameters for *bidentate* decarboxylation are markedly sensitive to these changes.

Reduction by Iodide. Stoichiometry. When an analyzed solution of *cis*-$Co(py)_2(CO_3)(H_2O)_2^+$ was added to a deoxygenated, acidic solution containing excess potassium iodide, the solution turned yellow over a period of several minutes. The final visible spectrum corresponded closely to that of iodine formed in a reaction with the stoichiometry of eq 17. This

$$2cis\text{-}Co(py)_2(CO_3)(H_2O)_2^+ + 2I^- \xrightarrow{H^+} 2Co^{2+}(aq) + 4pyH^+ + 2CO_2 + I_2 \qquad (17)$$

stoichiometry was checked by titration of reacted solutions with thiosulfate and was invariant over the following concentration

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ranges: $[Co^{III}] = (4.03-36.3) \times 10^{-4}$ M, $[I^-] = (1.0 - 20.0) \times 10^{-2}$ M, and $[H^+] = 0.1-1.8$ M at 25 °C and ionic strength 2.0 M.

Kinetics. Kinetic measurements were made under identical conditions used for stoichiometry measurements. The appearance of iodine (as I_3^-) was monitored at fixed wavelength in the range 388–460 nm with iodide in sufficient excess to ensure first-order conditions. Plots of ln $(A_\infty - A_t)$ vs. time were linear for at least 4 half-lives, indicating that the formation of iodine is first order in $[Co^{III}]$. Derived first-order rate constants k_{obsd} at three different acidities at 25.0 °C and I = 2.0 M are collected in Table IV. At each acidity the data are well described by rate law 18, where $k_{obsd} = k_e + k_f[I^-]$.

$$d[I_2]/dt = -\tfrac{1}{2}d[Co^{III}]/dt = k_{obsd}[Co^{III}] \qquad (18)$$

Values of k_e and k_f from a linear regression fit are given in Table IV. The first-order rate constant k_e increases with increasing acidity, while the rate constant k_f is acid independent. The mechanism of eq 19–22 predicts the observed stoichiometry and rate law.

$$Co(py)_2(CO_3)(H_2O)_2^+ \xrightarrow[H^+]{k_4} Co(py)_2(H_2O)_4^{3+} + CO_2 \qquad (19)$$

$$Co(py)_2(CO_3)(H_2O)_2^+ + I^- \xrightarrow[H^+]{k_5} Co^{2+}(aq) + 2pyH^+ + I\cdot + CO_2 \qquad (20)$$

$$Co(py)_2(H_2O)_4^{3+} + I^- \xrightarrow[H^+]{} Co^{2+} + 2pyH^+ + I\cdot \qquad (21)$$

$$2I\cdot \xrightarrow{fast} I_2 \qquad (22)$$

The rate constant for reaction 21 (1.60 $M^{-1}\ s^{-1}$) at 25 °C and I = 2.0 M)[25] is much higher than that for reaction 20, ensuring that reactions 19 and 20 are the rate-determining steps. For this mechanism, $2k_e = k_4$ and $2k_f = k_5$. The value of $2k_e = k_a + k_b[H_3O^+]$ calculated from the data in Table I for decarboxylation of $Co(py)_2(CO_3)(H_2O)_2^+$ at each experimental acidity used for the reaction with iodide is in agreement, within experimental error, with the observed value. This confirms (within the precision limits of the data) that the k_e terms corresponds to decarboxylation reaction 19 and that the k_f term arises from direct reduction of $Co(py)_2(CO_3)(H_2O)_2^+$ by iodide (reaction 20).

The rate constant k_5 is about 40 times less than that for the corresponding reduction of $Co(py)_2(H_2O)_4^{3+}$ by I^- (reaction 21) at 25 °C.[25] The rate constants for reduction of $Co(py)_2(CO_3)(H_2O)_2^+$, $Co(py)_2(H_2O)_4^{3+}$,[25] and $Co(NH_3)_2(H_2O)_4^{3+}$ [26] by iodide are all independent of reaction acidity, indicating that they all proceed through outer-sphere mechanisms.[25,26]

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Registry No. *cis*-$K[Co(py)_2(CO_3)_2]$, 54967-61-2; *cis*-$Co(py)_2(CO_3)(H_2O)_2$, 73104-76-4; *cis*-$Co(py)_2(H_2O)_4^{3+}$, 73136-37-5; I^-, 20461-54-5.

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Kinetics and Mechanism of the Complex Formation between Iron(III) and Some (Salicylato)pentaaminecobalt(III) Ions

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Kinetic studies by the stopped-flow technique were made at 20–30 °C and I = 1.0 M (ClO_4^-) of the formation and the dissociation of the binuclear complex of Fe(III) with (salicylato)pentaaminecobalt(III) ions, where the pentaamine residues are 5 NH_3, $(en)_2(NH_3)$, and tetraethylenepentamine. The formation of $N_5CoSalFe^{4+}$ involves the reaction of the phenol form of the cobalt(III) substrates with $Fe(OH_2)_6^{3+}$ and $Fe(OH_2)_5(OH)^{2+}$. The rate constants and the activation parameters for both the paths are reported and compared with the available data for the corresponding reaction of the Fe(III) species with various other ligands. The carboxylate-bound (salicylato)pentaaminecobalt(III) substrates behave effectively as phenol with regard to their rate of complexation with the Fe(III) species. The rate data for the formation reactions are virtually independent of the nature of the amine function attached to the cobalt(III) center. It is concluded that the I_d mechanism applies in the reaction with $Fe(OH_2)_5(OH)^{2+}$, while for the corresponding reaction with $Fe(OH_2)_6^{3+}$, the mechanism is most likely of the I_a type. The binuclear species $N_5CoSalFe^{4+}$ undergoes dissociation to yield the cobalt(III) substrates and the Fe(III) species via spontaneous and acid-catalyzed paths. The rate parameters for both the paths are sensitive to the nature of the amine function and decrease in the sequence tetren > $(en)_2(NH_3)$ > 5 NH_3. A comparison of the rate data for the spontaneous dissociation of the binuclear complexes with that for the mono(phenolato)iron(III) species ($C_6H_5OFe^{2+}$) reveals that the former are $\sim 10^3$ times kinetically less labile than the latter. This suggests that Fe(III) is chelated by the salicylate moiety through the Co(III)-bound carboxylate group and the free phenol group after deprotonation. The chelate ring opening appears to be rate determining in both the spontaneous and the acid-catalyzed paths. To make possible the comparisons just mentioned, we have made a separate study of the formation and decomposition reactions of the mono(salicylato)iron(III) complex in perchlorate media. Previous work on this system involved only the formation reaction and was done in nitrate media, which we have found to exhibit moderate catalytic behavior.

Introduction

In earlier studies, kinetic data for the metal ion catalyzed aquation of the (carboxylato)pentaamminecobalt(III) complexes derived from oxalic,[2] malonic,[3] and salicylic acids[4] have been reported. It was postulated that the metal ions associated with the cobalt(III) substrates to form binuclear complexes in a rapid and reversible step. These species, however, undergo ligand substitution at the cobalt(III) center at rates charac-

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