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Studies of Carbonatocobaltate(III) Complexes. Stoichiometry and Kinetics of the Reaction between Tris(carbonato)cobaltate(III) Species and Pyridine in Aqueous Sodium Bicarbonate Media[1]

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Spectral and reaction properties of green "Field–Durrant" solutions prepared by dissolving $Na_3[Co(CO_3)_3]\cdot 3H_2O$ in aqueous sodium bicarbonate are reported. The reaction of these green solutions with excess pyridine was found to produce only *cis*-$Co(CO_3)_2py_2^-(aq)$, which was isolated as a pale blue, moisture-sensitive hydrate $K[Co(CO_3)_2(py)_2]\cdot 0.5H_2O$ and as the purple crystalline salt $K[Co(CO_3)_2(py)_2]\cdot 2H_2O$. The behavior of these product salts in water, ethanol, and aqueous acid was investigated. The kinetics of the title reaction were monitored by conventional spectrophotometry at 525 and 635 nm over the following concentration ranges: $[Co^{III}] = (5.7–11.4) \times 10^{-4}$ M, $[H^+] = (0.15–9.52) \times 10^{-9}$ M, $[HCO_3^-] = 0.14–0.865$ M, and $[py] = (1.2–29.8) \times 10^{-2}$ M at 25 °C and ionic strength 1.0 M ($NaHCO_3$, $NaClO_4$). The rate law was found to be $-d[\text{green reactants}]/dt = d[cis\text{-}Co(CO_3)_2(py)_2^-]/dt = (A + B/[HCO_3^-])[H^+][\text{green reactants}][py]/(1 + C[H^+])$. A computerized fit of the data to this rate law gave $A = (1.70 \pm 0.22) \times 10^9\ M^{-2}\ min^{-1}$, $B = (8.41 \pm 0.42) \times 10^8\ M^{-1}\ min^{-1}$, and $C = (1.31 \pm 0.12) \times 10^9\ M^{-1}$. Spectral scanning during the course of the reaction showed that the rate-determining steps involve the formation of the first cobalt(III)–pyridine bond, followed by rapid addition of pyridine to form the bis(carbonato)bis(pyridine)cobaltate(III) product. A reaction mechanism is proposed which involves rapid equilibria between $Co(CO_3)_3^{3-}(aq)$, $Co(CO_3)_2(H_2O)(HCO_3)^{2-}(aq)$, and $Co(CO_3)_2(H_2O)_2^-(aq)$ species with substitution of pyridine at these centers as the rate-determining processes. The equilibrium constants for the processes $Co(CO_3)_3^{3-}(aq) + H_3O^+ \rightleftharpoons Co(CO_3)_2(HCO_3)(H_2O)^{2-}$ and $Co(CO_3)_2(HCO_3)(H_2O)^{2-} \rightleftharpoons Co(CO_3)_2(H_2O)_2^- + HCO_3^-$ are $(1.31 \pm 0.12) \times 10^9\ M^{-1}$ and less than 0.06 M at 25 °C, respectively. The rate constants for pyridine substitution were estimated to be $k_0 \leq 0.4$, $k_1 = 1.3 \pm 0.2$, and $k_2 \geq 10\ M^{-1}\ min^{-1}$ for $Co(CO_3)_3^{3-}(aq)$, $Co(CO_3)_2(HCO_3)(H_2O)^{2-}(aq)$, and $Co(CO_3)_2(H_2O)_2^-(aq)$, respectively.

Introduction

Reactions based on the substitution of amines and other ligands at the green cobalt(III) center produced by oxidizing cobalt(II) salts with hydrogen peroxide in the presence of excess alkali metal bicarbonate have been employed for many years in the synthesis of cobalt(III) complexes.[2,3] The synthetic utility of this green "Field–Durrant" precursor is the result of its relatively high lability and its weakly oxidizing character.

Surprisingly, little appears to be known about the structure of the green species in solution, except for the fact that excess bicarbonate is necessary for its stabilization.[2,3] Recently, Gillard and his coworkers[4] suggested that solid salts of the "$Co(CO_3)_3^{3-}$" anion could be classified according to their molecular formulas and infrared spectra. Thus, sparingly soluble salts, e.g., $[Co(en)_3][Co(CO_3)_3]$, are indefinitely stable in the anhydrous state and have the infrared spectra expected for fully chelated carbonate ligands in the anion, while alkali metal salts[5] $K_3[Co(CO_3)_3]\cdot 3H_2O$ and $Na_3[Co(CO_3)_3]\cdot 3H_2O$ are only stable as hydrates and show infrared evidence for at least one monodentate carbonate group both in the solid state and in solution.[4]

Typical synthetic conditions for preparation of the Field–Durrant solution involve the low-temperature oxidation of 25–50 mmol of a cobalt(II) salt in saturated aqueous potassium bicarbonate, which acts as a source of carbonate ligands and also serves to stabilize the product.[6,7] The dark green reaction mixture is usually protected from light because it is believed to be subject to photodecomposition.[2,3] The stability of such solutions decreases markedly with increasing temperature and decreasing bicarbonate concentration. We have observed[8] that the initial products of reaction of ammonium carbonate with such preparations include dimeric carbonatoamminecobalt(III) species whose proportions increase with decreasing bicarbonate concentration. These observations suggest that a mixture of monomeric and dimeric cobalt(III) complexes exists at the high concentrations used for synthesis[2,3] and in infrared measurements on solutions.[4]

By contrast, we have found that solutions of the much less soluble sodium salt $Na_3[Co(CO_3)_3]\cdot 3H_2O$ in 0.1–1.0 M aqueous sodium bicarbonate are stable under ordinary laboratory conditions and can be used for mechanistic studies. In this paper we report an investigation of the kinetics and mechanism of reaction of such solutions with excess pyridine, which forms the *cis*-bis(carbonato)bis(pyridine)cobaltate(III) anion, *cis*-$Co(CO_3)_2(py)_2^-(aq)$.[9]

Experimental Section

Reagents. Water which had been deionized and fractionally distilled from alkaline permanganate in an all-glass still was used throughout this work. Sodium tris(carbonato)cobaltate(III) trihydrate was synthesized by the literature method[10] and stored in a desiccator over P_2O_5 in the dark. Small amounts of moisture were found to cause decomposition to a black, insoluble residue, necessitating the maintenance of rigorously dry storage conditions. Saturated stock solutions of this complex were prepared by adding small amounts of the solid to 1.0 M $NaHCO_3$ and stirring the mixture for ca. 40 min. After filtration through a medium-porosity glass sinter, the filtrate was allowed to stand overnight at room temperature and then refiltered. The resulting stock solution, which contained $[Co^{III}] \approx 3 \times 10^{-3}$ M, was subsequently stored at 0 °C.

Hydrated potassium *cis*-bis(carbonato)bis(pyridine)cobaltate(III) salts $K[Co(CO_3)_2(py)_2]\cdot xH_2O$ ($x = 0.5$ or 2), were synthesized as follows. An ice-cold solution of $Co(NO_3)_2\cdot 6H_2O$ (7.3 g, 0.025 mol) in 10 ml of water was mixed with ice-cold hydrogen peroxide (30% w/v, 5 ml, 0.05 mol) and the mixture was then added at a rate of 0.5 ml min^{-1} to a constantly stirred, ice-cold slurry of $KHCO_3$ (50 g, 0.5 mol) in 50 ml of water. After addition of all of the cobalt(II)–peroxide mixture, the resulting green solution was allowed to warm to 25 °C and the supernatant was decanted from excess solid $KHCO_3$ into a stoppered Erlenmeyer flask. Pyridine (2–20 ml, 0.025–0.25 mol) was then added and reaction was allowed to proceed for 100 h at 25 °C, at which time no further spectral changes were evident.

The dark purple product mixture was poured into 2 l. of ice-cold acetone and stirred for 30 min; excess solvent was then removed from the solid by decantation. The wet, purple solid (ca. 65 g) was then washed by decantation with three 200-ml portions of anhydrous acetone and extracted with a minimum volume of ice-cold ethanol (ca. 30 ml) and the solution was quickly poured into 1 l. of ice-cold, anhydrous acetone. The pale blue, highly deliquescent[11] precipitate was then washed by decantation with two 200-ml portions of anhydrous acetone and dried under vacuum over P_2O_5 (product yields: 2.3 g (23%) with initial molar py:Co = 1; 4.0–4.8 g (39–47%) with py:Co = 2–10). The product was analyzed as follows. Small portions (20–100 mg) of the dry solid were dissolved in the minimum volume of anhydrous ethanol and immediately reprecipitated by addition to a large excess of anhydrous acetone. The solid was washed by centrifugation with several portions of anhydrous acetone and then transferred as a slurry to a weighed volumetric flask. After evacuation to constant weight at 30 °C, the flask was reweighed and the solid was then treated with excess concentrated $HClO_4$ and reduced to cobalt(II) with one or two crystals of KI, and the solution was then made up to the mark with water. The resulting solution was analyzed for cobalt by the Kitson procedure:[12] equiv wt calcd for $K[Co(CO_3)_2(py)_2]\cdot 0.5H_2O$, 385.2; found, 386 ± 4 (six determinations). Elemental analyses (Galbraith Laboratories, Knoxville, Tenn.) of samples prepared as above gave very erratic results, presumably due to the extreme moisture sensitivity of this complex.

A crystalline sample of the product was obtained as follows. Sufficient water was added to a suspension of $K[Co(CO_3)_2(py)_2]\cdot 0.5H_2O$ in acetone to impart a pale blue color to the supernatant. The mixture was then allowed to stand in a refrigerator at 0 °C for 3 weeks. The purple, needle crystals which formed were washed with anhydrous acetone and dried under vacuum. Anal. Calcd for $K[Co(CO_3)_2(py)_2]\cdot 2H_2O$ (equiv wt 412.2): C, 34.93; H, 3.40; N, 6.79; K, 9.48. Found (equiv wt 409 ± 5 (three determinations)): C, 35.22; H, 3.37; N, 6.80; K, 9.30. Smaller crystals were obtained by allowing a saturated ethanolic solution of the complex to stand overnight at −5 °C.[9] These crystalline samples were stable under normal laboratory conditions.

Studies of the thermal stability of $K[Co(CO_3)_2(py)_2]\cdot 0.5H_2O$ were conducted on preweighed samples at 30–210 °C in a vacuum oven (liquid N_2 trap). Although weight loss was apparent at temperatures in excess of ca. 50 °C, erratic results were obtained at intermediate temperatures and subsequent determinations were made by heating the solid to constant weight at 210 °C. The brown-black product was dissolved in boiling 1 M $HClO_4$ and analyzed for cobalt as described above: equiv wt calcd for $K[Co(O)(CO_3)]$, 174.0; found, 177.4 ± 0.1 (three determinations).

Pyridine was fractionally distilled from BaO at atmospheric pressure. All other chemicals were of reagent grade and were used as supplied.

Spectral and Kinetic Measurements. Spectral scans of reactants and products and absorbance–time curves for the title reaction were made at 25.0 ± 0.2 °C with a Beckman DK-1 ratio-recording spectrophotometer which was fitted with a temperature-controlled cell housing. Measurements were also made of the very early stages of the title reaction in a stopped-flow apparatus at 0 °C; these latter experiments were directed at detecting any fast equilibria or intermediate complex formation in the overall reaction. The acidity of thermostated solutions was determined by pH measurements from an Orion Model 801 digital pH meter equipped with Orion Model 91-01-00 Ag–AgCl internal standard glass and Orion Model 90-01 single-junction reference electrodes. The instrument was calibrated with standard borate and phosphate buffers over the experimental acidity range and readings were accurate to ±0.002 pH unit. In all cases, the measured acidity of a solution of given total analytical bicarbonate concentration was used together with appropriate equilibrium data[13] in the calculation of the actual bicarbonate concentration, $[HCO_3^-]$.

The kinetics of the title reaction were monitored spectrophotometrically at 525 (a wavelength of large absorbance change) or 635 nm (a wavelength of maximum absorbance for the green reactant) over the following analytical concentration ranges: $[Co^{III}] = (5.7\text{–}11.4) \times 10^{-4}$ M, $[H^+] = (0.1\text{–}9.5) \times 10^{-9}$ M, $[HCO_3^-] = 0.14\text{–}0.865$ M, and $[py] = (1.2\text{–}29.8) \times 10^{-2}$ M. In all cases the ionic strength was made up to 1.0 M by addition of $NaClO_4$ and pyridine was present in sufficient excess to ensure pseudo-first-order conditions. Solutions to be mixed were thermostated at 25.0 °C and transferred to the spectrophotometer within 30 s of mixing.

Each absorbance–time curve, consisting of 30–40 points over 90–95% reaction, was fitted by means of a nonlinear least-squares routine to the expression

$$A_t = \epsilon_R[Co]_T \exp(-k_{obsd}t) + \epsilon_P[Co]_T(1 - \exp(-k_{obsd}t)) \tag{1}$$

where A_t is the absorbance at time t, ϵ_R and ϵ_P are the molar absorptivities of reactant R and product P, respectively, $[Co]_T$ is the analytical cobalt(III) concentration, and k_{obsd} is the pseudo-first-order rate constant for the sequence

$$R \xrightarrow{k_{obsd}} P \tag{2}$$

under fixed experimental conditions. These calculations were made with A_t and t as the dependent and independent variables, respectively, at known fixed $[Co]_T$. The computer program provided the calculated values of ϵ_R, k_{obsd}, and ϵ_P, together with their standard deviations.

Final absorbances were obtained for each run. Repeated runs under fixed experimental conditions gave kinetic parameters with an average uncertainty of ±4%.

Results

Properties of the Green Carbonatocobalt(III) Species in Aqueous Sodium Bicarbonate Solutions. The solubility of the salt $Na_3[Co(CO_3)_3]\cdot 3H_2O$ at 25 °C and ionic strength 1.0 M was found to be proportional to the analytical bicarbonate concentration in the range 0.1–1.0 M. Solutions prepared as described in the Experimental Section exhibited spectral maxima at 260 ($\epsilon \sim 10^5$ M^{-1} cm^{-1} [14]), 440 (ϵ 166 ± 2 M^{-1} cm^{-1}), and 635 nm (ϵ 154 ± 2 M^{-1} cm^{-1}) and Beer's law was obeyed at $8 \lesssim pH \lesssim 10$. However, reaction studies were subsequently limited to $pH \lesssim 10$ because of large, irreproducible spectral changes in the 300–400 nm region and eventual precipitation under more alkaline conditions.

The green stock solution in 1 M $NaHCO_3$ was used in preliminary reactivity studies. A substantial, immediate, and reproducible absorbance increase in the near-uv region occurred on addition of excess ethylenediamine, 1,2-propanediamine, and 1,3-propanediamine dissolved in sodium bicarbonate. These brown solutions gradually turned purple on standing.[6] By contrast, addition of ammonia, 1,6-hexanediamine, and pyridine under similar conditions did not result in the rapid brown coloration, the solutions simply changing from green to purple over periods of 5–60 min, depending on solution conditions. Addition of all of the above ligands, except pyridine, to the stock solution caused an increase in pH, but separate experiments showed that the brown coloration with the first three diamines was not due to this pH increase, since the initial absorbance increase at 380 nm was independent of the concentration of ligand at $pH \lesssim 10$ and addition of 1,6-hexanediamine, another basic ligand, did not result in the brown coloration. The comparatively weak basicity of pyridine ($pK_a \approx 5.3$ at 25 °C[15]) and the high buffer capacity of concentrated sodium bicarbonate allowed the study of spectra and reaction kinetics over wide [py] ranges at constant $[H^+]$ and $[HCO_3^-]$ in the title reaction. The concentrations $[H^+]$ and $[HCO_3^-]$ also could be varied over substantial ranges without significant changes in the form of the pyridine ligand, commending a detailed kinetic study of this system.

On adding excess pyridine to the stock solution,[16] the visible spectrum changed with time from that for the green reactant (maxima at 635 and 440 nm) to a purple product solution with absorption maxima at 561 (ϵ 165 ± 5 M^{-1} cm^{-1}) and 388 nm (ϵ 232 ± 15 M^{-1} cm^{-1}) and minima at 468 (ϵ 32 ± 1 M^{-1} cm^{-1}) and 350 nm (ϵ 130 ± 6 M^{-1} cm^{-1}). This spectrum is identical with that for solutions of analyzed samples of $K[cis\text{-}Co(CO_3)_2(py)_2]\cdot 2H_2O$ in 1 M $NaHCO_3$ (see above and ref 9). The spectrum of the purple product did not change with time even in the presence of a large excess of pyridine. Spectral scans during the course of the reaction revealed isosbestic points at 590, 495, 410, and 355 nm, and theoretical spectra generated on the assumption that the reacting solution contained only various proportions of the green reactant and the bis(carbonato)bis(pyridine)cobaltate product were identical, within experimental error, with those obtained experimentally.

In addition, chromatography of isolated products on Sephadex G-25 (ethanol eluent) and Biobeads SX-12 (water and 50% v/v aqueous pyridine) indicated the presence of only one component.

Properties of the Bis(carbonato)bis(pyridine) Product. Dissolution of the hydrates $K[Co(CO_3)_2(py)_2]\cdot xH_2O$ (x = 0.5

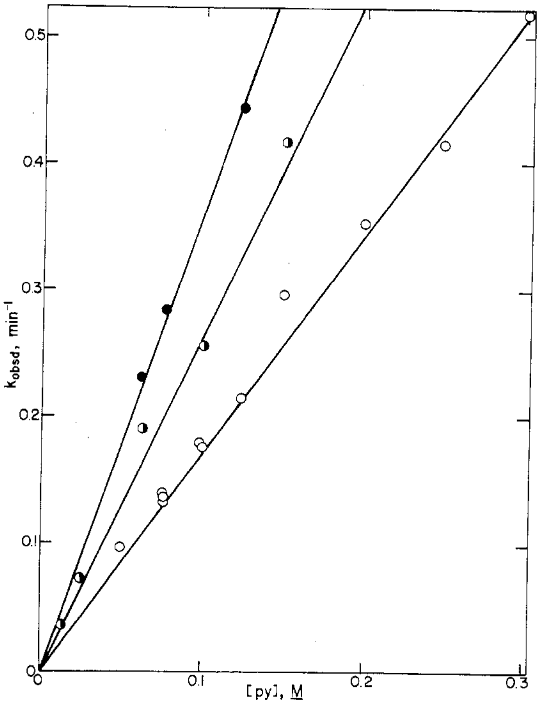

Figure 1. Variation of k_{obsd} with [py] at 25.0 °C, ionic strength 1.0 M, pH 8.2 ± 0.1, and the following free bicarbonate concentrations: ○, $[HCO_3^-] = 0.83 \pm 0.02$ M; ◑, $[HCO_3^-] = 0.41$ M; ●, $[HCO_3^-] = 0.21$ M.

or 2) in water and anhydrous ethanol gave identical solution spectra but the solutions were unstable, precipitating an unidentified brown solid. However, dissolution in water containing excess pyridine and/or sodium bicarbonate or in ethanol–pyridine mixtures gave solutions with identical spectra but with greatly increased stability. The solid hydrates were essentially insoluble in pyridine, dioxane, chloroform, and benzene.

Addition of the solid hydrates to excess $HClO_4$ caused evolution of CO_2 and resulted in a shift of the long-wavelength spectral maximum from 561 to 540 nm (ϵ 50 ± 1 M^{-1} cm^{-1}) with the appearance of a new spectral shoulder at 375 nm (ϵ ~85 M^{-1} cm^{-1}). These initial spectral parameters for the acidified product are similar to those for *cis*-$Co(NH_3)_2^{3+}(aq)$.[8] However, at $[H^+] \geq 1$ M, the long-wavelength maximum absorbance shifted to 550 nm (ϵ ~30 M^{-1} cm^{-1}) at a rate which increased with increasing acidity; at $[HClO_4] \approx 2 \times 10^{-2}$ M the final product was aquocobalt(II) with no evidence for the formation of the absorbance maximum at 550 nm. All solutions finally decomposed to $Co^{2+}(aq)$, with no evidence for the intermediacy of $Co^{3+}(aq)$.[17] These properties are those expected of a complex which is undergoing acid-catalyzed loss of pyridine, with the appearance of the 550-nm band perhaps indicating the formation of $Co(py)^{3+}(aq)$, which may undergo base-catalyzed reduction by water, as does $Co^{3+}(aq)$.[17] Acidified solutions were found to oxidize I^- to I_2 and Cl^- to Cl_2, properties which are again reminiscent of $Co^{3+}(aq)$ species.[17] In any event, these oxidizing properties of the acidified product prevented further characterization of the aquobis(pyridine)cobalt(III) complex by cation-exchange techniques.[8]

Kinetics. Experiments on the stopped-flow time scale at 0 °C gave no evidence for any rapid preequilibria in the reaction of the green reactant with pyridine. Absorbance–time curves obtained at 525 and 635 nm could be fitted to eq 1 within an average uncertainity of ±1% for at least 90% of all reactions, indicating that the reaction is first order in [Co^{III}] (eq 2). The observed first-order rate constant was independent of the monitoring wavelength and [Co^{III}] over the experimental concentration ranges and obeyed the empirical function

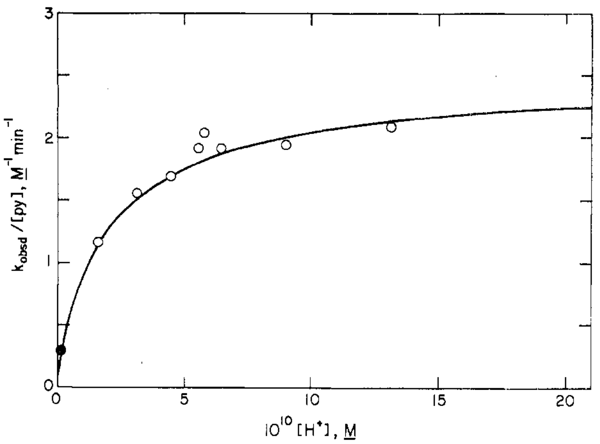

Figure 2. Variation of k_{obsd}/[py] with [H$^+$] at 25.0 °C and ionic strength 1.0 M with $[HCO_3^-] = 0.23 \pm 0.07$ M. The filled circle refers to data at low $[HCO_3^-]$ and pH 10.2 (see text).

Table I. Kinetic Data for the Reaction of Green Carbonatocobaltate(III) Species with Pyridine at 25.0 °C and Ionic Strength 1.0 M[a]

10^2[py]	$[HCO_3^-]$	10^9[H$^+$]	k_{obsd}[b,c]	k_{calcd}[b,d]
7.45	0.83	7.22	0.141 (0.007)	0.14
9.93	0.82	6.90	0.183 (0.005)	0.18
4.97		6.74	0.097 (0.007)	0.092
12.4	0.83	7.39	0.214 (0.003)	0.23
14.9	0.79	5.74	0.296 (0.005)	0.28
24.8	0.78	5.35	0.414 (0.003)	0.46
12.4	0.21	7.22	0.44 (0.03)	0.49
6.21	0.20	5.87	0.23 (0.02)	0.24
7.45	0.21	6.74	0.28 (0.02)	0.29
	0.29	0.59	0.114 (0.005)	0.11
	0.86	9.30	0.131 (0.005)	0.14
	0.87	9.52	0.143 (0.004)	0.14
29.8	0.82	7.56	0.524 (0.008)	0.56
19.9	0.83	7.74	0.354 (0.004)	0.37
9.93	0.41	6.15	0.261 (0.005)	0.25
14.9		6.29	0.424 (0.006)	0.38
1.24		6.44	0.036 (0.006)	0.032
6.21		6.29	0.190 (0.008)	0.16
24.8		6.01	0.668 (0.009)	0.63
9.93	0.098	0.15	0.116 (0.006)	0.13
	0.68	0.43	0.201 (0.005)	0.19
	0.22	0.45	0.168 (0.009)	0.16
	0.73	6.15	0.178 (0.006)	0.19
	0.53	1.99	0.184 (0.006)	0.18
9.31	0.39	1.31	0.194 (0.004)	0.17
	0.31	0.89	0.180 (0.005)	0.17
	0.14	0.31	0.146 (0.006)	0.15
29.8	0.20	0.55	0.585 (0.015)	0.57
24.8		0.57	0.506 (0.006)	0.47
7.45	0.22	0.64	0.143 (0.007)	0.14

[a] All concentrations are M. [b] Units are min^{-1}. [c] Errors shown in parentheses are one standard deviation. [d] Calculated from a nonlinear least-squares fit of the data to eq 3.

$$k_{obsd} = \left(\frac{A[H^+] + B[H^+]/[HCO_3^-]}{1 + C[H^+]}\right)[py] \qquad (3)$$

where A, B, and C are empirical parameters.

Thus, at pH 8.2 ± 0.1 and approximately constant $[HCO_3^-]$, k_{obsd} was a linear function of [py], while at the same acidity the slopes of k_{obsd} vs. [py] increased with $1/[HCO_3^-]$ (Figure 1). The observed second-order rate constant, k_{obsd}/[py], at approximately constant $[HCO_3^-]$ approached a limiting value at high [H$^+$] (Figure 2). The kinetic data in Table I were fitted to eq 3 by means of a nonlinear least-squares routine with A, B, and C as parameters, whose respective values were found to be $(1.7 \pm 0.22) \times 10^9$ M^{-2} min^{-1}, $(8.41 \pm 0.42) \times 10^8$ M^{-1} min^{-1}, and $(1.31 \pm 0.12) \times 10^9$ M^{-1} at 25.0 °C and ionic strength 1 M. Pseudo-first-order rate constants calculated from this fit of the data are included in Table I for comparison with k_{obsd}.

Mechanism. The mechanism shown by eq 4–9 is consistent

$$Co(CO_3)_3{}^{3-} + H_3O^+ \overset{fast}{\rightleftharpoons} Co(CO_3)_2(HCO_3)(H_2O)^{2-} \quad K_h \tag{4}$$

$$Co(CO_3)_2(HCO_3)(H_2O)^{2-} \overset{fast}{\rightleftharpoons} Co(CO_3)_2(H_2O)_2{}^- + HCO_3{}^- \quad K_{H_2O} \tag{5}$$

$$Co(CO_3)_3{}^{3-} + py \xrightarrow{k_0} Co(CO_3)_2(CO_3)(py)^{3-} \tag{6}$$

$$Co(CO_3)_2(HCO_3)(H_2O)^{2-} + py \xrightarrow{k_1} Co(CO_3)_2(HCO_3)(py)^{2-} + H_2O \tag{7}$$

$$Co(CO_3)_2(H_2O)_2{}^- + py \xrightarrow{k_2} Co(CO_3)_2(H_2O)(py)^- + H_2O \tag{8}$$

$$Co^{III}py + py \xrightarrow[fast]{k_3} Co(CO_3)_2(py)_2{}^- \tag{9}$$

with the observed kinetic dependences. Here, reaction 9 represents the rapid reactions of the three initial carbonatopyridinecobaltate(III) products with pyridine to give a common *cis*-bis(carbonato)bis(pyridine)cobaltate(III) product (see below); steps 6–8 are postulated to be rate determining.

The rate law predicted by this mechanism is given in eq 10.

$$k_{obsd} = \left(\frac{k_0 + k_1K_h[H^+] + k_2K_hK_{H_2O}[H^+]/[HCO_3{}^-]}{1 + K_h[H^+] + K_hK_{H_2O}[H^+]/[HCO_3{}^-]}\right)[py] \tag{10}$$

Attempts to fit the experimental data to eq 10 by nonlinear least squares gave a much worse fit than that provided by eq 3, suggesting that some of the terms in eq 10 are too small to be determined under the experimental conditions. Equation 10 reduces to the same form as eq 3 if the terms k_0 and $K_hK_{H_2O}[H^+]/[HCO_3{}^-]$ are much smaller than the other terms in the numerator and denominator of eq 10, respectively. Comparison of reduced eq 11 with eq 3 then gives $A = k_1K_h$,

$$k_{obsd} = \left(\frac{k_1K_h[H^+] + k_2K_hK_{H_2O}[H^+]/[HCO_3{}^-]}{1 + K_h[H^+]}\right)[py] \tag{11}$$

$B = k_2K_hK_{H_2O}$, and $C = K_h$, respectively, corresponding to the assignments $K_h = (1.31 \pm 0.12) \times 10^9$ M^{-1}, $k_1 = A/C = 1.3 \pm 0.2$ M^{-1} min^{-1}, and $k_2K_{H_2O} = 0.64 \pm 0.07$ min^{-1} at 25.0 °C and ionic strength 1.0 M.

Estimates for K_{H_2O}, k_2, and k_0 can be obtained as follows. If $K_hK_{H_2O}[H^+]/[HCO_3{}^-] \leq 0.1(1 + K_h[H^+])$ at the lowest experimental acidity, then $K_{H_2O} \leq 6 \times 10^{-2}$ M. With this estimate for K_{H_2O}, $k_2 \geq 10$ M^{-1} min^{-1}. Similarly, if $k_0 \leq 0.1(k_1K_h[H^+] + k_2K_hK_{H_2O}[H^+]/[HCO_3{}^-])$ at the lowest experimental acidity, then $k_0 \leq 0.4$ M^{-1} min^{-1}, consistent with the small intercept at low $[H^+]$ in Figure 2. Finally, since the reaction is first order in [py] while the product is a bis(pyridine)cobaltate(III) species, we may conclude that the apparent[18] rate constant k_3 for reaction 9 is at least 10 times greater than the largest value of $k_{obsd}/[py]$ (Figure 2). Thus, $k_3 \geq 20$ M^{-1} min^{-1} at 25.0 °C and ionic strength 1.0 M.

Discussion

Solutions prepared by dissolving $Na_3[Co(CO_3)_3]\cdot 3H_2O$ in aqueous sodium bicarbonate are sufficiently stable under normal laboratory conditions to allow accurate spectral and kinetic measurements to be made. It would appear that the spectrum of the green reactant solution essentially is invariant with pH and $[HCO_3{}^-]$ over the ranges $8 \leq pH \leq 10$ and $[HCO_3{}^-]_T \approx 0.1$–$1.0$ M, respectively.

The rate of reaction of this green cobalt(III) solution with pyridine is first order in both $[Co^{III}]$ and [py] and spectral scans of the reaction mixture indicate that the rate-determining steps involve formation of pyridinecobalt(III) species. However, the single product of the reaction is *cis*-$Co(CO_3)_2(py)_2{}^-$, which can be confidently identified from its visible[9,19] and ir[9] spectra and by comparison of the spectrum of the acidified product (presumably $Co(py)_2{}^{3+}(aq)$) with that of $Co(NH_3)_2{}^{3+}(aq)$.[8] The spectral, chromatographic, and kinetic data (the latter obtained by computer fitting of absorbance–time curves at two different wavelengths) provide no evidence for the formation of any other products; in particular, *trans*-$Co(CO_3)_2(py)_2{}^-$ [9] is not observed as a detectable product under the experimental conditions used for synthesis or spectral measurements in this study.

The dependences of the rate constant on $[H^+]$ and $[HCO_3{}^-]$ in the reaction with pyridine and the adherence of the green reactant solutions to Beer's law are consistent with the existence of different, monomeric carbonatocobaltate(III) species in aqueous sodium bicarbonate in the pH range 8–10. The mechanism proposed involves rapid equilibria between fully chelated $Co(CO_3)_3{}^{3-}$ and ring-opened $Co(CO_3)_2(HCO_3)(H_2O)^{2-}$ and $Co(CO_3)_2(H_2O)_2{}^-$. If $K_{H_2O} << 0.06$ and $[Co(CO_3)_2(H_2O)_2{}^-]$ is neglected, then the ratio $[Co(CO_3)_2(HCO_3)(H_2O)^{2-}]/[Co(CO_3)_3{}^{3-}] = K_h[H^+]$ varies from 0.2 to 12.4 over the experimental conditions. The fraction of cobalt(III) in the fully chelated form thus varies from ca. 10 to 80% over the experimental pH range. If $K_{H_2O} = 0.06$ M (the upper limit), then the corresponding fraction of $Co(CO_3)_2(H_2O)_2{}^-(aq)$ varies from 3 to 20%. Although the latter must be regarded as an upper limit under the experimental conditions, it is worth noting that this fraction would be observed at low $[HCO_3{}^-]$ even at low pH (in this case $[HCO_3{}^-] = 0.20$ M and $[H^+] = 7.22 \times 10^{-9}$ M (Table I)). Our experimental observations are consistent with very similar spectra for $Co(CO_3)_3{}^{3-}(aq)$ and $Co(CO_3)_2(HCO_3)(H_2O)^{2-}(aq)$ in aqueous sodium bicarbonate.

The existence of ring-opened species is supported by the infrared spectra[4] of both solid samples and aqueous solutions of $K_3[Co(CO_3)_3]\cdot 3H_2O$, which contain more absorption bands than are found in the ir spectra of anhydrous salts, e.g., $[Co(en)_3][Co(CO_3)_3]$, whose stoichiometry demands the existence of fully chelated carbonate. In addition, the stoichiometry of the reaction with pyridine indicates that two cis positions in the cobalt(III) reactant are much more readily substituted than are the other four at $8 \leq pH \leq 10$. It is worth noting in this regard that the synthesis[20] of the more highly substituted carbonatopyridinecobalt(III) complex $Co(py)_3(CO_3)Cl$ requires addition of a mixture of pyridine and HCl (molar ratio 1:2.8) to the Field–Durrant solution. Ring opening in $Co(py)_4CO_3{}^+$ is very slow even at $[H^+] = 5.00$ M.[21]

We now turn to specific kinetic aspects of the proposed reaction mechanism. Reaction 4 is postulated to involve a rapid, overall equilibrium between the two species $Co(CO_3)_3{}^{3-}$ and $Co(CO_3)_2(HCO_3)(H_2O)^{2-}$; the proton-assisted formation of the latter complex involves ring opening and protonation, but the order in which these processes occur is unknown.[3] However, Dasgupta and Harris[22] have measured the rate constants k_4, k_5, and k_6 for the overall processes 12–14, where

$$Co(NTA)CO_3{}^{2-} + H_2O \xrightarrow{k_4} Co(NTA)(OH)(HCO_3)^{2-} \tag{12}$$

$$Co(NTA)CO_3{}^{2-} + H_3O^+ \xrightarrow{k_5} Co(NTA)(H_2O)(HCO_3)^- \tag{13}$$

$$Co(NTA)(H_2O)(HCO_3)^- \xrightarrow{k_6} Co(NTA)(H_2O)(OH)^- + CO_2 \tag{14}$$

NTA is the nitrilotriacetate ion and $Co(NTA)CO_3{}^{2-}$ contains a chelated carbonate ligand. Steps 13 and 14 are formally analogous to those postulated in the tris(carbonato)cobaltate(III) system.

The magnitudes of these measured rate constants[22] ($(3.00 \pm 0.80) \times 10^{-3}$ s^{-1}, 41.9 ± 0.8 M^{-1} s^{-1}, and 51.7 ± 2.5 s^{-1}, respectively, at 25.0 °C) are much greater than those for analogous processes at cationic carbonatocobalt(III) centers; since the rate of reaction of the green reactants with pyridine is strictly second order, it would appear that the overall forward rates of reactions 4 and 5 are sufficiently great to prevent these processes from becoming rate determining.[23] However, since K_h is actually the product of equilibrium constants for ring opening and protonation of $Co(CO_3)_3{}^{3-}$ and since K_{H_2O} is only available as an upper limit, we cannot come to any firm conclusions concerning the actual rates of interconversion in reactions 4 and 5. The only definite requirement would seem to be that these processes occur at significantly higher rates than does substitution by pyridine under our experimental conditions.

The assignment of the kinetic $[H^+]$ and $[HCO_3^-]$ dependences of the pyridine reaction in terms of equilibria 4 and 5 is further supported by the observation of very low reaction rates at high pH, i.e., under conditions which favor $Co(CO_3)_3{}^{3-}$. The fully chelated species is expected to be much more inert to substitution than are $Co(CO_3)_2XY^{n-}$ (X, Y = H_2O or HCO_3^-) complexes. However, high-pH conditions also decrease $[HCO_3^-]$, which, according to the postulated equilibria, also favor the formation of $Co(CO_3)_2(H_2O)_2{}^-$. Although the latter species is never analytically significant under our conditions, it should be emphasized again that spectral and kinetic data at pH $\gtrsim 10$ (such as that for the filled circle in Figure 2 at pH 10.2) are often made comparatively uncertain by the slow formation of varying amounts of insoluble material, which could well be formed by dimerization of $Co(CO_3)_2(H_2O)_2{}^-$ species.[8]

The most readily substituted carbonatocobaltate(III) centers would appear to be those which contain one coordinated pyridine ligand. The indication that $k_2 >> k_1$ suggests that aquo ligands are more readily replaced by pyridine than is inner-sphere bicarbonate, although this conclusion must be tentative because different centers ($Co(CO_3)_2(HCO_3)(H_2O)^{2-}$ and $Co(CO_3)_2(H_2O)_2{}^-$) are being compared. However, the conclusion that replacement of water, rather than bicarbonate, predominates in the reaction of $Co(CO_3)_2(HCO_3)(H_2O)^{2-}$ with pyridine is mildly supported by direct observation of HCO_3^- loss from the half-bonded bis(carbonato)ethylenediaminecobaltate(III) complex $Co(CO_3)_2(en)(HCO_3)^{2-}$.[25]

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Registry No. $Co(CO_3)_3{}^{3-}$, 15245-10-0; $Co(CO_3)_2(HCO_3)(H_2O)^{2-}$, 57918-79-3; $Co(CO_3)_2(H_2O)_2{}^-$, 57918-80-6; $Co(CO_3)_2(CO_3)(py)^{3-}$, 57918-81-7; $Co(CO_3)_2(HCO_3)(py)^{2-}$, 57918-82-8; $Co(CO_3)_2(H_2O)(py)^-$, 57918-83-9; $K[Co(CO_3)_2(py)_2]$, 54967-61-2; py, 110-86-1.

References and Notes

(1) This work was supported by a Cottrell Grant from the Research Corp., which is gratefully acknowledged.

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(23) The complex $Co(NTA)CO_3{}^{2-}$ contains four- and five-membered chelate rings while those in $Co(CO_3)_3{}^{3-}$ are all four-membered. If the relief of steric strain[3,24] is an important factor favoring the opening of a chelate ring in $Co(CO_3)_3{}^{3-}$, then the forward rate constant for reaction 4 might be expected to be even higher than that for the analogous process in $Co(NTA)(CO_3)^{2-}$ (reaction 13).[22]

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