Table III. Stability Constants of Co(III) Complexes at $I = 0.1$, 25 °C

Co(III) complex	log $(K_{Co^{III}L}/K_{Co^{II}L})$	log $K_{Co^{II}L}$	log $K_{Co^{III}L}$
[Co(edta)]$^-$	24.89	16.03[a-c]	40.92
[Co(trdta)]$^-$	26.31	15.39[a,c,d]	41.70
[Co(tdta)]$^-$	22.0	15.58[a,c,d]	37.6
[Co(pdta)]$^-$	25.01	17.40[e]	42.41
[Co(ms-bdta)]$^-$	25.49	16.9[f]	42.4
[Co(cydta)]$^-$	25.20	18.73[a,b,g]	43.93
[Co(dpot)]$^-$	25.35	13.92[h]	39.27
[Co(hedtra)(H$_2$O)]	22.65	14.8[i]	37.5

[a] Calculated from the value of $K_{Co^{II}L}$ at 20 °C, $I = 0.1$ by use of the $\Delta H°$ value. [b] Schwarzenbach, G.; Gut, R.; Anderegg, G. *Helv. Chim. Acta* **1954**, *37*, 937. [c] Anderegg, G. *Ibid.* **1964**, *47*, 1801. [d] L'Eplattenier, F.; Anderegg, G. *Ibid.* **1964**, *47*, 1792. [e] Ogino, H. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 771. [f] Calculated from the value of $K_{Co^{II}L}$ at 20 °C, $I = 0.1$ (Majer, J.; Novak, V.; Svicekowa, M. *Chem. Zvesti* **1964**, *18*, 481). The $\Delta H°$ value was estimated by the present authors. [g] Anderegg, G. *Helv. Chim. Acta* **1963**, *46*, 1833. [h] Thompson, L. C.; Kundra, S. K. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2945. [i] Calculated from the value of $K_{Co^{II}L}$ at 30 °C, $I = 0.1$ (Chaberek, S., Jr.; Martell, A. E. *J. Am. Chem. Soc.* **1955**, *77*, 1477). The $\Delta H°$ value was estimated by the present authors.

magnitude of free energies of (aminopolycarboxylato)cobalt(III/II) couples is the entropies, which in turn are dependent primarily on the charge of the complexes.

Quite recently, the enthalpy of the oxidation reaction of [Co^{II}(edta)]$^{2-}$ by MnO$_4^-$ was determined by a direct thermometric titration to be −101.4 kJ mol^{-1} by Doi.[28] The thermodynamic parameters of reaction 5 were also calculated by combining the $\Delta H°$ value of the oxidation reaction of [Co(edta)]$^{2-}$ by MnO$_4^-$ with those of related reactions, the results obtained by the nonelectrochemical method being $\Delta G° = −37.1$ kJ mol^{-1}, $\Delta H° = −69.9$ kJ mol^{-1}, and $\Delta S° = −110$ J K^{-1} mol^{-1} at $I = 0.1$, 25 °C. These are in a reasonably good agreement with those in Table II, supporting the validity of

the experimental procedure employed in this work.

D. Stability Constants of Co(III) Complexes. The number of stability constants reported for cobalt(III) complexes is limited because of the experimental difficulty due to the inertness of the cobalt(III) complexes. As the formal potentials of (aminopolycarboxylato)cobalt(III/II) couples were determined (Table II), the stability constants of the cobalt(III) complexes, $K_{Co^{III}L}$, can be caluclated by using the redox potential of Co(aq)$^{3+}$/Co(aq)$^{2+}$ [29] and the stability constants of the cobalt(II) complexes, $K_{Co^{II}L}$. The results are summarized in Table III. It is seen that the stability order is almost parallel for Co(III) and Co(II) complexes of tetraacetate, though the order is reversed for the edta and the trdta complexes.[23] The $K_{Co^{III}L}$ values of triacetato complexes were not obtained except for that of the hedtra complex because of the absence of the $K_{Co^{II}L}$ data. The stability constant of [Co^{III}(hedtra)(H$_2$O)] is much smaller than that of [Co^{III}(edta)]$^-$ as compared with the stability constants of the cobalt(II) complexes. The relative destabilization of the Co(III) complex of the triacetate is manifested in its more negative $\Delta G°$ value. As has been stated in the previous section, the magnitude of $\Delta G°$ is governed by the entropy term; that is to say, the relative destabilization of the (triacetato)cobalt(III) complex compared with (tetraacetato)cobaltate(III) complexes is attributable to the effect of the entropy, which is governed mainly by the charge of the complexes.

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Rates of Decarboxylation of the Bis(carbonato)(ethylenediamine)cobaltate(III) Ion in Phosphoric Acid Buffer Solutions and Aqueous Perchloric Acid

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The kinetics of the complete decarboxylation of the bis(carbonato) complexes K[Co(en)(CO$_3$)$_2$]·H$_2$O and Na[Co(en)(CO$_3$)$_2$]·H$_2$O in aqueous acidic solutions have been investigated. The interpretation of the data is that only the second decarboxylation has been studied at the experimental conditions. The rate data for the ring-opening step that is related to the loss of the second CO$_2$ from the title complex are described by a pseudo-first-order rate constant of the form $k_{obsd} = k_a + k_b[H_3O^+]$. Rate parameters at 5 °C and $I = 1.0$ M (NaClO$_4$) are $k_a = (5.7 \pm 1.0) \times 10^{-4}$ s^{-1} and $k_b = (4.37 \pm 0.12) \times 10^{-2}$ M^{-1} s^{-1} with activation parameters for the acid-catalyzed pathway of $\Delta H_b^* = 12 \pm 2$ kcal mol^{-1} and $\Delta S_b^* = -21 \pm 8$ cal deg^{-1} mol^{-1}. An induction period noted during the decarboxylation reaction is ascribed to the formation of the ring-opened monodentate carbonato aquo species Co(en)(CO$_3$)(HCO$_3$)(H$_2$O) or Co(en)(HCO$_3$)(H$_2$O)$_3$$^{2+}$. We have been unable to isolate a stable bidentate Co(en)(CO$_3$)(H$_2$O)$_2$$^+$ intermediate as has been found for the analogous pyridine complex. The kinetic results are compared with those for the decarboxylation of other mono(carbonato)cobalt(III) and bis(carbonato)cobaltate(III) complexes.

Introduction

Bidentate carbonato complexes decarboxylate at rates that are quite sensitive to the nature of the "nonparticipating" ligands, metal center, and charge on the complex itself.[1,2]

Indeed, reported rate constants for the acid-catalyzed ring-opening step vary over approximately 7 orders of magnitude,

(1) There have been numerous studies. Reference 2 is a recent investigation and cites much of the previous work.

Table I. Spectral Data for the Reactant Bis(carbonato)(ethylenediamine)cobaltate(III) Anion and the Product Tetraaquo(ethylenediamine)cobalt(III) Cation

medium^a	λ_{max} $(\epsilon)^b$	λ_{max} (ϵ)	ref
	$Co(en)(CO_3)_2^-$		
1 M NaHCO$_3$	570 (148)	390 (214)	8
water?	567 (159)	394 (164)	6
water?	565 (148)	386 (213)	7
water^c	568 (154)	395 (173)	this work^d
	$Co(en)(H_2O)_4^{3+}$		
~0.1 M HClO$_4$	511 (44)	367 (32)	8
~0.05 M HClO$_4$	510 (59)	373 (49)	6
1 M HClO$_4$ ^{c}	516 (50.0)	378 (43.1)	this work^d

^{a} Solution prepared by use of the potassium salt unless indicated otherwise. ^{b} All wavelengths in nm and extinction coefficients in M^{-1} cm^{-1}. ^{c} The sodium salt of the complex anion was used to prepare the solution. ^{d} The extinction coefficients are calculated from cobalt(III) concentrations determined by analyses[5] of the solutions.

and it appears that, for the *total* series of carbonato complexes, the factors that affect reactivity are not amenable to simple correlation.[2,3]

The decarboxylation reactions of bis(carbonato) complexes have been investigated only recently.[3-5] The loss of carbon dioxide from the bidentate bis(carbonato) complex $Co(py)_2(CO_3)_2^-$ occurs in two distinct decarboxylation processes, both of which may be studied independently.[3,5] In contrast to this observation, the loss of both carbon dioxide molecules from a monodentate bis(carbonato) complex appears to be simultaneous.[4]

In the present study, we have investigated the decarboxylation reactions of the triply bidentate bis(carbonato) complex $Co(en)(CO_3)_2^-$. The stable intermediate mono(carbonato) complex $Co(en)(CO_3)(H_2O)_2^+$ was not isolated as it had been for the corresponding pyridine complex, $Co(py)_2(CO_3)_2^-$. An interesting aspect of the current work is that at certain experimental conditions the usual first-order plots of ln (A_t – A_∞) vs. time are initially nonlinear. This spectral evidence and some limited kinetic evidence tend to support the existence of a transient ring-opened (bicarbonato)aquocobalt(III) complex, $Co(en)(CO_3)(HCO_3)(H_2O)$ or $Co(en)(HCO_3)(H_2O)_3^{2+}$.

Experimental Section

Preparative Methods. Crystals of $K[Co(en)(CO_3)_2]\cdot H_2O$ were prepared by the procedure reported by Rowan, Storm, and Hunt.[6] Our minor modification of this procedure was that ethanol was used to precipitate the product from the eluate of the cation-exchange column. Several additional recrystallizations of the initial product were required to obtain adequate purity. A comparison of the spectral parameters of an aqueous solution of the potassium salt with those previously reported[6] indicated good agreement with regard to positions of the wavelength maxima in the visible region, but our calculated extinction coefficients, based on an independent cobalt(III) analysis, tended to be approximately 10% higher at the longer wavelength. See Table I for the experimental spectral parameters of the bis(carbonato) complex.

A new synthesis for the desired anionic complex was developed that produced the sodium salt and avoided the presence of the KHCO$_3$ contaminant that was present during the synthesis of the potassium

salt. The procedure is a combination of portions of several reports[6-8] and involves the addition of the carbamate of ethylenediamine to $Na_3Co(CO_3)_3\cdot 3H_2O$.[9] The carbamate of ethylenediamine was prepared by the method of Jensen and Christensen.[10] The carbamate was washed by swirling the crude solid with several portions of 95% ethanol. Each time, the solid was collected by filtration. This procedure was followed by several similar washings with anhydrous ether. The isolated white powder was stored in a desiccator and showed no discoloration after several months.

The desired $Na[Co(en)(CO_3)_2]\cdot H_2O$ product was prepared by slowly adding 12.9 g (0.05 mol) of the carbamate to a 0 °C slurry of 36.2 g (0.10 mol) of $Na_3[Co(CO_3)_3]\cdot 3H_2O$ in 175 mL of water. The reaction mixture was stirred at 0 °C for 3 h, stirred at 40 °C for an additional 2.5 h, cooled to room temperature, and filtered. The filtrate volume was reduced to 75 mL by use of a rotary evaporator. This solution was filtered and charged onto a cation-exchange column (Dowex 50W-X2 resin, approximately 50 cm in length and 3 cm in diameter) in the Na$^+$ form and eluted with water. The column acted to retain the cationic side product $Co(en)_2CO_3^+$. Approximately 150 mL of a dark blue eluate was collected, and its volume was reduced to about 30 mL by the rotary evaporator. A 2-mL portion of absolute ethanol was added, and the mixture was allowed to stand overnight. An impure purple-white solid was obtained upon filtration and discarded. Additions of larger volumes of absolute ethanol tended to produce oils. The second addition of 2 mL of absolute ethanol produced a reddish purple product. This solid was analyzed and found to contain carbonate but no ethylenediamine. It was water insoluble, and no further attempts were made to identify it. Additional 2-mL portions of absolute ethanol added to the solution produced crystals of the desired $Na[Co(en)(CO_3)_2]\cdot H_2O$ product. These crystals were further purified by dissolving in the minimum amount of water and reprecipitating by the dropwise addition of about 1 mL of absolute ethanol. Only one recrystallization was required. Yield of the purified $Na[Co(en)(CO_3)_2]\cdot H_2O$ product was low but comparable to that obtained for the corresponding potassium salt. Anal. Calcd for $Na[Co(en)(CO_3)_2]\cdot H_2O$: C, 17.15; H, 2.88; N, 10.00; Co, 21.04. Found:[5,11] C, 17.23; H, 3.40; N, 10.01; Co, 20.00.

The UV–visible spectral maxima of both the reactant carbonato complex $Na[Co(en)(CO_3)_2]\cdot H_2O$ and the expected final decarboxylation product $Co(en)(H_2O)_4^{3+}$ are reported in Table I. The spectrum of this latter ion was obtained by dissolving an appropriate amount of the carbonato complex in 1 M HClO$_4$. Rapid decarboxylation occurred, and the desired aquo complex was stable toward reduction in the 1 M HClO$_4$ medium. Spectra of both complexes were recorded on a Bausch & Lomb Spec 2000.

Kinetic Experiments. Absorbance–time measurements were obtained at 570 nm on decomposing solutions of the bis(carbonato) complex by use of a Cary 14 spectrophotometer with a thermostated cell holder. Dry nitrogen was passed through the cell compartment if fogging of the cell windows was observed during low-temperature kinetic runs. A kinetic run was initiated by adding a weighed quantity of the sodium or potassium salt of the $Co(en)(CO_3)_2^-$ anion into a thermostated cell that contained a solution of perchloric acid or phosphoric acid buffer at the appropriate temperature, acidity, and ionic strength. Absorbance–time data were obtained immediately after stirring to dissolve the solid. For the fastest reactions it was necessary to add and stir the solid into the reaction medium concurrent with the spectrometer operating in the absorbance–time drive mode. This permitted reactions with half-lives up to about 1 min to be monitored.

In our initial studies at 0 °C and in perchloric acid solutions with complex concentrations about 5×10^{-3} M, the decarboxylation reaction was experimentally inconvenient outside the hydrogen ion concentration range described by 0.10 M < [H$_3$O$^+$] < 0.25 M. At higher acidities the reaction was too fast to study by our conventional techniques, and at lower acidities a change in the pH of the reaction mixture by approximately 0.5 pH unit was observed to occur during the decarboxylation reaction. This latter observation indicated that perchloric

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(3) Hyde, K. E.; Fairchild, G. H.; Harris, G. M. *Inorg. Chem.* **1976**, *15*, 2631.
(4) van Eldik, R.; Palmer, D. A.; Kelm, H.; Harris, G. M. *Inorg. Chem.* **1980**, *19*, 3679.
(5) Hyde, K. E.; Hyde, E. W.; Moryl, J.; Baltus, R.; Harris, G. M. *Inorg. Chem.* **1980**, *19*, 1603.
(6) Rowan, N.; Storm, C. B.; Hunt, J. B. *Inorg. Chem.* **1978**, *17*, 2853.

(7) Mori, M.; Shibata, M.; Kyuno, E.; Hoshiyama, K. *Bull. Chem. Soc. Jpn.* **1958**, *31*, 291.
(8) Davies, G.; Hung, Y. *Inorg. Chem.* **1976**, *15*, 1358.
(9) Bauer, H. F.; Drinkard, W. C. *J. Am. Chem. Soc.* **1960**, *82*, 5031.
(10) Jensen, A.; Christensen, R. *Acta Chem. Scand.* **1955**, *9*, 486.
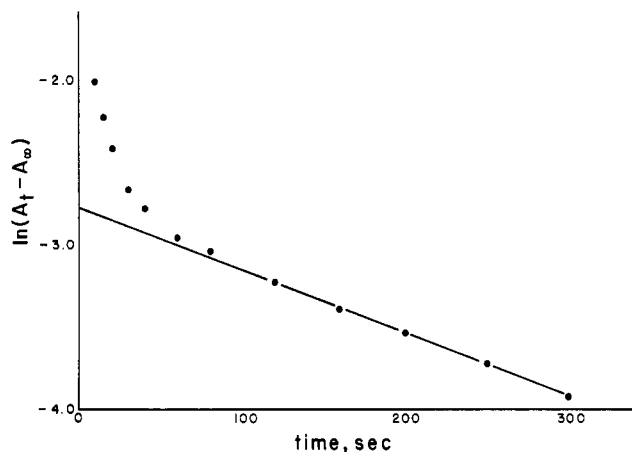(11) Analyses for C, H, and N by Galbraith Laboratories, Inc., Knoxville, TN.

Figure 1. Plot of ln $(A_t - A_\infty)$ for selected points obtained from the experimental absorbance vs. time curve for the total decarboxylation of the $Co(en)(CO_3)_2^-$ ion at 0 °C and $[H^+]$ = 0.145 M (phosphoric acid buffer) with I = 1.0 M $(NaClO_4)$. The straight-line result from the linear-regression analysis of data points obtained at times greater than 60 s has a slope of $-k$(slow). The difference between the line and the data at times less than 60 s may be used to obtain k(fast).

acid at this concentration and for this reaction stoichiometry was not self-buffering. A phosphoric acid buffer system of appropriate capacity was used to extend the kinetic studies to solutions with hydrogen ion concentrations as low as 0.01 M. Attempts to obtain kinetic data for the decarboxylation reaction at still lower acidities provided by a mixed phosphate/citrate buffer were unsuccessful since the spectrum of the final product was not that of the product $Co(en)(H_2O)_4^{3+}$ ion. These results may be attributed to the polymerization[6] of the aquo ion in solutions with the higher pH values and/or the anation of the aquo ion.[6]

The experimental absorbance–time data at 570 nm were computer fitted, with first-order kinetics assumed, to obtain both an observed rate constant and a calculated value of A_∞. This procedure produced an A_∞ value that was within 5% or less of the experimentally observed absorbance measured after several hours. At the lowest temperature and acidities, plots of log $(A_t - A_\infty)$ vs. time clearly indicated an initial curvature before the expected linear behavior. This behavior is illustrated in Figure 1 and is reminiscent of that expected for a consecutive reaction sequence. An attempt was made to extract rate parameters for the faster reaction by computer fitting the absorbance–time data to the functional form expected for a consecutive first-order process.[12]

pH Measurements and Solution Acidities. A double-junction Orion Model 90-02-00 reference electrode and a Corning Triple Purpose Ag/AgCl pH electrode were calibrated to read true hydrogen ion concentrations by use of 0.1 and 0.01 M $HClO_4$ solutions brought to a constant ionic strength of 1.0 with $NaClO_4$. The response of the electrode appeared to be linear in this region. All pH measurements were recorded on an Orion Model 611 digital pH meter.

Phosphoric acid buffer solutions with an ionic strength of 1.0 M and with hydrogen ion concentrations in the range 0.10–0.010 M were prepared by mixing a known quantity of a standardized phosphoric acid solution with standard sodium hydroxide and sodium perchlorate solutions and water. Accurate hydrogen ion concentrations of the buffer solutions were determined at 0, 5, 10, and 20 °C by pH measurements with the meter calibrated as described above. In addition to providing accurate measurements of the true hydrogen ion concentration of the phosphate buffer solution, the data provided values for the first dissociation constant (K_1) of phosphoric acid at I = 1.0 $(NaClO_4)$. The average values of K_1 at 0, 10, and 20 °C are 0.049, 0.039, and 0.029, respectively. A plot of ln K_1 vs. temperature is linear, and $\Delta H°$ = −4.3 kcal/mol may be obtained from the slope. Our relatively crude results are in reasonable agreement with the values predicted by the nine-parameter expression of Mesmer and Baes.[13]

Table II. Observed Rate Constants for the Fast Step in the Total Decarboxylation of the $Co(en)(CO_3)_2^-$ Ion in Phosphoric Acid Buffers at 0 °C[a]

$10^2[H_3O^+]$, M	1.3	4.9	8.1	14.5
10^2k_{obsd}, s^{-1}	4.7	6.8 ± 0.4	6.5 ± 0.6	8.1 ± 0.8

[a] Except for the value at $[H^+]$ = 0.013 M, the k_{obsd} values represent the average of three or more determinations. The uncertainties represent the calculated standard deviations.
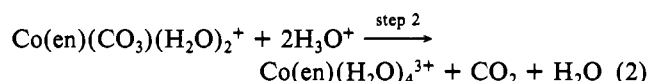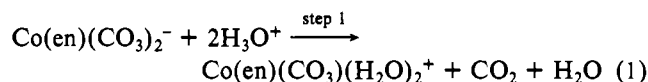
Results

Two points seem particularly pertinent in summarizing the kinetic results. First, for the 0 °C runs at higher acidities, an induction period persisted long enough to encourage treatment of the rate data with a consecutive first-order model. This procedure has been used successfully to obtain rate constants for the decarboxylation and reduction steps in the total decomposition of the cis-$Co(py)_2(CO_3)_2^-$ ion.[2,5] In the present case the induction period was of short duration and convergence of our nonlinear least-squares computer program for series first-order reactions was obtained when k(slow) was fixed at a value obtained from simple first-order treatment of data after the induction period terminated. This procedure permitted an estimation of k(fast) and ϵ_B (the extinction coefficient at 570 nm of the presumed intermediate). The values of k(fast) at several different acidities are shown in Table II. The average of ϵ_B is 55 ± 5 M^{-1} cm^{-1}, based on 11 determinations.

Second, after the induction period all kinetic runs produced absorbance–time data consistent with a first-order reaction. Plots of ln $(A_t - A_\infty)$ were linear over at least 3 half-lives, and pseudo-first-order rate constants, k(slow), could be obtained from the slopes of such plots. These observed rate constants are collected in Table III. At 0 °C, kinetic data were collected in both perchloric acid and phosphoric acid/dihydrogen phosphate buffer solutions. The table indicates that good agreement exists between the rate constants determined in the two different media. Likewise, the results are not dependent on whether the sodium or the potassium salt was used as the source of the $Co(en)(CO_3)_2^-$ anion.

Discussion

The reaction stoichiometry, observed within the time frame of our experiments on the decomposition of the $Co(en)(CO_3)_2^-$ ion in solutions with pH <2, corresponds to the loss of both carbonate ligands from the reactant. By analogy with previous reports[2,5] on the similar $Co(py)_2(CO_3)_2^-$ complex, the decarboxylation is expected to occur in two distinct steps:

$$Co(en)(CO_3)_2^- + 2H_3O^+ \xrightarrow{\text{step 1}}$$
$$Co(en)(CO_3)(H_2O)_2^+ + CO_2 + H_2O \quad (1)$$

$$Co(en)(CO_3)(H_2O)_2^+ + 2H_3O^+ \xrightarrow{\text{step 2}}$$
$$Co(en)(H_2O)_4^{3+} + CO_2 + H_2O \quad (2)$$

Whether or not both steps are individually observable will depend on the nature of the complex and the range of experimental conditions investigated. In addition, viewing each decarboxylation step as containing only a single rate-determining mechanistic step may be an oversimplification.
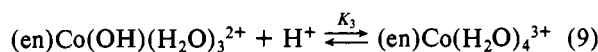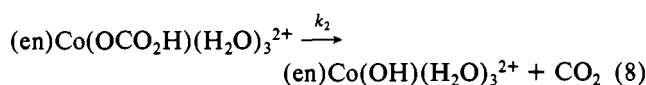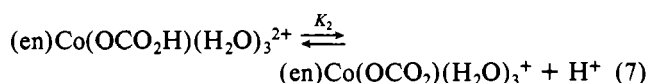
Our observations may be discussed with reference to the well-established mechanism[3,14] for the decarboxylation of a chelated carbonato complex. This mechanism is shown after step 1 in Scheme I, where k_0 and k_1 control the parallel and

(12) Wilkins, R. G. "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes"; Allyn and Bacon: Boston, MA, 1974; p 22.

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(14) Hyde, K. E.; Harris, G. M. *Inorg. Chem.* **1978**, *17*, 1892.

Scheme I

$$(en)Co(CO_3)_2^- + 2H_3O^+ \xrightarrow{\text{(step 1)}}$$
$$(en)Co(O_2CO)(H_2O)_2^+ + CO_2 + H_2O \quad (3)$$

$$(en)Co(O_2CO)(H_2O)_2^+ + H_2O \xrightarrow{k_0}$$
$$(en)Co(OCO_2)(H_2O)_3^+ \quad (4)$$

$$(en)Co(O_2CO)(H_2O)_2^+ + H^+ \underset{}{\overset{K_1}{\rightleftarrows}}$$
$$(en)Co(O_2COH)(H_2O)_2^{2+} \quad (5)$$

$$(en)Co(O_2COH)(H_2O)_2^{2+} + H_2O \xrightarrow{k_1}$$
$$(en)Co(OCO_2H)(H_2O)_3^{2+} \quad (6)$$

$$(en)Co(OCO_2H)(H_2O)_3^{2+} \underset{}{\overset{K_2}{\rightleftarrows}}$$
$$(en)Co(OCO_2)(H_2O)_3^+ + H^+ \quad (7)$$

$$(en)Co(OCO_2H)(H_2O)_3^{2+} \xrightarrow{k_2}$$
$$(en)Co(OH)(H_2O)_3^{2+} + CO_2 \quad (8)$$

$$(en)Co(OH)(H_2O)_3^{2+} + H^+ \underset{}{\overset{K_3}{\rightleftarrows}} (en)Co(H_2O)_4^{3+} \quad (9)$$
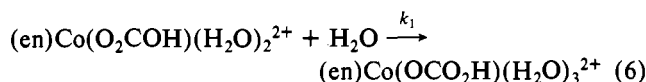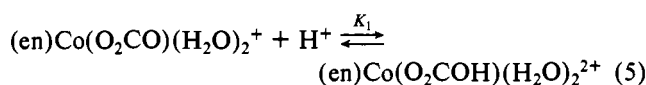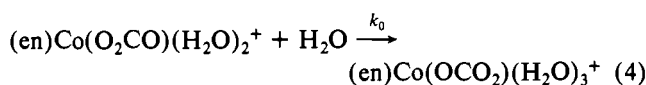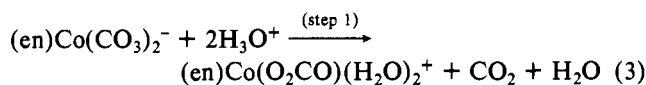
rate-determining ring-opening mechanistic steps and k_2 is *usually* the relatively rapid carbon–oxygen bond-breaking decarboxylation step. When k_2 is relatively fast, simple first-order kinetics are observed in buffered solutions and the pseudo-first-order rate constant should have the form[14] shown in eq 10. Our experimental conditions are such that $1 \gg$

$$k_{obsd} = \frac{k_0 + k_1 K_1 [H^+]}{1 + K_1 [H^+]} \quad (10)$$

$K_1 [H^+]$; thus, eq 10 reduces to eq 11.

$$k_{obsd} = k_0 + k_1 K_1 [H^+] \quad (11)$$

A similar detailed mechanism could be given for step 1 (eq 1, or eq 3 in Scheme I), but we consider the first decarboxylation to be much faster than the second and hence summarize the net result as step 1. For the only other bidentate bis(carbonato)cobaltate(III) complex that has been investigated,[2,5] the rate of the first ring-opening reaction, at a particular acidity, is approximately 4 orders of magnitude greater than the rate of the second (i.e., $[k_b(\text{step } 1)/k_b(\text{step } 2)] \sim 10^4$ where k_b's are experimental rate constants and are related to the mechanistic steps as $k_b = k_1 K_1$). In the discussion that follows, we will consider and evaluate the possibility that other mechanistic steps within the net first decarboxylation are kinetically significant.

The observation of an induction period during the production of the totally decarboxylated $Co(en)(H_2O)_4^{3+}$ is consistent with the formation of a transient intermediate. Probable intermediates are $Co(en)(CO_3)(H_2O)_2^+$ (a bidentate mono(carbonato) complex) and $Co(en)(CO_3)(HCO_3)(H_2O)$ or $Co(en)(HCO_3)(H_2O)_3^{2+}$ (monodentate bicarbonato complexes). The former type of intermediate has been isolated and characterized in solution during the two-step decarboxylation of the $Co(py)_2(CO_3)_2^-$ ion.[2] At our experimental conditions, such a bidentate carbonato intermediate would be expected[14] to undergo ring opening with a rate that is linearly dependent on the $[H_3O^+]$. The latter type of intermediate (aquo bicarbonato ring-opened species) is similar to the carbonato pentaamine complex[15] and has been identified during the decarboxylation of several chelated (tetraamine)(carbona-
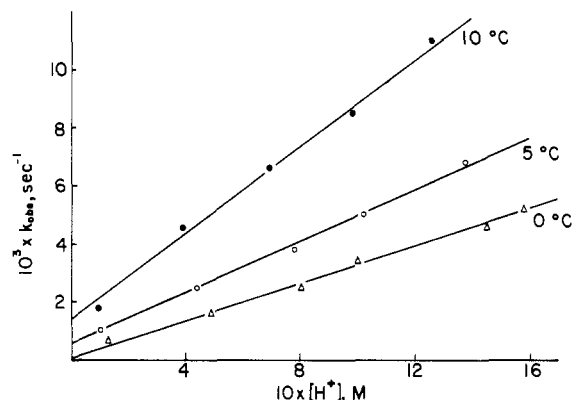

Figure 2. Plots of the average k_{obsd} vs. $[H_3O^+]$ for the slow step in the total decarboxylation of the $Co(en)(CO_3)_2^-$ ion at three temperatures, each with ionic strength $I = 1.0$ M.

to)metal(III) complex ions under high-acidity conditions.[16–18] Our concern here is to speculate on the identity of the intermediate responsible for the induction period observed during the low-temperature kinetic runs.

An examination of the observed rate constants in Table II for the faster reaction that occurs during the total decarboxylation suggests that the $[H_3O^+]$ dependence of the rate is minimal at best. The usual form[19] observed for ring opening of bidentate carbonato complexes ($k_{obsd} = k_a + k_b[H_3O^+]$, with $k_b/k_a \sim 10^3$) is not realized in the present study, and we consider this as evidence that the fast reaction cannot be assigned to a carbonato ring-opening reaction and that the doubly bidentate species $Co(en)(CO_3)_2^-$ is not kinetically significant. We assume that the data in Table II indicate that the observed rate constants are independent of acidity. This lack of a $[H_3O^+]$ dependence for the rate of the faster reaction suggests that it may involve, as a kinetically significant intermediate, ring-opened complexes formulated as $Co(en)-(CO_3)(HCO_3)(H_2O)$ or $Co(en)(HCO_3)(H_2O)_3^{2+}$. At the acidities used in the present investigation, bicarbonato complexes would decarboxylate at rates that are independent of the $[H_3O^+]$. Further evidence for this assignment comes from the realization that the activation parameters for the decarboxylation of protonated monodentate carbonato complexes are reasonably independent[4,20] of the nature of both the central metal(III) ion and the nonparticipating ligands. Values[21] of $\Delta H^* \sim 16.5 \pm 0.5$ kcal/mol and $\Delta S^* \sim -4.5 \pm 2.9$ cal/(mol K) are the average reported values with standard deviations for a series of monodentate (carbonato)(amine)cobalt(III) complexes. A typical decarboxylation rate constant (k_2 in the reaction mechanism) of $\sim 4 \times 10^{-2}$ s^{-1} at 0 °C may be estimated by use of these activation parameters. This value is the same order of magnitude as the $k_{obsd}(\text{fast})$ presented in Table II.

The kinetic analysis of the spectrophotometric data for our series first-order reaction results in the usual ambiguity.[22] The

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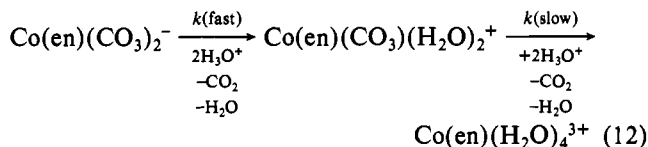(22) Espenson, J. H. "Chemical Kinetics and Reaction Mechanisms"; McGraw-Hill: New York, 1981; p 70.

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Table III. Observed Rate Constants (s^{-1}) for the Slow Step in the Total Decarboxylation of the [Co(en)(CO$_3$)$_2^-$]^a Ion in Perchloric Acid and Phosphoric Acid Buffer Solutions[b,c]

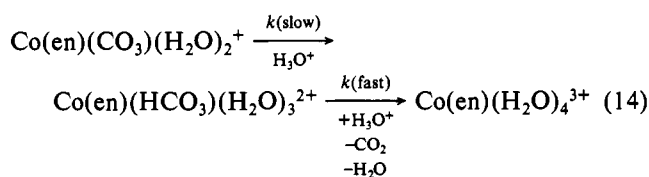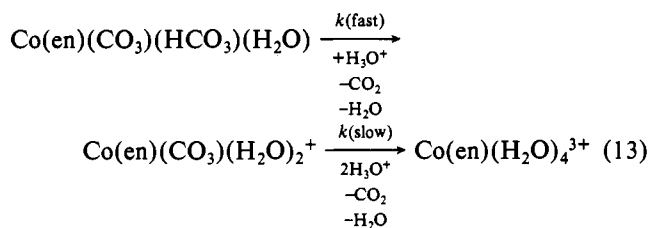|	0.0 °C		5.0 °C		10.0 °C	
	[H$_3$O$^+$]	10^3k_{obsd}	[H$_3$O$^+$]	10^3k_{obsd}	[H$_3$O$^+$]	10^3k_{obsd}
	0.251^d	8.37	0.138	6.75	0.126	11.1
	0.251^d	8.38	0.138	6.31	0.126	10.1
	0.158^d	5.02	0.138	6.45	0.126	10.2
	0.158^d	5.24	0.138	7.23	0.098	8.79
	0.158^d	5.07	0.102	5.06	0.098	8.41
	0.145	4.73	0.102	4.72	0.098	8.54
	0.145	4.42	0.102	5.29	0.098	8.25
	0.145	4.85	0.102	5.06	0.069	6.47
	0.100^d	3.38	0.078	3.48	0.069	6.87
	0.100^d	3.48	0.078	4.07	0.069	6.33
	0.081	2.75	0.078	3.95	0.069	7.10
	0.081	2.66	0.078	3.73	0.039	4.36
	0.081	2.30	0.043	2.55	0.039	4.35
	0.049	1.80	0.043	2.50	0.039	4.73
	0.049	1.52	0.043	2.41	0.039	4.39
	0.013	0.623	0.043	2.60	0.0098	1.83
	0.013	0.738	0.0095	0.998	0.0098	1.80
	0.013	0.593	0.0095	1.03	0.0098	1.64
			0.0095	1.01	0.0098	1.94
			0.0095	1.08		
k_a, s^{-1}	(9.4 ± 8.2) × 10^{-5}		(5.8 ± 1.0) × 10^{-4}		(1.36 ± 0.16) × 10^{-3}	
k_b, M^{-1} s^{-1}	(3.23 ± 0.06) × 10^{-2}		(4.37 ± 0.12) × 10^{-2}		(7.36 ± 0.20) × 10^{-2}	

$$\Delta H_{b\pm}^{\ddagger} = 12.1 \pm 2.1 \text{ kcal mol}^{-1}$$
$$\Delta S_b^{\ddagger} = -20.9 \pm 7.6 \text{ cal mol}^{-1} \text{ deg}^{-1}$$

^{a} The majority of the tabulated results refer to the sodium salt. At both 5 and 10 °C at least one run at each acidity was made with the potassium salt. No cation-dependent trends were observed. ^{b} $I = 1.0$ M (NaClO$_4$). All hydrogen ion concentrations as molarity. ^{c} The solution acidity was maintained by the phosphoric acid buffer system unless otherwise noted. ^{d} Solution acidity maintained by HClO$_4$ self-buffering.

first reaction need not be the fast reaction. The lack of an appreciable [H$_3$O$^+$] dependence for k(fast) would eliminate the case where ring opening is the rate-limiting mechanistic step in each decarboxylation reaction.

$$\text{Co(en)(CO}_3)_2^- \xrightarrow[\substack{2\text{H}_3\text{O}^+ \\ -\text{CO}_2 \\ -\text{H}_2\text{O}}]{k(\text{fast})} \text{Co(en)(CO}_3)(\text{H}_2\text{O})_2^+ \xrightarrow[\substack{+2\text{H}_3\text{O}^+ \\ -\text{CO}_2 \\ -\text{H}_2\text{O}}]{k(\text{slow})}$$

$$\text{Co(en)(H}_2\text{O})_4^{3+} \quad (12)$$

However, neither the lack of a [H$_3$O$^+$] dependence for k(fast) nor the magnitude of k(fast) serves to distinguish between the reactions in which a kinetically significant bicarbonato intermediate appears during the first (eq 13) or second (eq 14) decarboxylation steps.

$$\text{Co(en)(CO}_3)(\text{HCO}_3)(\text{H}_2\text{O}) \xrightarrow[\substack{+\text{H}_3\text{O}^+ \\ -\text{CO}_2 \\ -\text{H}_2\text{O}}]{k(\text{fast})}$$

$$\text{Co(en)(CO}_3)(\text{H}_2\text{O})_2^+ \xrightarrow[\substack{2\text{H}_3\text{O}^+ \\ -\text{CO}_2 \\ -\text{H}_2\text{O}}]{k(\text{slow})} \text{Co(en)(H}_2\text{O})_4^{3+} \quad (13)$$

$$\text{Co(en)(CO}_3)(\text{H}_2\text{O})_2^+ \xrightarrow[\text{H}_3\text{O}^+]{k(\text{slow})}$$

$$\text{Co(en)(HCO}_3)(\text{H}_2\text{O})_3^{2+} \xrightarrow[\substack{+\text{H}_3\text{O}^+ \\ -\text{CO}_2 \\ -\text{H}_2\text{O}}]{k(\text{fast})} \text{Co(en)(H}_2\text{O})_4^{3+} \quad (14)$$

The rate constants for the slow step in the consecutive sequence may be interpreted in a straightforward manner and are related to the ring opening of the bidentate mono(carbonato) complex Co(en)(CO$_3$)(H$_2$O)$_2^+$. The data in Table III reveal that the pseudo-first-order rate constants clearly increase with increasing [H$_3$O$^+$] at each temperature. Plots of k_{obsd} vs. [H$_3$O$^+$] are linear (see Figure 2) and thus are adequately

Table IV. Rate Parameters for the Acid-Catalyzed Decarboxylation of Co(en)(CO$_3$)$_2^-$ and Some Related Ring-Closed (Carbonato)metal(III) Complexes

complex species^a	I, M	k_b, s^{-1} M^{-1} ^{b}	$\Delta H_b^{\ddagger}$, kcal mol^{-1}	$\Delta S_b^{\ddagger}$, cal mol^{-1} deg^{-1}	ref
Co(en)(CO$_3$)(H$_2$O)$_2^+$	1.0	0.2	12 ± 2	−21 ± 8	this work
Co(en)$_2$(CO$_3$)$^+$	0.5	0.6	14 ± 1	−7 ± 3	23
Co(pn)$_2$(CO$_3$)$^+$	0.5	0.5	14 ± 3	−13 ± 9	23
Co(tn)$_2$(CO$_3$)$^+$	0.5	0.8	12 ± 4	−19 ± 9	23
Rh(en)$_2$(CO$_3$)$^+$	0.5	1.0 × 10^{-5}	25 ± 4	2 ± 11	20
Co(py)$_2$(CO$_3$)(H$_2$O)$_2^+$	1.0	3.4 × 10^{-4}	20 ± 1	−9 ± 4	2
Co(py)$_2$(CO$_3$)$_2$	0.5	5.9	17 ± 1	2 ± 4	5

^{a} Abbreviations used: en, ethylenediamine; pn, propylenediamine; tn, trimethylenediamine; py, pyridine. ^{b} Values listed are for 25 °C. If experimental results were not available at this temperature, then the activation parameters were used to calculate k_b at 25 °C.

described by the simple first-order hydrogen ion concentration dependence of eq 15. This is consistent with that expected

$$k_{obsd} = k_a + k_b[\text{H}_3\text{O}^+] \quad (15)$$

for the ring-opening step of a bidentate carbonato complex (eq 11 with $k_a = k_0$ and $k_b = k_1 K_1$). The values of k_a and k_b calculated from a linear-regression treatment of k_{obsd} vs. [H$_3$O$^+$] data at the various temperatures are listed at the bottom of Table III.

The activation parameters measured in the present study and assigned to the ring-opening step that occurs during the decarboxylation of the Co(en)(CO$_3$)(H$_2$O)$_2^+$ ion are presented at the bottom of Table III. The values of $\Delta H_b^{\ddagger} = 12$ kcal/mol and $\Delta S^{\ddagger} = -21$ cal/(mol K) are at the low end of the range of values previously observed for the decarboxylation of bidentate carbonato complexes ($\Delta H_b^{\ddagger} = 11$–34 kcal/mol and

$\Delta S_b^{\ddagger}$ = -20 to +26 cal/(mol K)].[2] For discussion purposes, rate parameters for the decarboxylation of the Co(en)-$(CO_3)(H_2O)_2^+$ and a few related complexes are presented in Table IV. Within the limits of experimental uncertainty, the parameters for the $Co(en)(CO_3)(H_2O)_2^+$ complex are identical with those of the (carbonato)bis(alkylamine) complexes Co-$(en)_2CO_3^+$, $Co(pn)_2CO_3^+$, and $Co(tn)_2CO_3^+$. This implies that the ring-opening mechanistic step is not much affected by the replacement of the nitrogen donor atoms of simple alkylamines by the oxygen donor atoms of simple ligands. If this implication is correct, then it is possible to rationalize the other entries in Table IV. The $Rh(en)_2(CO_3)^+$ complex is considerably less reactive than $Co(en)(CO_3)(H_2O)_2^+$ or the carbonato bis(alkylamine) complexes because of the enhanced strength of the metal–oxygen bond in the rhodium complex.

The $Co(py)_2CO_3(H_2O)_2^+$ ion is less reactive than the corresponding ethylenediamine complex because amine ligands with π systems tend to decarboxylate at very slow rates.[2] For the $Co(py)_2(CO_3)_2^-$ complex, the reduced rates expected by the presence of ligand pyridine are offset by the enhancement due to a negative charge on the complex and the possible straining of the metal–oxygen bond that is related to the presence of two carbonate chelate rings and two bulky pyridine molecules.

Metal Complex Catalysts Interlayered in Smectite Clay. Hydroformylation of 1-Hexene with Rhodium Complexes Ion Exchanged into Hectorite
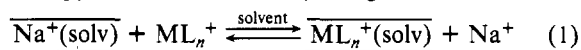
FAEZEH FARZANEH and THOMAS J. PINNAVAIA*

The cationic hydroformylation catalyst precursor $Rh(COD)(PPh_3)_2^+$, where COD = 1,5-cyclooctadiene, readily intercalates into the swelling layered silicate clay mineral hectorite by replacement of Na^+ ions initially present on the interlamellar surfaces. Under hydroformylation conditions, however, the active rhodium complex desorbs from the clay interlayers due to the formation of neutral $RhH(CO)_x(PPh_3)_2$ (x = 1, 2) species. Rhodium complexes containing the positively charged phosphinophosphonium ligand $Ph_2P(CH_2)_2^+PPh_2(CH_2Ph)$, abbreviated P–P+, are shown to be much more suitable for catalyst intercalation. $[Rh(COD)Cl]_2$, $[Rh(CO)_2Cl]_2$, and $Rh(COD)^+$ all form cationic complexes with P–P+ which bind to the clay interlayers and catalyze the hydroformylation of 1-hexene at 100 °C and 600 psi CO/H_2 when acetone is the solvating medium. Under these conditions, >95% of the 1-hexene is hydroformylated in the clay interlayers. The ratios of normal- to branched-chain aldehydes (n/b) are somewhat higher for the intercalated catalysts (2.4–3.0) than for the homogeneous catalysts under analogous conditions (1.5–2.1). In addition, the intercalated catalyst tends to lower the extent of 1-hexene isomerization relative to homogeneous solution. Spatial factors may influence the relative stabilities of primary and secondary metal alkyls formed as intermediates in the restricted interlayer regions of the layered silicate. The polarity of the solvating medium is important in promoting hydroformylation in the interlayer regions of the intercalated clay catalysts. No hydroformylation activity is observed for the intercalated catalyst in benzene, since this solvent fails to swell the hectorite interlayers and provide access to the metal centers. Solvation by DMF causes extensive dissociation of Rh–(P–P+) bonds in the clay interlayers and loss of a neutral rhodium carbonyl to solution.

Introduction

Earlier reports from our laboratory[1-3] have demonstrated that metal complex catalysts can be immobilized by intercalation in swelling layered silicate clay minerals such as montmorillonite and hectorite. Under appropriate conditions of swelling by adsorbed solvents, the interlayers occupied by the intercalant are accessible to substrates, and catalytic hydrogenation reactions analogous to those that occur in homogeneous solution can be accomplished in the solid state. Since these intercalated layered silicate intercalation catalysts are ordered in the 00*l* direction and since the degree of swelling can be controlled within rather narrow limits, they offer the potential for influencing catalyst selectivity based on the spatial requirements of substrate–metal complex intermediates formed in the restricted interlamellar space.[1]

The objective of the present study was to examine the properties of clay-intercalated hydroformylation catalysts. Most hydroformylation catalyst precursors are neutral species[4-6] that can be immobilized on polymer[7-9] and inorganic oxide[10,11] supports by covalent attachment mechanisms. However, the mechanism of catalyst intercalation in layered silicates involves an exchange reaction of Na^+ ions that normally occupy the solvated interlayer regions:

$$\overline{Na^+(solv)} + ML_n^+ \underset{\xleftarrow{\hspace{1cm}}}{\overset{solvent}{\xrightarrow{\hspace{1cm}}}} \overline{ML_n^+(solv)} + Na^+ \qquad (1)$$

where the lines represent the negatively charged silicate layers and ML_n^+ is the catalyst precursor. Therefore, a positively charged precursor is required for catalyst immobilization in layered silicates.

Cationic complexes of the type $Rh(diene)(PPh_3)_2^+$ have been reported by Oro et al.[12,13] to have hydroformylation activity

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