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Decarboxylation Kinetics for the Carbonatotris(pyridine)cobalt(III) Ion in Perchloric Acid Solutions

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Abstract

The kinetics of the decomposition reactions of the $Co(py)_3(CO_3)(H_2O)^+$ ion have been investigated in aqueous perchloric acid solutions over a range of hydrogen ion concentrations (0.10 to 5.0 M) and at two ionic strengths ($I = 1.0$ and 5.0 M). At the lower ionic strength, plots of ln $(A_t - A_\infty)$ *versus* time show a nonlinearity that is consistent with that expected for consecutive first-order reactions. The rates of the faster reaction are similar to those reported for the spontaneous reduction of aquopyridinecobalt(III) cations. At the higher ionic strength, the above noted curvature is not apparent and the decarboxylation kinetics of the title complex may be described by a pseudo-first-order rate constant: $k_{obs} = k[H_3O^+]$. At 20 °C, $k = (1.75 \pm 0.09)$ s^{-1} M^{-1} with activation parameters of $\Delta H^{\ddagger} = (97 \pm 4)$ kJ mol^{-1} and $\Delta S^{\ddagger} = -(54 \pm 32)$ J deg^{-1} mol^{-1}. These kinetic parameters are compared with those previously reported for the similar complexes, $Co(py)_4CO_3^+$ and $Co(py)_2(CO_3)(H_2O)_2^+$.

Introduction

The robustness of the cation $Co(py)_4(CO_3)^+$ toward decarboxylation in strongly acid solutions was first noted over a decade ago [1]. Detailed kinetic studies indicated that the cation was indeed the most resilient carbonato cobalt(III) complex yet investigated [2]. In this particular cation, the slow decarboxylation rate could be related to steric factors associated with the four coordinated pyridines [3] and the presence of a π system in these same ligand. Both $Co(bipy)_2(CO_3)^+$ and $Co(phen)_2(CO_3)^+$ would be considered relatively slow with respect to their rate of decarboxylation in acidic solution [4] but neither ranked with the $Co(py)_4(CO_3)^+$ cation.

During the course of investigations on the decarboxylation kinetics of the dicarbonato cobalt(III) complex $Co(py)_2(CO_3)_2^-$, the intermediate $Co(py)_2(CO_3)(H_2O)_2^+$ [5] was isolated and characterized in acidic solution [5]. Kinetic studies of this carbonato complex [6] in which steric factors associated with bulky pyridine ligands should be minimal, indicated that it decarboxylated at about the same rate as $Co(bipy)_2(CO_3)^+$ and $Co(phen)_2(CO_3)^+$. This rate would be considered relatively slow when compared with carbonato cobalt(III) cations.

Our present investigation reports the kinetic study associated with the decarboxylation of $Co(py)_3(CO_3)(H_2O)^+$. The results are to be compared with those for $Co(py)_4(CO_3)^+$ and $Co(py)_2(CO_3)(H_2O)_2^+$ in an attempt to establish a correlation between the number of coordinated pyridine ligands and the decarboxylation rate.

Experimental

The complex $[Co(py)_3(CO_3)(H_2O)]ClO_4 \cdot 2H_2O$ was prepared by a method similar to that reported by Loan [7]. An alternative synthesis of this compound has been reported by Laier *et al.* [8]. A quantity (20 g) of $[Co(py)_3CO_3Cl]$ [1] was added to 80 ml of a cooled (~5 °C) 1 M $HClO_4$ solution. The solution was allowed to stir on a cooling plate for 1 h. The reddish-purple crystals that formed were collected by suction filtration and washed with ice cold water (100 ml). In the recrystallization procedure, the crude product was dissolved in 10 ml warm (45 °C) methanol and an aspirator suction was used to reduce the volume by half. The resulting solution was cooled in ice and the product was precipitated by adding 20–30 ml of anhydrous diethylether. The reddish crystals were collected by suction filtration, washed with ice cold methanol twice, and allowed to air dry.

The purity of this compund was determined by comparison of its solution spectral parameters with those reported in the literature [8]. Reported (medium is water): $(\epsilon,\lambda)_{max}$: (119, 540 nm), (138, 380 nm); $(\epsilon,\lambda)_{min}$: (20,453 nm), (113,358 nm). Found (medium 0.01 M $HClO_4$): $(\epsilon,\lambda)_{max}$: (116,542

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nm), (140,380 nm); $(\epsilon,\lambda)_{min}$: (23,453 nm), (129,361 nm).

The solid form of the decarboxylation product, triaquatris(pyridine)cobalt(III) perchlorate dihydrate, $[Co(py)_3(H_2O)_3](ClO_4)_3 \cdot 2H_2O$, was prepared by the method described by Laier [8].

Purity of this compound was established spectrophotometrically. Reported (4 M $HClO_4$) [8]: $(\epsilon,\lambda)_{max}$: (52.2, 518 nm); $(\epsilon,\lambda)_{min}$: (16.1, 445 nm). Found (1.0 M $HClO_4$, $I = 5.0$ M [$NaClO_4$]): $(\epsilon,\lambda)_{max}$: (46.6, 521 nm); $(\epsilon,\lambda)_{min}$: (16.6, 446 nm).

Stock solutions of sodium perchlorate and perchloric acid were prepared from reagent grade chemicals and appropriately standardized [5]. The stock solutions were used to prepare the solutions of varying acidity and constant ionic strength ($[H_3O^+] =$ 0.10 to 1.0 M at $I = 1.0$ M ($NaClO_4$) or $[H_3O^+] =$ 1.0 M to 5.0 M at $I = 5.0$ M ($NaClO_4$)) that were used for the kinetic runs.

Kinetic data was obtained by use of a Cary 14 Spectrophotometer in its time drive mode. Solutions were degassed and thermostated at the desired temperature before a kinetic run was initiated. A kinetic run was initiated by dissolving the solid compound in the cooled reaction medium. Because of the low solubility of the compound, it was often necessary to filter the solution before initiating a kinetic run. Absorbance-time data was recorded only after a thermistor temperature probe indicated that appropriate temperature had been obtained within the sample cell. Temperatures remained constant to ±0.1 °C and at least three kinetic runs were performed at each temperature and acidity in the high ionic strength experiments ($I = 5.0$ M).

Results and Discussion

Some preliminary kinetic experiments on the decomposition reactions of the $Co(py)_3(CO_3)(H_2O^+)$ ion were obtained at 25 °C and $I = 1.0$ M ($NaClO_4$). At the highest acidity ($[H_3O^+] = 1.0$ M), an isosbestic point was evident at about 372 nm. The observation and position of this isosbestic point is consistent with decarboxylation of the carbonato complex to form the aquo complex, *mer*-$Co(py)_3(H_2O)_3^{3+}$. At lower acidities the reaction became inconvenient to study because the isosbestic point held for less than two decarboxylation half-lives or was not observed at all. This observation is consistent with the increased importance of the spontaneous reduction [9] of the initial decarboxylation product relative to the decarboxylation reaction itself.

In order to study the consecutive reactions involved in the decomposition of $Co(py)_3(CO_3)(H_2O)^+$, in a convenient time frame, absorbance-time data were collected at 45 °C at several acidities ($I = 1.0$ M). At these conditions, it was possible to treat the data based on the assumption of consecutive first-order processes [10]. A reasonable value for k(slow) and a rough estimate for k(fast) were obtained by the usual procedure for the treatment of such data. This data is collected in Table I. The values of k(fast) show a reciprocal $[H_3O^+]$ ($k = k_c + k_d/[H_3O^+]$) dependence while those for k(slow) suggest a linear $[H_3O^+]$ dependence ($k = k_a + k_b[H_3O^+]$). This acid dependence is adequate to assign the fast reaction to the spontaneous reduction of $Co(py)_3(H_2O)_3^{3+}$ to $Co^{2+}(aq)$ and the slow reaction to the actual decarboxylation of $Co(py)_3(CO_3)(H_2O)^+$. In addition, the values of k_c and k_d shown at the foot of Table I are reasonably consistent with those obtained at different temperatures for the reduction reaction of *cis*-$Co(py)_2(H_2O)_4^{3+}$. By this we mean that the data fall on the same straight line when ln k_c or ln k_d is plotted against reciprocal temperature.

TABLE I. Observed Rate Constants for the Decomposition of the $Co(py)_3(CO_3)H_2O^+$ Ion in Aqueous Perchloric Acid, $I = 1.0$ M ($NaClO_4$) and $T = 45.0$ °C.

$[H_3O^+]$	$10^3 \times k_{obs}$ (fast) $(s^{-1})^a$	$10^5 \times k_{obs}$ (slow $(s^{-1})^b$
0.100	1.09 ± 0.10	7.65 ± 0.40
0.300	0.697	
0.500	0.529 ± 0.042	10.9 ± 0.30

[a] $k(\text{fast}) = 4.3 \times 10^{-4} + 6.7 \times 10^{-5}/[H_3O^+] = k_c + k_d/[H_3O^+]$. [b] $k(\text{slow}) = 6.8 \times 10^{-5} + 8.1 \times 10^{-5}[H_3O^+] = k_a + k_b[H_3O^+]$.

The bulk of the kinetic data was collected at an ionic strength of 5.0 M ($NaClO_4$) rather than at the $I = 1.0$ M that was used in our preliminary studies. Rates of decarboxylation reactions increase with increasing ionic strength and increasing acidity while those for the spontaneous reduction of $Co(py)_2(H_2O)_4^{3+}$ decrease with increasing ionic strength and increasing acidity. The decarboxylation reaction could be studied separately at this ionic strength when $[H_3O^+] \geqslant 1.0$ M. Absorbance-time data was collected at 540 nm and over a range of temperatures (5 to 20 °C) and acidities (1.0 to 5.0 M). Plots of $\log(A_t - A_\infty)$ indicated good linearity over two or more half-lives and the value of A_∞ observed, estimated by a best-fit procedure, or calculated from the spectral parameters reported for $Co(py)_3(H_2O)_3^{3+}$ generally agreed to within 5 percent.

Values of the observed rate constants for the decarboxylation reaction at $I = 5.0$ M are summarized in Table II. The data in this Table indicates that the decarboxylation rate constant increases with increasing $[H_3O^+]$. Figure 1 suggests that plots of k_{obs} *versus* $[H_3O^+]$ are reasonably linear at each of the temperatures studied. These observations are consistent with the rate law generally observed for the

TABLE II. Observed Rate Constants for the Decarboxylation of the $Co(py)_3(CO_3)(H_2O)^+$ Ion in Aqueous Perchloric Acid at I = 5.0 M ($NaClO_4$) and Various Temperatures[a]

$[H_3O^+]$	5.0 °C $10^3 \times k_{obs}$	10.0 °C $10^3 \times k_{obs}$	15.0 °C $10^3 \times k_{obs}$	20.0 °C $10^3 \times k_{obs}$
1.0	0.213	0.474	0.848	1.91
	0.262	0.483	0.825	1.84
	0.234	0.431	0.873	1.62
2.0	0.455	0.990	1.57	3.16
	0.500	0.990	1.69	3.77
	0.500	0.926	1.61	3.76
3.0	0.920	1.65	3.53	5.38
	0.790	1.51	3.46	4.72
	0.090	1.56	2.84	4.92
4.0	1.14	2.26	4.08	6.49
	1.14	1.88	4.05	6.32
	1.42	2.07	3.66	6.12
5.0	1.88	2.75	5.67	8.84
	1.81	2.64	5.71	9.61
	1.49	2.48	6.38	9.02
k_b (s^{-1} M^{-1})	$(3.74 \pm 0.23) \times 10^{-4}$	$(5.40 \times 0.18) \times 10^{-4}$	$(1.25 \pm 0.71) \times 10^{-3}$	$(1.75 \pm 0.87) \times 10^{-3}$

[a] $\Delta H_b^{\ddagger} = (71.5 \pm 9.2)$ kJ mol^{-1}; $\Delta S_b^{\ddagger} = (-53.6 \pm 31.8)$ J mol^{-1} K^{-1}.

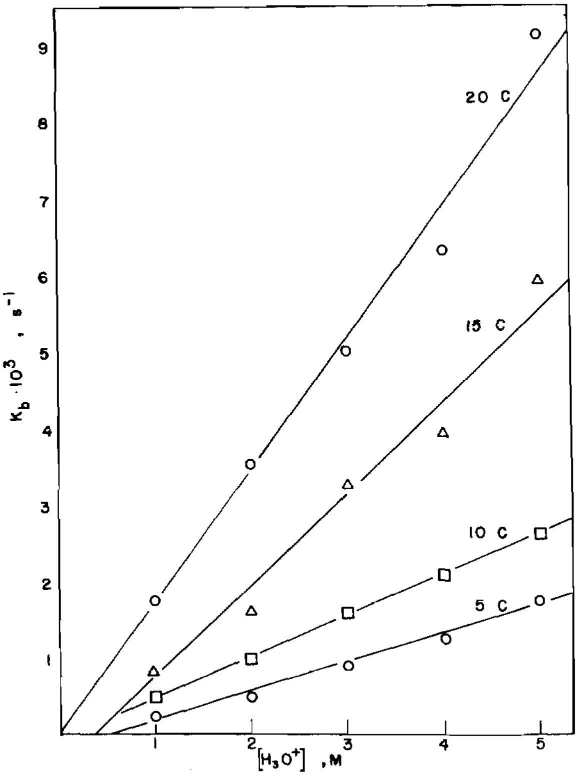
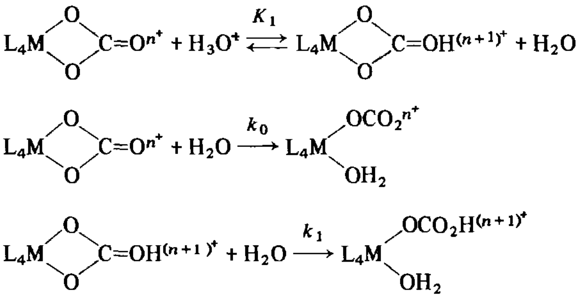


Fig. 1. Plot of the average value of the observed rate constant (I = 5.0 M) *vs.* the hydrogen ion concentration at each temperature investigated.

decarboxylation reactions of carbonato cobalt(III) complexes shown below.

$$k_{obs} = k_a + k_b[H_3O^+] \quad (1)$$

This simple form of the observed rate constant is to be associated with the generally accepted form of the mechanism for the decarboxylation reactions of bidentate carbonato complexes. This mechanism is shown below but the steps after the generally rate determining ring opening step [11] have not been included.



The expected observed rate constant is of the form

$$k_{obs} = \frac{k_0 + k_1 K_1 [H_3O^+]}{1 + K_1 [H_3O^+]} \quad (2)$$

TABLE III. Rate Constants at 25 °C and Activation Parameters for the Acid Catalyzed Decarboxylation Path for Carbonatopyridinecobalt(III) Ions

Complex	$I = 1.0$ M			$I = 5.0$ M		
	$10^5 \times k_b$ (s^{-1} M^{-1})	$\Delta H_b^{\ddagger}$ (kJ/mol)	$\Delta S_b^{\ddagger}$ (J/mol K)	$10^5 \times k_b$ (s^{-1}) M^{-1})	$\Delta H_b^{\ddagger}$ (kJ/mol)	$\Delta S_b^{\ddagger}$ (J/mol K)
$Co(py)_4CO_3^+$	0.036	142 ± 50	109 ± 151	0.83	97 ± 4	−17 ± 13
$Co(py)_3(CO_3)(H_2O)^+$	8.1^a			300	72 ± 9	−54 ± 32
$Co(py)_2(CO_3)(H_2O)_2^+$	34.0	82 ± 5	−36 ± 18			

[a] Value is from the 45 °C measurements (see Table I).

which reduces to

$$k_{obs} = k_o + k_1 K_1 [H_3O^+] \qquad (3)$$

at our experimental conditions. It is expected that $K_1 [H_3O^+] < 1$ since K_1 from the protonation of the carbonyl oxygen should be quite small.

Unweighted at each temperature linear regression analysis of the data in Table II to the equation $k_{obs} = k_a + k_b[H_3O^+] = k_o + k_1 K_1 [H_3O^+]$ yield the values k_b shown at the bottom of the Table. Values for k_a are not reported since they are slightly negative and not much different than zero. The activation parameters associated with k_b (the acid catalyzed decarboxylation path) are also found at the foot of Table II.

In Table III we have collected rate constants at 25 °C and activation parameters for the acid catalyzed decarboxylation path of several $Co(py)_n(CO_3)(H_2O)_{4-n}^+$ complexes for which kinetic results are available. The $Co(py)_4CO_3^+$ ion still remains the most robust toward decarboxylation when compared with the two carbonatoaquopyridinecobalt(III) ions. Clearly the replacement of coordinated pyridine by ligand water increases the rate of decarboxylation but all the carbonatopyridinecobalt(III) complexes are much less reactive toward decarboxylation when compared with similar complexes containing aliphatic amines as 'nonparticipating' ligands. This point has been made before [6].

Our particular interest in the present study was to investigate whether the rate of decarboxylation would increase with a decrease in the number of coordinated pyridine ligands in $Co(py)_n(CO_3)(H_2O)_{4-n}^+$ complexes. Unfortunately, the need to separate the decarboxylation process from the reduction process necessitated that the majority of the data was obtained at the higher ionic strength. The value of k_b reported in Table III, estimated from a limited number of results at $I = 1.0$ and at 45 °C, for $Co(py)_3(CO_3)(H_2O)^+$ lies between those shown for the $Co(py)_4(CO_3)^+$ and $Co(py)_2(CO_3)(H_2O)_2^+$ complexes at 25 °C. Activation parameters are not available at this ionic strength but this crude comparison would suggest that the rate of decarboxylation increases with decreasing numbers of coordinated pyridine ligands. At the higher ionic strength ($I = 5.0$ M) no kinetic results are available for the $Co(py)_2(CO_3)(H_2O)_2^+$ complex. Previous work [6] has suggested that the rate of decarboxylation of this complex is not much altered by small changes in the ionic strength. If this is the case, then the $Co(py)_3(CO_3)H_2O^+$ complex decarboxylates approximately an order of magnitude faster than the $Co(py)_2(CO_3)(H_2O)_2^+$ complex and the idea that robustness toward decarboxylation in carbonato complexes is simply related to the number of pyridine ligands must be discarded. On the other hand, ionic strength strongly influences the rate of the decarboxylation reaction of $Co(py)_4(CO_3)^+$. A change of $I = 1.0$ to 5.0 M causes a greater than 20 fold

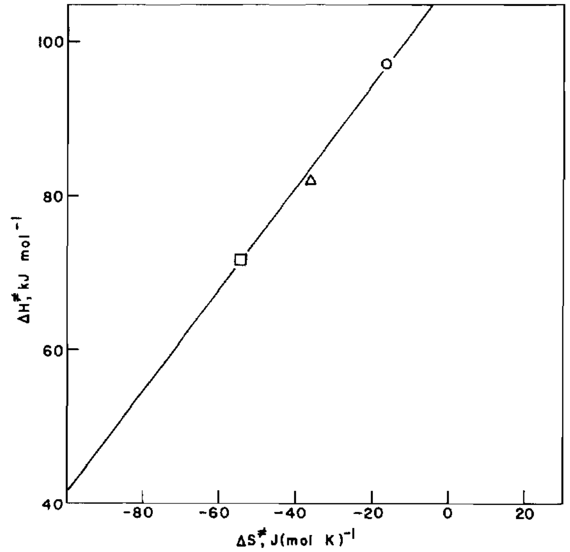


Fig. 2. Isokinetic plot of $\Delta H_b^{\ddagger}$ vs. $\Delta S_b^{\ddagger}$ of the acid-catalyzed ring-opening decarboxylation path for the three pyridinecarbonatocobalt(III) cations. ○, $Co(py)_4(CO_3)^+$; △, $Co(py)_3(CO_3)(H_2O)^+$; □, $Co(py)_2(CO_3)(H_2O)_2^+$.

increase in the value of k_b. If this same factor holds for the variation of k_b with ionic strength for the $Co(py)_2(CO_3)(H_2O)_2^+$ ion, then a value of $k_b > 300$ s^{-1} M^{-1} would be estimated. Again, the rate of acid catalyzed decarboxylation would decrease with replacement of coordinated pyridine with water in the series $Co(py)_n(CO_3)(H_2O)_{4-n}^+$.

Lastly, it has been noted [11] that activation parameters ΔH_b and ΔS_b for the various acid-catalyzed ring-opening reactions of bidentate carbonato complexes results in a poor isokinetic plot. Figure 2 shows such a plot for the three carbonatopyridinecobalt(III) complexes. The isokinetic plot is quite linear with all three points falling on the same straight line. This suggests that all three complexes decarboxylate by the same process and that the relative values of the various effects (stereochemical, electronic, steric and other) on the decarboxylation process are similar.

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