The Kinetics and Mechanism of Aquation of Carbonato Complexes of Cobalt(III). II. The Acid-Catalyzed Aquation of Carbonatotetraamminecobalt(III) Ion

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Abstract: The aquation of $Co(NH_3)_4CO_3^+$ ion exhibits a first-order dependence on (H^+) over most of the acidity range $1 < pH < 5$. This behavior is in sharp contrast with that of the previously studied monodentate analog, $Co(NH_3)_5CO_3^+$, the aquation of which is acidity independent throughout the range defined. Rates of the tetraammine aquation reaction have been determined at 20, 25, and 30° and $I = 0.5$ M for $HClO_4$ concentrations between 0.1 and 0.5 M by means of stopped-flow technique, and by time-drive chart spectrophotometry in the range $1 < pH < 5$. The pseudo-first-order rate constants are directly proportional to (H^+) for $2 < pH < 3$, beyond which point the slow residual rate tends to independence of acidity. Acidometric rate studies at the same ionic strength (0.5 M), utilizing stoichiometric mixtures of carbonato complex ion and perchloric acid, substantiate a two-step concept for the reaction. The first and rate-determining step, characterized by k_1, is acid-catalyzed ring opening of the chelated carbonato ligand, followed by rapid decarboxylation of the bicarbonatoaquo product ion. The acid-independent portion of the reaction results from the slow direct attack by H_2O on the chelate with rate constant k_0, so that the resultant observed pseudo-first-order rate constant is given by $k = k_0 + k_1(H^+)$. At 25° and $I = 0.5$ M, $k_0 = 1.3 \times 10^{-4}$ sec^{-1}, $k_1 = 1.5$ M^{-1} sec^{-1}, and the temperature variation parameters describing these constants are, respectively, $\Delta H^{\ddagger}$, 12 ± 5 and 15.3 ± 1.0 kcal/mole and $\Delta S^{\ddagger}$, -37 ± 19 and -6.3 ± 3.8 eu.

In our previous paper in this series,[2] we have shown that the rate of the aquation reaction of carbonatopentaamminecobalt(III) ion is independent of acidity in the range $1 < pH < 5$. At lower acidities, the rate falls off rapidly and asymptotically approaches a very small or zero limiting value beyond pH 9. This limiting rate does not become observably supplemented by base-catalyzed hydrolysis[3] until the pH exceeds 12. The facts of the aquation process are consistent with a mechanism for which the significant steps are

$$Co(NH_3)_5CO_3H^{2+} + H_2O \rightleftharpoons Co(NH_3)_5CO_3^+ + H_3O^+ \quad K \quad (1)$$

$$Co(NH_3)_5CO_3H^{2+} \longrightarrow Co(NH_3)_5OH^{2+} + CO_2 \quad k_1 \quad (2)$$

At 25° and $I = 0.5$ M, $K = 4 \times 10^{-7}$ M and $k_1 = 1.25$ sec^{-1}. The observed pseudo-first-order rate constant is closely described over the whole range $1 < pH < 9$ by the relation derived from the mechanism

$$k = k_1(H^+)/[(H^+) + K] \quad (3)$$

The pentaammine behavior contrasts sharply with the acid-catalyzed hydrolysis of the bidentate analogs, $Co(NH_3)_4CO_3^+$ and $Co(en)_2CO_3^+$ (en = $NH_2CH_2CH_2NH_2$), as is apparent from our own preliminary reports[4,5] and from other earlier work.[6-8] In these, a first-order dependence on acid concentration is found over the range $2 < pH < 3$, above which the rate tends to an independence of the acidity. As with the pentaammine compound, base-catalyzed hydrolysis becomes observable only as the pH exceeds 12.[9-11]

Another interesting contrast between pentaammine and tetraammine carbonato complexes is apparent from oxygen-18 tracer studies of their decomposition in strongly acid media, as reported by Taube and coworkers. The Co–O bond remains intact during aquation of the $Co(NH_3)_5CO_3^+$ species,[12] but for $Co(NH_3)_4CO_3^+$, one of the Co–O bonds remains intact while the other is severed.[13] Previous carbonate exchange studies of the tetraammine complex[14] had led to the suggestion that its aquation consisted of a rapid ring-opening equilibration promoted by proton addition to the carbonato ligand, followed by rate-determining elimination of CO_2 from the monodenate bicarbonatoaquo intermediate. However, as pointed out by Posey and Taube,[13] the tetraammine aquation data are perhaps more consistently explained in terms of the reverse of the earlier suggestion, *i.e.*, rate-determining acid-catalyzed ring opening and fast decarboxylation. The reactions would be

$$Co(NH_3)_4CO_3^+ + H_3O^+ \longrightarrow cis\text{-}Co(NH_3)_4(H_2O)(CO_3H)^{2+} \quad k_1 \quad (4)$$

$$cis\text{-}Co(NH_3)_4(H_2O)(CO_3H)^{2+} \longrightarrow cis\text{-}Co(NH_3)_4(H_2O)(OH)^{2+} + CO_2 \quad k_2 \quad (5)$$

with the condition that $k_2 \gg k_1(H^+)$. It would be expected that Co–O bond fission would occur in reaction 4 and C–O fission in reaction 5, the latter process being a close analog to reaction 2 above, for which Co–O

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[1] To whom correspondence concerning this paper should be addressed.

[2] Part I: T. P. Dasgupta and G. M. Harris, *J. Am. Chem. Soc.*, **90**, 6360 (1968).

[3] D. J. Francis and R. B. Jordan, *ibid.*, **89**, 5591 (1967).

[4] T. P. Dasgupta and G. M. Harris, Proceedings of the XIth International Conference on Coordination Chemistry, Haifa, Israel, 1968, p 180.

[5] G. M. Harris and V. S. Sastri, *Inorg. Chem.*, **4**, 263 (1965).

[6] K. J. Pedersen, *J. Am. Chem. Soc.*, **53**, 18 (1931).

[7] J. Y. Tong, E. St. A. Kean, and B. B. Hall, *Inorg. Chem.*, **3**, 1103 (1964).

[8] R. Ralea, G. Burlacu, and D. Giurgiu, *Rev. Chim. Acad. Rep. Populaire Roumaine*, **7**, 1187 (1962).

[9] H. A. Scheidegger and G. Schwarzenbach, *Chimia*, **19**, 166 (1965).

[10] H. A. Scheidegger, Doctoral Thesis, Eidgenössischen Technischen Hochschule, Zürich, 1966.

[11] M. E. Farago, *Coord. Chem. Rev.*, **1**, 66 (1966).

[12] J. P. Hunt, A. C. Rutenberg, and H. Taube, *J. Am. Chem. Soc.*, **74**, 268 (1952); see also C. A. Bunton and D. R. Llewellyn, *J. Chem. Soc.*, 1692 (1953).

[13] F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, **75**, 4099 (1953).

[14] G. M. Harris and D. R. Stranks, *Trans. Faraday Soc.*, **48**, 137 (1952); D. R. Stranks and G. M. Harris, *J. Phys. Chem.*, **56**, 906 (1952); D. R. Stranks, *Trans. Faraday Soc.*, **48**, 911 (1952); G. Lapidus and G. M. Harris, *J. Am. Chem. Soc.*, **85**, 1223 (1963).

Table I. Spectrophotometrically Determined Rate Constants[a]

A. 20°			B. 25°			C. 30°		
pH	10^4k, sec^{-1}	k', M^{-1} sec^{-1}	pH	10^4k, sec^{-1}	k', M^{-1} sec^{-1}	pH	10^4k, sec^{-1}	k', M^{-1} sec^{-1}
1.0	880	0.9	−0.3	9600	0.5[b]	2.0	245	2.5
1.45	310	0.9	−0.1	5400	0.5[c]	2.2	156	2.5
1.75	200	1.0	0.3	3200	0.6	2.4	99	2.5
1.95	140	1.2	1.0	1200	1.2	2.45	81	2.3
2.0	110	1.1	1.8	270	1.7	2.55	73	2.6
2.2	69	1.1	2.0	160	1.6	2.8	43	2.7
2.4	43	1.1	2.2	100	1.6	3.05	22	2.5
2.65	27	1.2	2.4	58	1.5	3.25	14	2.5
2.8	18	1.1	2.6	39	1.6	3.3	12	2.4
3.0	10	1.0	3.05	13	1.5	3.4	10	2.5
3.4	4.1	1.0	3.1	12	1.5	3.5	8.2	2.6
3.5	3.5	1.1	3.2	10	1.6	3.6	7.0	2.8
3.8	2.4	1.5	3.3	8.2	1.6	3.75	5.2	2.9
3.9	2.05	1.6	3.4	6.4	1.6	3.85	5.0	3.5
4.1	1.6	2.0	3.5	5.6	1.8	4.0	4.5	4.5
4.3	1.15	2.3	3.75	3.5	2.0	4.2	4.2	6.7
4.5	1.15	3.6	4.0	2.8	2.8	4.4	4.0	10.0
4.75	1.0	5.6	4.2	3.0	4.8	4.6	3.8	15.1
			4.4	2.2	5.5	4.8	3.6	22.7
			4.6	2.2	8.8			
			4.8	2.1	13.2			

[a] $(Co(NH_3)_4CO_3^+) = 0.005$ M; $I = 0.5$ M. [b] Ionic strength 2.0 M. [c] Ionic strength 1.26 M.

breakage does *not* occur. Furthermore, some streaming apparatus experiments by Scheidegger and Schwarzenbach show that ring-opening protonation of the closely similar $Co(en)_2CO_3^+$ ion is relatively slow,[9,10] but that decarboxylation of the resultant bicarbonatoaquo complex has a half-life only of the order of a fraction of a second[10] at 20°.

It was our purpose in the present work to reinvestigate the kinetics and mechanism of aquation of the carbonatotetraamminecobalt(III) complex ion as thoroughly as possible over a wide range of acidity. This has been effected by use of three different rate-study procedures: stopped-flow at high acidities (0.1 $M < (HClO_4) < 0.5$ M) where the rate is very rapid, and time-drive chart-recorded spectrophotometry or potentiometric acidimetry of the reactant solution over the rest of the range within which reaction is observable ($1 < pH < 5$). The identification of the rate-determining process as ring-opening according to reaction 4 within the acid range $2 < pH < 3$ has been established, and some details of the aquation mechanism outside these limits have been clarified.

Experimental Part

Carbonatotetraamminecobalt(III) nitrate was prepared according to standard procedure.[15] Diaquotetraamminecobalt(III) nitrate was prepared by adding HNO_3 (concentrated acid–water in 1:1 ratio) to the carbonato complex until effervescence ceased and crystallizing out the desired product by evaporating the solution. The purity of the complexes was checked by analyzing for cobalt by the $CoSO_4$ method.[16] *Anal.* Calcd for $[Co(NH_3)_4CO_3]NO_3 \cdot 0.5H_2O$: Co, 22.8. Found: Co, 22.6. Calcd for $[Co(NH_3)_4(H_2O)_2](NO_3)_3 \cdot 2H_2O$: Co, 15.3. Found: Co, 15.2. Further purity checks were provided by visible and infrared spectrophotometry,[17] using Cary 15 and Beckman IR5A instruments, respectively. All other chemicals used were of reagent grade, and the laboratory distilled water was purified by passage through a mixed-bed ion-exchange column.

The low-acid spectrophotometric rate studies were carried out at 20, 25, and 30° and $I = 0.5$ M ($NaClO_4$) on a Cary 15 spectrophotometer with a time-drive chart recorder, utilizing the wavelength 520 mμ, at which the absorbance change during reaction is conveniently large.[17] Temperature control of the optical cells within ±0.1° was achieved by a thermostated metal-block cell holder. The pH of the reactant solutions was stabilized by use of McIlvaine phosphate–citric acid buffer,[18] correcting for its contribution to the total ionic strength by means of the data of Elving, *et al.*[19] Solutions were preequilibrated with respect to temperature prior to addition of the requisite amount of solid complex salt. Rates of reaction at the higher acidities (where buffering was unnecessary) were determined by the stopped-flow technique described previously,[2] utilizing the same wavelength as in the Cary 15 work above. Pseudo-first-order rate constants were derived in the conventional manner from semilogarithmic plots of the fraction of reactant remaining as a function of time. The acidities of the buffered reaction media were measured with a Beckman Research Model pH Meter.

The acidometric rate data was obtained at 5, 10, and 15° and the same ionic strength as before.[20] The reaction vessel was a jacketed beaker through the annular space of which water at the desired temperature was continuously circulated. Thermostated solutions of carbonato complex and perchloric acid were mixed in such proportions as to provide the 1:2 stoichiometric ratio, enabling evaluation of the rate constants from the simplified second-order plot of $[(H^+)_0 - (H^+)_t]/(H^+)_t$ *vs.* time. The required (H^+) values were derived from the automatically recorded pH *vs.* time curves[21] obtained from the Beckman pH meter combined with a Sargent Model SRL recorder. Typical plots of one set of pH–time data and of the resultant second-order rate analysis are presented in Figure 1. Particularly evident is the essentially nonbasic character of the $Co(NH_3)_4CO_3^+$ ion, as shown by the instantaneous decrease of the pH from ~7 to ~2 when the complex salt solution is made 0.01 M in acid at the commencement of reaction.

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(15) G. Schlessinger, *Inorg. Syn.*, **6**, 173 (1960).

(16) A. B. Lamb and E. B. Damon, *J. Am. Chem. Soc.*, **59**, 383 (1937).

(17) The molar absorbance of our $Co(NH_3)_4CO_3^+$ is 104 at 520 mμ (*cf.* 105 reported by J. P. Mathieu, *Bull. Soc. Chim. France*, [5] **3**, 468 (1936)). The aquation product, $Co(NH_3)_4(H_2O)_2^{3+}$, has a molar absorbance of 52 at the same wavelength. The C–O stretching frequencies of $Co(NH_3)_4CO_3^+$ are 1598, 1035, and 765 cm^{-1} (*cf.* 1593, 1030, and 760 cm^{-1} reported by K. Nakamoto in "Infra-red Spectra of Inorganic Co-ordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 163).

(18) T. C. McIlvaine, *J. Biol. Chem.*, **49**, 183 (1921).

(19) P. J. Elving, J. M. Markwitz, and I. Rosenthal, *Anal. Chem.*, **28**, 1179 (1956).

(20) These runs were made at lower temperatures because of limitations on the rate of response of the pH measuring device and the consequent necessity of lowering the reaction rate.

(21) The readings made on the pH meter were converted to *molar concentrations* of hydrogen ion (rather than activities) by calibrating the instrument against solutions of known molar concentration of perchloric acid in the 0.5 M total ionic strength medium.

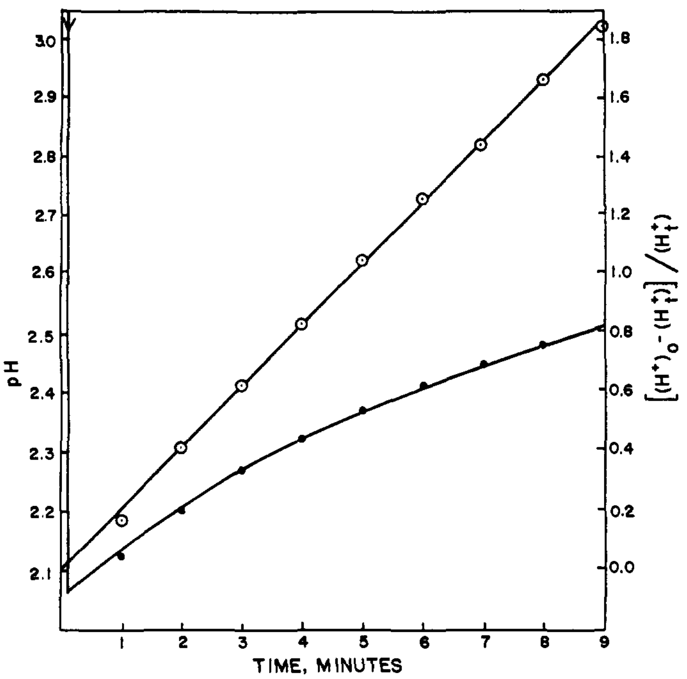

Figure 1. Plots of acidometric rate data: closed circles, pH *vs.* time; open circles, $[(H^+)_0 - (H^+)_t]/(H^+)_t$ *vs.* time (as derived from given pH plot).

Results and Discussion

The spectrophotometrically determined pseudo-first-order rate constant k (including both stopped-flow and Cary 15 results) are recorded in Table I, together with the calculated second-order constants $k' = k/(H^+)$. There are seen to be three regions insofar as rate dependence on acidity is concerned. The dominant one is the central range of $2 < pH < 3$, within which there is a clean first-order dependence on (H^+) and k' is apparently a true second-order rate constant. However, for $pH < 2$ k appears to fall off somewhat, while in excess of pH 3, k approaches constancy so that k' appears to increase dramatically. The data at the high end of the pH scale have been examined on the assumption that the observed rate constant k is the sum of two terms, as previously suggested[6] for this acidity range.

$$k = k_0 + k_1(H^+) \qquad (6)$$

This treatment is illustrated in Figure 2, where data at three temperatures in the range $3 < pH < 4$ are shown as a k *vs.* (H^+) plot. Good straight lines are obtained with intercepts and slopes such that k_0 and k_1 values are as recorded in Table II. Also given are the k_1 values[22] derived acidometrically at the lower temperatures and $2 < pH < 3$ (as illustrated in Figure 1), and the average values from the data of Table I in the same acidity range. The parameters $\Delta H_0^{\ddagger}$, $\Delta S_0^{\ddagger}$, $\Delta H_1^{\ddagger}$, and $\Delta S_1^{\ddagger}$ presented at the foot of Table II refer to k_0 and k_1, respectively, and were derived in the conventional manner by a least-squares analysis of the linear Eyring–Polanyi plots of the relevant tabulated data (see Figure 3). A noteworthy feature of this analysis is that the

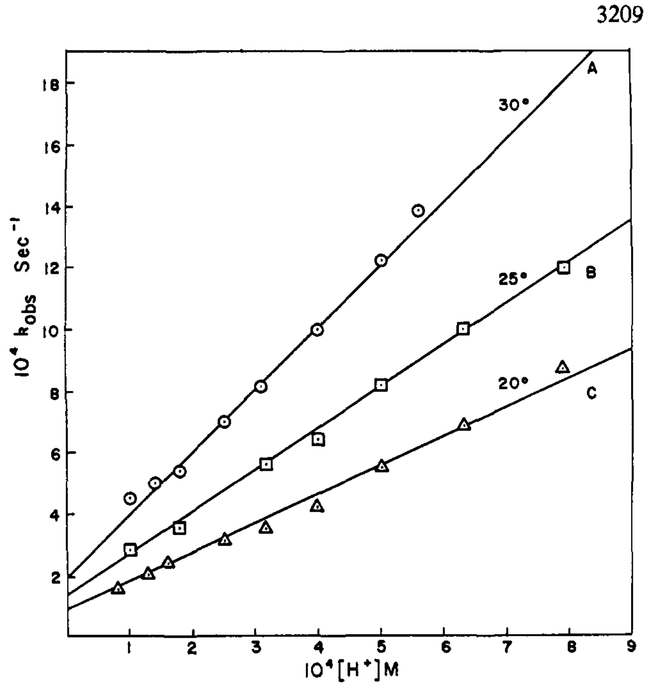

Figure 2. Plots of observed rate constant k *vs.* (H^+): △, at 20°; ⊡, at 25°; ⊙, at 30°.

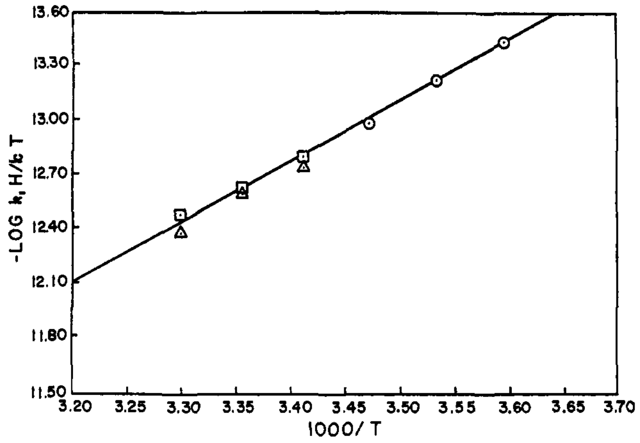

Figure 3. Temperature variation of k_1: ⊙, acidometric data; △, average values in $2 < pH < 3$ range of Table I; ⊡, values from slopes of curves in Figure 2.

acidometric and spectrophotometric data for k_1 all fit the same straight line with a high degree of consistency. The acidometric runs clearly illustrate the initial low basicity of the $Co(NH_3)_4CO_3^+$ ion (as already pointed out) and also that the time-dependent consumption of acid occurs at the same rate as the spectrophotometrically observed over-all conversion of carbonato complex to diaquo complex. The obvious conclusion is that acid-catalyzed ring opening of the chelated carbonato ligand is the rate-determining process in the $2 < pH < 3$ range of these experiments.

A very satisfactory interpretation of the rate data can be made in terms of a mechanism consisting of reactions 4 and 5 above, together with[23] reactions 7–9 below.

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(22) These k_1 values were derived by use of eq 6 in the form $k_1 = (k - k_0)/(H^+)$ and the assumption that k_0 has the values given in the second column of Table II. In any case, the k_0 contribution to k soon becomes negligible as the pH becomes less than 3.

(23) Conversion of the *cis* complexes to the *trans* forms need not be considered, since the process is exceedingly slow for the aquocarbonato species[10] and is not only slow but thermodynamically unfavorable for the diaquo species (at equilibrium, the *cis/trans* ratio[24] is 58 at 25°).

(24) J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, 6, 1265 (1952).

Table II. Summary of Aquation Rate Constant Data at $I = 0.5\ M$

Temp, °C	$10^4 k_0$, sec^{-1}	k_1, M^{-1} sec^{-1}	k_1, M^{-1} sec^{-1}
5	$(0.3)^a$		0.21 ± 0.05^c
10	$(0.4)^a$		0.35 ± 0.05^c
15	$(0.6)^a$		0.62 ± 0.1^c
20	0.9 ± 0.2^b	1.0 ± 0.1^b	1.1 ± 0.1^d
25	1.3 ± 0.2^b	1.4 ± 0.1^b	1.5 ± 0.1^d
30	1.8 ± 0.3^b	2.1 ± 0.1^b	2.5 ± 0.2^d

[a] Estimated by use of the derived temperature parameters. [b] Obtained from the intercepts and slopes of Figure 2. [c] Values obtained by acidometric technique as illustrated in Figure 1 (each value is an average of three determinations). [d] Average values from the 2 < pH < 3 range of Table I.

$\Delta H_0^{\ddagger} = 12 \pm 5$ kcal/mole $\qquad \Delta H_1^{\ddagger} = 15.3 \pm 1.0$ kcal/mole

$\Delta S_0^{\ddagger} = -37 \pm 19$ eu $\qquad \Delta S_1^{\ddagger} = -6.3 \pm 3.8$ eu

Table III. Effect of Ionic Strength Variation on k_1 at 25°

I, M	0.025	0.03	0.04	0.05	0.06	0.10	0.18	0.29	0.50
k_1, M^{-1} sec^{-1} ^{a}	0.83	1.01	0.99	1.08	1.07	1.13	1.33	1.33	1.50^b

[a] Calculated from eq 6 assuming k_0 constant and equal to 1.3×10^{-4} sec^{-1}. [b] "Best value" from Table I.

$$\mathrm{Co(NH_3)_4CO_3^+ + H_2O \longrightarrow} \quad cis\text{-}\mathrm{Co(NH_3)_4(OH)(CO_3H)^+} \quad k_0 \qquad (7)$$

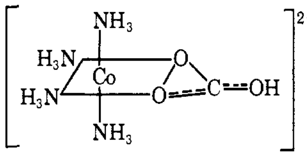
$$cis\text{-}\mathrm{Co(NH_3)_4(H_2O)(CO_3H)^{2+} + H_2O \rightleftharpoons} \quad cis\text{-}\mathrm{Co(NH_3)_4(OH)(CO_3H)^+ + H_3O^+} \quad K_1 \qquad (8)$$

$$cis\text{-}\mathrm{Co(NH_3)_4(H_2O)_2^{3+} + H_2O \rightleftharpoons} \quad cis\text{-}\mathrm{Co(NH_3)_4(H_2O)(OH)^{2+} + H_3O^+} \quad K_2 \qquad (9)$$

The magnitude of pK_1 is not exactly known but must be close to 6, since the corresponding value[9] for the species $\mathrm{Co(en)_2(H_2O)(CO_3H)^{2+}}$ is 5.3 at 20° and $I = 0.1\ M$, while the value for the pentaammine analog[2] is 6.4 at 25° and $I = 0.5\ M$. Thus, even at the highest pH values of the present study, the monodentate carbonato species will be nearly all in the protonated form *cis*-$\mathrm{Co(NH_3)_4(H_2O)(CO_3H)^{2+}}$, and will decompose only according to reaction 5.[25] Reactions 4, 5, and 7, together with the reasonable assumption[26] that $k_2 \gg k_1(\mathrm{H^+})$ in the range 2 < pH < 5, yield a rate law exactly of the form observed experimentally (eq 6). The few data obtained at higher acidities (first three entries at 20° and first four entries at 25°, Table I) show that k' begins to show a decrease as the pH falls below 2. This, of course, is the expectation as $k_1(\mathrm{H^+})$ approaches and surpasses k_2 in magnitude, when the latter becomes the limiting rate constant and $k' = k_2$. As noted already,[26] k_2 undoubtedly lies between 1 and 2 sec^{-1}.

A factor of concern in determining the limiting value of k at high acidity is the effect of the increased ionic strength in such systems. The influence of ionic strength variation has therefore been investigated in the range $0.025\ M < I < 0.5\ M$ at pH 2.65 and 25°. Under these conditions, the effect can be identified with k_1, since k_0 makes a very small contribution to k at the quoted acidity, and k_0 is not likely to be very sensitive to ionic strength changes in any case, since it describes an ion–molecule reaction. The values of k_1 obtained are recorded in Table III. The data exhibit considerable scatter, but yield a straight line of unit positive slope when plotted in the form of $\log k_1$ *vs.* $\sqrt{I}/(1 + \sqrt{I})$. This is in keeping with expectation for a reaction between two unipositive ions.[27] Since k_1 does, in fact, increase markedly as the ionic strength increases, the apparent fall-off in k at the high acidities (where $I > 0.5\ M$) is even more conclusively ascribable to a rate limitation set by k_2, as suggested above.

The temperature dependence parameters identified with k_0 and k_1 (Table II) are significant in that $\Delta S^{\ddagger}$ is much more negative for the former than for the latter. This is what one would predict, since the transition state for reaction 7 must include a very specifically oriented water molecule positioned in such a manner that its oxygen atom can promote replacement of the O atom of the carbonate group, and enable dechelation to take place. In contrast, for reaction 4, only proton addition is necessary to form the transition state, perhaps in the following fashion



The resultant weakening of one of the Co–O bonds facilitates its fission and provides easy entry for a water molecule from the solvation sheath, to form the aquobicarbonato complex ion. It is significant that the observed $\Delta S_1^{\ddagger}$ value (-6.3 ± 4 eu) is what one would predict for reaction between unipositive ions on the basis of electrostatic theory (between −5 and −10 eu, depending on the radius assigned to the transition state[28]).

Finally, it is of interest to make some direct comparisons of the rate constant values at 25° obtained in this work with the results derived from the data of the earlier investigators. The various k_0 and k_1 values appear in Table IV,[29] and can be seen to be in very good agreement. Two important conclusions may be drawn

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(25) The value of pK_2 is also close to 6 under our experimental conditions,[24] so practically all of the hydroxoaquo species produced in reaction 5 is immediately protonated to give the diaquo analog according to the reverse of reaction 9.

(26) The rates of acid hydrolysis of $\mathrm{Co(NH_3)_5Cl^{2+}}$ and $\mathrm{Co(NH_3)_4(H_2O)Cl^{2+}}$ differ only by a small factor at 25°: F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, p 164. One would thus expect k_2 for the tetraammine carbonato system to be close to k_1 for the pentaammine system (1.3 sec^{-1}).[2] An estimate[10] of 0.3 sec has in fact been given for the half-time of decarboxylation of the species *cis*-$\mathrm{Co(en)_2(OH_2)(CO_3H)^{2+}}$, suggesting $k_2 \sim 2$ sec^{-1} for this type of tetraammine complex ion.

(27) G. M. Harris, "Chemical Kinetics," D. C. Heath and Co., Boston, Mass., 1966, p 102.

(28) K. J. Laidler, "Chemical Kinetics," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1965, p 215.

(29) Pedersen's paper[6] gives the acid dependence in equations of the form $k = k_0 + k_1Kh$, where K is the dissociation constant of the buffer acid at the specified ionic strength, h is the acid–base ratio of the buffer mixture, and the k's are defined in "decadic logarithms." The appropriate factors were used to convert his numbers to conform to our eq 6. The work of Ralea, *et al.*,[8] was limited to two acidities only (pH's of 3.29 and 4.10, respectively). Their two recorded k values were used in our eq 6, with the appropriate values of ($\mathrm{H^+}$) to yield the k_0 and k_1 figures which appear in Table IV.

Table IV. Comparison with Rate Constant Data of Earlier Workers

	Pedersen[6]	Ralea, *et al.*[8]	This work
10^4k_0, sec^{-1}	1.0,[a] 1.0,[b] 1.0[c]	0.7[d]	1.3[e]
k_1, $M^{-1}\ \text{sec}^{-1}$	1.0,[a] 1.1,[b] 1.8[c]	1.2[d]	1.5[e]

[a] I = 0.11 M, glycolate buffer. [b] I = 0.21 M, glycolate buffer. [c] I = 0.98 M, acetate buffer. [d] I = 0.25 M, Britton–Robinson buffer.[30] [e] I = 0.5 M, phosphate–citrate buffer.

from these data: first, that our earlier assumption that k_0 is rather insensitive to ionic strength variation is well substantiated by Pedersen's work; second, that the nature of the buffer used has little effect on the rate of reaction, ruling out the possibility of buffer–ion substitution reactions as contributing in any way to the observed reactions.

A further significant correlation is possible in connection with our work on the exchange of carbon-14-labeled carbonate ions with the $Co(NH_3)_4CO_3^+$ ion.[14,31] This study was made in the range $9 < pH < 10$, where no net acid- or base-catalyzed aquation of the complex is observable. However, one portion of the exchange proceeds at a rate, R_A, which is independent of the carbonate ion concentration. This rate can be explained in terms of an aquo-dechelation equilibration (reaction 7 and its reverse)[32]

$$Co(NH_3)_4CO_3^+ + H_2O \rightleftarrows Co(NH_3)_4(OH)(CO_3H)^+ \quad k_0, k_0' \tag{10}$$

together with reaction 8 and the equilibrations

$$Co(NH_3)_4(OH_2)(CO_3H)^{2+} \rightleftarrows Co(NH_3)_4(OH_2)(OH)^{2+} + CO_2 \quad k_2, k_2' \tag{11}$$

$$Co(NH_3)_4(OH)(CO_3H)^+ \rightleftarrows Co(NH_3)_4(OH)_2^+ + CO_2 \quad k_3, k_3' \tag{12}$$

Since $k_0 = 1.3 \times 10^{-4}\ \text{sec}^{-1}$ at 25°, faster by a factor of 10 than the observed total carbonate exchange rate, reaction 10 can be ruled out as the rate-limiting process. The rate-constant ratio $k_0/k_0' = K_0$ is known[33] to be close to 10^{-3}, so k_0' must be about 0.1 sec^{-1}, and equilibration according to reaction 10 must have a half-time of much less than 1 min.[34] The proposed mechanism to account for R_A (reactions 8 through 12), with the assumption that the rate-determining exchange processes are those described by k_2 and k_3, leads to the expression

$$R_A = k_2[Co(NH_3)_4(OH_2)(CO_3H)^{2+}] + k_3[Co(NH_3)_4(OH)(CO_3H)^+] \tag{13}$$

Symbolizing the total concentration of all forms of the carbonato complex, chelated or not, by a, and recalling that K_0 is very small, one can recast eq 13 in the form

$$R_A = \frac{k_2K_0(H_3O^+)a}{K_1} + k_3K_0a \tag{14}$$

Since all quantities are approximately known[35] except k_2 and k_3, one can evaluate the latter from experimental observations at two acidities. While our data for the $Co(NH_3)_4CO_3^+$ case is not as extensive as in some of our later studies where greater assurance concerning this revised interpretation is possible,[31] using eq 14 one derives that, at 25°, $k_2 \sim 2\ \text{sec}^{-1}$ and $k_3 \sim 1 \times 10^{-2}\ \text{sec}^{-1}$. The former value is as expected on the basis of the aquation data above, while k_3, for which a value is not otherwise obtainable, exhibits the considerable decrease in decarboxylation reactivity one would predict for the less protonated species.[36]

Acknowledgment. Financial support of this work through Grant No. GP-6708 from the National Science Foundation is gratefully acknowledged. Also appreciated is the cooperation of the Computer Center of the State University of New York at Buffalo, supported under NSF Grant No. 0789B.

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(30) H. T. S. Britton and R. A. Robinson, *J. Chem. Soc.*, 458 (1931).

(31) A more complete reconsideration of the carbonate exchange studies will appear in R. Dobbins and G. M. Harris, in preparation; see also K. V. Krishnamurty, V. S. Sastri, and G. M. Harris, *Chem. Rev.*, in press.

(32) The product can also be written in the form $Co(NH_3)_4(OH_2)(CO_3)^+$. However, the hydroxobicarbonato form has been adopted here and above in this paper on the basis of studies of the closely related oxalatotetraamminecobalt(III) complex. It has been shown (S. C. Chan, private communication) that the water ligand is much more acidic than the monodentate C_2O_4 ligand, and one would expect similar behavior for the CO_3 ligand. But there is undoubtedly some degree of sharing of the proton between OH and CO_3 (or C_2O_4) by means of internal hydrogen bonding.

(33) This is the value for the closely similar complex ion, $Co(en)_2CO_3^+$, at 20° and I = 0.1 M (see ref 9).

(34) Contributions to the dechelation process by reaction 4 or the analogous OH^--promoted reaction need not be considered, since they are both very slow in the pH range of the exchange studies.

(35) K_1 is taken to be 5×10^{-6}, or about the same as for $Co(en)_2CO_3^+$ under comparable conditions (ref 9).

(36) A significant comparison here is between the rate constants for decarboxylation of H_2CO_3 and HCO_3^-, which are 2 and $5 \times 10^{-6}\ \text{sec}^{-1}$, respectively (see ref 2). However, such a wide difference is not to be expected for the aquobicarbonato and hydroxobicarbonato comparison, since in this instance the removed proton is on the *adjacent* molecule, H_2O, not on the carbonate group itself.