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

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Abstract: Stopped-flow technique has enabled a study of the reaction over the range $1 < \text{pH} < 8$ and $25° < T < 45°$ at $I = 0.5\ M$. The rate-determining reaction is $Co(NH_3)_5CO_3H^{2+} \rightarrow Co(NH_3)_5OH^{2+} + CO_2$, and is accompanied by various proton-transfer equilibria. The observed pseudo-first-order rate constant, k_{obsd}, is independent of the acidity for pH <5, up to which point it has a uniform maximum value. Above pH 5, the rate falls off rapidly and asymptotically approaches a very small value beyond pH 7. The data are satisfactorily interpreted in terms of a proton preequilibration–decarboxylation mechanism, such that $k_{obsd} = k_1(H^+)/[(H^+) + K_1]$, where k_1 is the rate constant of the reaction given above, and K_1 is the acid dissociation constant of $Co(NH_3)_5CO_3H^{2+}$. The constant k_1 is described by the Eyring–Polanyi parameters $\Delta H^{\ddagger} = 17.0 \pm 0.5$ kcal/mole and $\Delta S^{\ddagger} = -0.5 \pm 1.0$ eu, and has a value of 1.25 sec^{-1} at 25°. The corresponding figure for K_1 is $4 \times 10^{-7}\ M$ and is confirmed not only by the fit to the kinetic data but by independent titrimetric determinations. The relationship of our results to earlier findings is discussed.

The reaction by which carbonatopentaamminecobalt(III) salts lose carbon dioxide in acidic aqueous solution, thereby undergoing conversion to the aquopentaammine species, has been examined several times previously. Lamb and Stevens[2] studied the process conductometrically nearly 30 years ago under conditions such that the hydrogen ion concentration was not stabilized other than by the self-buffering of the complex ion system itself. Their limited observations concerning the acid dependence of the process led them to propose the following mechanism.

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

$$Co(NH_3)_5CO_3H^{2+} + H_2O \rightleftharpoons Co(NH_3)_5(H_2O)^{3+} + HCO_3^- \quad \text{(slow)} \qquad (2)$$

$$Co(NH_3)_5(H_2O)^{3+} + H_2O \rightleftharpoons Co(NH_3)_5OH^{2+} + H_3O^+ \quad \text{(fast)} \qquad (3)$$

$$HCO_3^- + H_3O^+ \rightleftharpoons H_2CO_3 + H_2O \quad \text{(fast)} \qquad (4)$$

Subsequent work by Lamb and Mysels[3] confirmed the earlier data and offered, in addition, measures of the acid dissociation constant, K_1, of the species $Co(NH_3)_5CO_3H^{2+}$ ($pK_1 = 7.1$ and 6.4 at 0 and 25°, respectively). More recently, tracer experiments utilizing oxygen-18 labeling[4] have proved conclusively that the acid-catalyzed aquation takes place *without* metal–oxygen fission.[5] The rate-determining reaction cannot, therefore, be looked upon as a substitution of a water molecule for bicarbonate ion, as given in reaction 2 above. It should rather be written

$$Co(NH_3)_5CO_3H^{2+} \rightleftharpoons Co(NH_3)_5OH^{2+} + CO_2 \qquad k_1, k_2 \quad (2')$$

with subsequent proton-transfer equilibration of the hydroxo complex product according to reaction 3, and escape, solvation, and/or hydrolysis of carbon dioxide.

The exchange of carbonate between the carbonatopentaamminecobalt(III) ion and "free" dissolved carbonate was studied by Stranks, utilizing carbon-14 labeling. Data obtained in the range $8.8 < \text{pH} < 10$ can be interpreted[6] in terms of a dual mechanism in which the predominant process is aquation equilibration according to either reaction 2 or 2′, yielding values for the rate constant of aquation, k_1, and for K_1. Very recently, the kinetics of acid-catalyzed aquation in the limited range $8.5 < \text{pH} < 9.4$ has been studied by spectrophotometric technique.[7] These results are in sharp disagreement with the earlier work, both with respect to the values of 25° of pK_1 (8.2 as compared to Lamb and Mysels' 6.4) and k_1 (2.3×10^{-2} sec^{-1} as compared to an approximate value[8] of 7×10^{-3} sec^{-1} deduced from the data of Lamb and coworkers and Stranks' figure[8] of 1.2×10^{-3} sec^{-1}). The present study was undertaken with the purpose of attempting to resolve these various discrepancies. A spectrophotometric study of the aquation has been carried out over a wide range of acidity ($1 < \text{pH} < 8$), utilizing stopped-flow technique at the higher acidities (pH < <7.5) where the reaction becomes very rapid. Independent titrimetric determinations of pK_1 have also been made, and a satisfactory rationalization of all the existing data has become possible.

Experimental Section

Carbonatopentaamminecobalt(III) nitrate monohydrate was prepared according to the method of Lamb and Mysels[3] and its purity checked by analyses for cobalt,[9] carbon, hydrogen, and nitrogen.[10] *Anal.* Calcd for $Co(NH_3)_5CO_3NO_3 \cdot H_2O$: Co, 20.75;

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

[2] A. B. Lamb and R. G. Stevens, *J. Am. Chem. Soc.*, **61**, 3229 (1939).

[3] A. B. Lamb and K. J. Mysels, *ibid.*, **67**, 468 (1945).

[4] (a) J. B. Hunt, A. C. Rutenberg, and H. Taube, *ibid.*, 74, 268 (1952); (b) C. A. Bunton and D. R. Llewellyn, *J. Chem. Soc.*, 1692 (1953).

[5] It is of interest that carbonate removal by Pb^{2+} or Hg^{2+} in aqueous solution also occurs without Co–O bond fission though the situation with respect to Ba^{2+} is not so clearly defined: R. B. Jordan, A. M. Sargeson, and H. Taube, *Inorg. Chem.*, **5**, 486 (1966).

[6] (a) D. R. Stranks, *Trans. Faraday Soc.*, **51**, 505 (1955); (b) G. Lapidus and G. M. Harris, *J. Am. Chem. Soc.*, **85**, 1223 (1963).

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

[8] See discussion below for origin of these numbers.

[9] Estimated as $CoSO_4$, using the method of A. B. Lamb and E. B. Damon, *J. Am. Chem. Soc.*, **59**, 383 (1937).

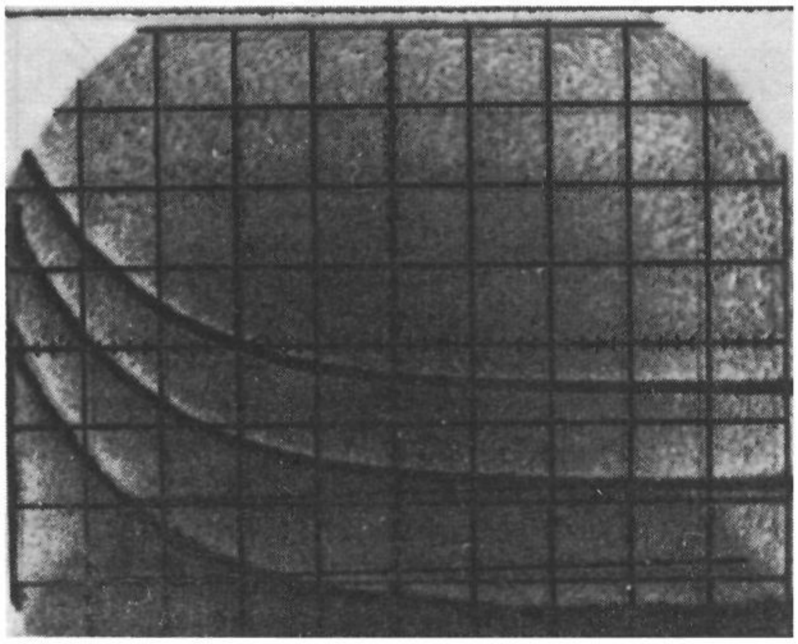

Figure 1. Typical oscilloscope trace: time scale, 0.5 sec per large division, along horizontal axis.

C, 4.22; H, 5.99; N, 29.58. Found: Co, 20.80; C, 4.30; H, 6.02; N, 29.70. Spectrophotometric measurements made on a Cary 15 spectrophotometer also confirmed the purity of the material.[11] During kinetic runs, the pH was controlled by means of a McIlvaine phosphate–citric acid buffer,[12] its contribution to the total ionic strength being derived from the data of Elving, *et al.*[13] All materials used were of reagent grade, and the distilled water was purified by passage through an ion-exchange column.

The glass–Lucite stopped-flow apparatus[14] was essentially the same as that described by Dulz and Sutin.[15] The wavelength 505 mμ offers a conveniently large absorbance change[11] and was selected for the kinetic measurements. The requisite buffer solution, containing sufficient sodium perchlorate to provide the standard ionic strength in the reaction mixture of 0.5 *M*, was thermostated in a container separate from that of the carbonato complex, samples being withdrawn into the syringes of the stopped-flow apparatus through a three-way stopcock. Transmittances were presented on the oscilloscope as a function of time and recorded by a Polaroid camera (see Figure 1 for a typical trace). Pseudo-first-order rate constants, k_{obsd}, were obtained in the conventional manner from semilogarithmic plots of the fraction of reactant remaining *vs.* time. pH measurements of the buffered reaction medium were made with a Beckman Research Model meter. Sodium corrections were neglected since below pH 9 they are very small.

Values of the acid dissociation constant of the bicarbonatopentaamminecobalt(III) complex were obtained by independent determinations. In these, equal volumes of thermostated solutions of the complex and perchloric acid (0.0050 and 0.0025 *M*, respectively) were mixed and the pH graphically recorded as a function of time over as short an interval of time as possible (10–12 sec) and back-extrapolated to zero time. Measurements at 15, 20, and 25° gave almost identical p*K* values of 6.7 ± 0.2. This result is only approximate due to the slow response of the recording pH device employed, as compared to the half-time of aquation of the carbonato species (see below).

Results and Discussion

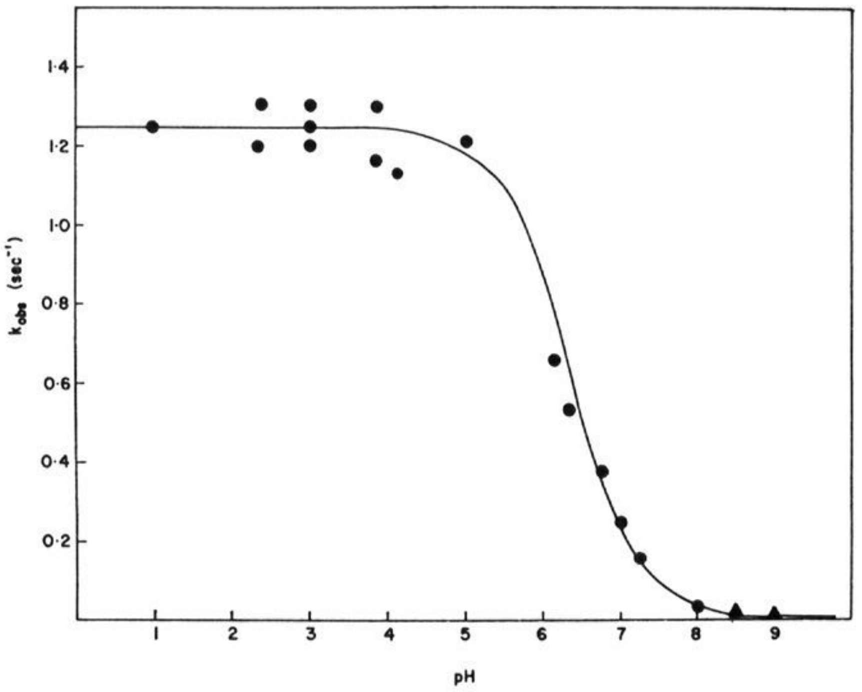

Figure 2. pH profile of observed first-order rate constant: ●, our data; ▲, data of Francis and Jordan.[7]

Our data at 25° are presented in the form of a k_{obsd} *vs.* pH plot in Figure 2. Below pH 5, k_{obsd} is essentially constant at 1.25 sec^{-1}, except for the appreciable experimental scatter. In the range $5 < \text{pH} < 8$, there is a rapid decline in the rate, followed by an asymptotic approach to the very low values recorded by Francis and Jordan[7] at pH ~9. This behavior is reminiscent of acid–base titration, as would be expected if reactions 1 and 2 represent the mechanism of the aquation. The corresponding rate law assuming a negligible back-reaction,[16] constant (H^+), and "instantaneous" proton transfer in reaction 1 is

$$\frac{d(\text{Co(NH}_3)_5\text{OH}_2{}^{3+})}{dt} = k_1(\text{Co(NH}_3)_5\text{CO}_3\text{H}^{2+}) = \frac{k_1(\text{H}^+)}{[(\text{H}^+) + K_1]}(\text{total carbonato complex})$$

Whence

$$k_{\text{obsd}} = k_1(\text{H}^+)/[(\text{H}^+) + K_1] \tag{5}$$

or

$$\frac{1}{k_{\text{obsd}}} = \frac{1}{k_1} + \frac{K_1}{k_1(\text{H}^+)} \tag{6}$$

A replot of the data of Figure 1 in the reciprocal form of eq 6 is shown in Figure 3, where the limiting value $k_{\text{obsd}} = k_1$ at high acidity is taken to be 1.25 sec^{-1}, as derived from Figure 2. The slope of the straight line of Figure 3 is K_1/k_1, and, using $k_1 = 1.25$ sec^{-1}, yields a value of $K_1 = 4 \times 10^{-7}$ *M* (pK_1 = 6.4). The solid curve of Figure 2 was calculated by use of these k_1 and K_1 values. Our "kinetic" pK_1 is in good agreement with that of Lamb and Mysels[3] and also with the accurate figure of 6.36 obtained at 20° and ionic strength 0.1 *M* by Scheiddegger and Schwarzenbach.[17] Our "titrimetric" pK_1 (~6.7) is not in such close agreement owing to the experimental difficulties mentioned, but does indicate small temperature variability in the 15–25° range. This accounts in part for the excellent agree-

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[10] Microanalyses for C, H, and N by Drs. Weiler and Strauss, Oxford, England.

[11] The molar absorbancy indexes of the hydrolysis product $\text{Co(NH}_3)_5(\text{H}_2\text{O})^{3+}$ are 49 and 18 at 491 and 555 mμ, respectively, as compared to 48.6 and 18.2, reported by C. H. Langford and W. R. Muir, *J. Am. Chem. Soc.*, **89**, 3141 (1967), for the same compound. For the carbonato complex, our data gave a maximum in the index of approximately 94 at 505 mμ. At this wavelength, the index of the product is 46.

[12] T. C. McIlvaine, *J. Biol. Chem.*, **49**, 183 (1921).

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

[14] Made available through the courtesy of Professor R. G. Wilkins of this department.

[15] G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

[16] We observed no spectrophotometric evidence for an equilibration up to pH ~7. Above that value, the reaction becomes an equilibration, and only the initial portion of the absorbance *vs.* time plots was used in evaluating k_{obsd}.

[17] Obtained by rapid-flow technique, as reported in Doctoral Thesis of H. A. Scheidegger, Eidgenossischen Technischen Hochschule, Zurich, 1966, p 18.

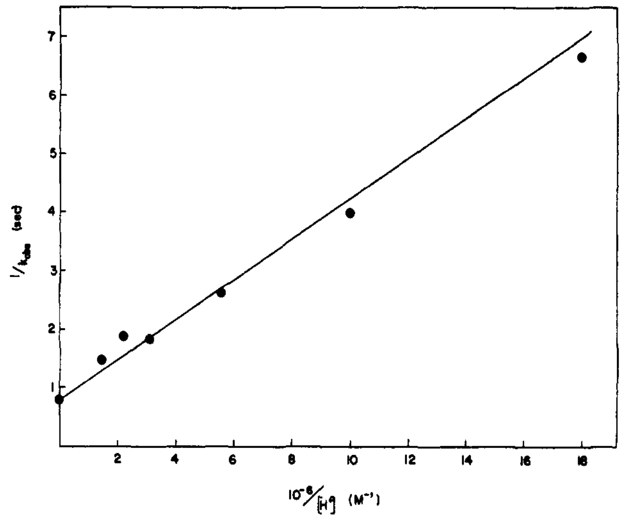

Figure 3. Reciprocal plot according to eq 6.

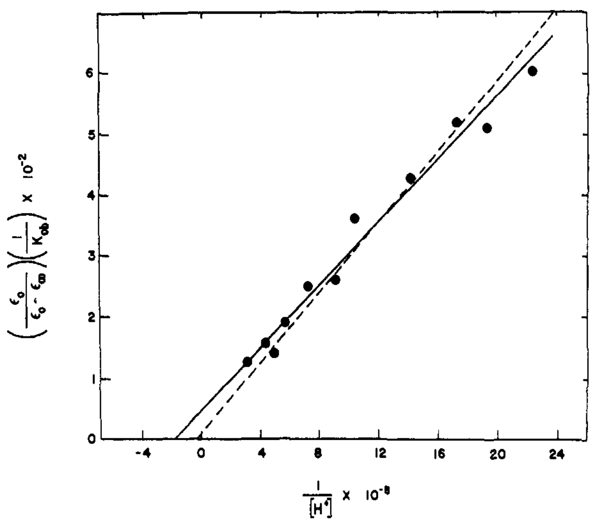

Figure 4. Comparison with data of Francis and Jordan: broken curve, our calculation.

ment between the 20 and 25° values noted above, though the ionic strength difference may also be a contributing factor.

The discrepancies between these data and the values of k_1 and K_1 reported by Francis and Jordan are readily explained. The latter results were obtained from least-squares determinations and the intercept and slope of a reciprocal plot similar to our Figure 3 (see ref 7, Figure 1). However, the intercept, $-1/K_1$, is a long extrapolation in their diagram and thus subject to great error. This then introduces a large error into k_1, since the slope of the plot is k_1/K_1. Actually, their data are well fitted by our values of $k_1 = 1.25$ sec^{-1} and $K_1 = 4 \times 10^7$, as shown in Figure 4, which is a replot of Francis and Jordan's Figure 1 including our calculated curve (broken line). It is noteworthy that while our value of the intercept (which determines $1/K_1$) is very much less than that of Francis and Jordan, our slope (k_1/K_1) of 3.1×10^6 is in fair agreement with their figure of 3.9×10^6.

We studied the temperature dependence of the aquation in the constant rate range (pH 3) where $k_{obsd} = k_1$. At 0.5 *M* ionic strength, $k_1 = 3.1$ sec^{-1} at 35° and 7.5 sec^{-1} at 44.5°. Coupled with the 25° data already given, a conventional Eyring–Polanyi plot leads to values for the parameters of $\Delta H^{\ddagger} = 17.0 \pm 0.5$ kcal/mole and $\Delta S^{\ddagger} = -0.5 \pm 1.0$ eu. Extrapolation of these data to 0° shows that at this temperature $k_1 = 7.9 \times 10^{-2}$ sec^{-1}. Lamb and coworkers' data suggest a value about $^1/_{11}$ as great at this,[18] but, since their solution was unbuffered, the actual pH of their equimolar reacting mixture of carbonato complex and acid is unknown.[19] Regarding Stranks' exchange data,[6] it has been suggested[7] that all the experiments can be interpreted in terms of aquation as the rate-limiting process.[20] One is thus dealing with a mechanism consisting of reactions 1 and 2 with the additional process

$$CO_2 + H^{14}CO_3^- \rightleftharpoons {}^{14}CO_2 + HCO_3^- \qquad (7)$$

If (2) is indeed the rate-determining reaction, the rate constant of exchange, k_{ex}, must be identical with k_{obsd} of eq 5. The data of ref 6a, Table 1, may be recalculated[21] on this basis, using the relation

$$R_{ex} = \frac{0.693}{t_{1/2}}\frac{ab}{a+b} = \frac{k_1(H^+)a}{[K_1 + (H^+)]} \qquad (8)$$

where *a* and *b* are the concentrations of complex and free carbonate, respectively. The average value of k_1 in the range $8.8 < pH < 9.3$ is deduced in this manner to be close to 1.2×10^{-3} sec^{-1}. This is smaller by a factor of about 66 than our extrapolated k_1 at 0° (7.9×10^{-2} sec^{-1}). Such a discrepancy is much too great to be accounted for by ionic strength effects, especially since the latter were shown to be very small in other experiments performed by Stranks (ref 5, Table 3). Clearly, reaction 2 cannot be rate determining in the exchange process, and one is forced to consider another possibility. The literature indicates that reaction 7 may in fact be the slow step, since it involves the processes

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \qquad k_3, k_4 \qquad (9)$$

$$CO_2 + OH^- \rightleftharpoons HCO_3^- \qquad k_5, k_6 \qquad (10)$$

The various rate constants have[22] the following approximate values at 0°: $k_3 = 2 \times 10^{-3}$ sec^{-1}, $k_4 = 2$ sec^{-1}, $k_5 = 900$ M^{-1} sec^{-1}, and $k_6 = 5 \times 10^{-6}$ sec^{-1}. In addition, the "instantaneous" equilibration of reaction 4 is also involved, so that CO_2–HCO_3^- carbon-exchange kinetics can become very complex indeed. However, near pH 9 (where most of Stranks' data were obtained), the rate-determining reactions by which "free" carbonate can become converted to CO_2 and thus provide a path for reentry of labeled carbon into

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(18) They show (ref 3, Figure 4) a figure of about 3.5×10^{-3} sec^{-1} for the sum of forward and reverse rate constants in a 1:1 carbonato complex/HCl solution at 0°. Assuming the reverse reaction to be relatively slight under these conditions[16] (pH $\sim$7), and since $K \sim (H^+)$, it follows from eq 5 that $k_1 \sim 2k_{obsd}$ or $k_1 = 7 \times 10^{-3}$ sec^{-1}.

(19) Their value of $k_{obsd} = 3.5 \times 10^{-3}$ sec^{-1} would yield a figure for k_1 equal to ours at pH 8.4, since they found pK_1 = 7.1 at 0°.

(20) Some of the figures quoted in support of this contention (ref 7, Table IV, column 3) are in fact in error. Using Stranks' original data at 25° (ref 6a, Table 2) one obtains hydrolysis rate values of 5.5, 11.3, 13.3, and 19.0×10^6 *M* sec^{-1}, respectively.

(21) Equation 8 can be rearranged to give $k_1 = R_{ex}[K_1 + (H^+)]/(H^+)a$. Using Lamb and Mysel's value for K_1 at 0° (8×10^{-8}), one obtains values for k_1 in the range 1.0×10^{-3} to 1.4×10^{-3} sec^{-1} independent of complex and free carbonate concentrations and of pH up to 9.3. Above pH 9.3, k_1 appears to increase, attaining a value of 1.9×10^{-3} sec^{-1} at pH 10.

(22) D. M. Kern, *J. Chem. Educ.*, 37, 14 (1960).

the carbonato complex are those governed by k_4 and k_6.[23] In these circumstances

$$R_{ex} = k_4(H_2CO_3) + k_6(HCO_3^-) = \\ k_4(H^+)b/[K_4 + (H^+)] + k_6K_4b/[K_4 + (H^+)] \quad (11)$$

where K_4 is the dissociation constant of H_2CO_3 ($\sim 2 \times 10^{-4}$ at 0°)[22] and b is as defined for eq 8. Since $K_4 \gg (H^+)$, it follows that

$$R_{ex}/b = k_4(H^+)/\delta K_4 + k_6\delta \quad (12)$$

Stranks' data on the variation of R_{ex} with acidity at constant complex ion and free carbonate concentration yield the following comparison.

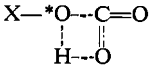
(H^+) $(M \times 10^{10})$	1.1	1.6	2.5	4.4	4.9	7.4
R_{ex}/b (obsd)[24] $\times 10^7$ (sec^{-1})	0.6	0.7	1.0	1.5	1.7	2.5
R_{ex}/b (calcd)[25] $\times 10^7$ (sec^{-1})	0.6	0.7	0.8	0.9	1.0	1.2

While the agreement does not appear to be good at the higher acidities it must be remembered that the figures for (H^+) are based on pH determinations in highly basic solution and could well be low by a factor of 2. If this is in fact assumed to be the case, the agreement between observed and calculated results becomes nearly perfect.

Finally, an interesting comparison may be made between the rate constant k_1 we have identified as that for aquation of the pentaamminecarbonatocobalt(III) complex and rate constants for similar reactions of organic carbonates. For the series of salts of the type $RO\cdot CO_2^-$ (R = ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, and *sec*-butyl), rate constants have been obtained[26] for the reaction proceeding as

$$RO\cdot CO_2^- + H^+ \rightleftarrows RO\cdot CO_2H \xrightarrow{k} ROH + CO_2$$

At 0° in aqueous solution, these are all close to 0.25 sec^{-1}, greater than our extrapolated value for k_1 at 0° by a factor of about 3. For carbonic acid itself, the corresponding rate constant (k_4 above) is 2 sec^{-1}, greater by a factor of 4 than that for the organic carbonates, due allowance being made for the fact that carbonic acid has two protons available for transfer. One can visualize a common transition state for all three reactions as



$$\begin{array}{l} X—{}^{*}O\cdots C{=}O \\ \qquad\ \vdots \qquad \vdots\vdots \\ \qquad\ H\cdots O \end{array}$$

where X = $(NH_3)_5Co^{3+}$, CH_3CH_2 (for ethyl carbonate), or H. The rate of CO_2 elimination should mainly be a function of the nature of the bonding to the *O atom in the transition state. Great differences in decarboxylation rate among the three species should therefore not be expected in spite of the residual positive charge on the cobaltic complex ion, since a large fraction of this charge is distributed throughout the ammine portion of the complex ion and is thus not centralized on the cobalt. The concept of the mechanism of carbonato complex ion acid decomposition as a decarboxylation appears to be quite reasonable from this point of view.

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(23) If k_3 and k_5 were rate determining, $R_{ex} = k_3(CO_2) + k_5(CO_2)(OH^-)$. The concentration of CO_2 would be fixed by reaction 2. The data of Francis and Jordan (ref 7, Table III) show that the equilibrium ratio of carbonato complex to aquo product is constant at about 65/35 at 25° over the range $8.3 < pH < 9.3$. That this ratio is not greatly temperature dependent is shown by Figure 1, curve B, of ref 6a, where it is seen that the extrapolated "zero-time equilibrium" aquated mixture has an activity of about 60% of the initial value. This represents a "dilution" of the radioactive "free" carbonate by "inactive" carbonate from the complex to an extent approximating the extent of complex decomposition at 25°. The (CO_2) is thus about one-third that of the total original carbonato complex. Utilizing the equation above and the quoted k_3 and k_5 values, one would predict R_{ex} values with (complex) ~ 0.04 M and pH 9 ($(OH^-) \sim 10^{-6}$ M at 0°) of about 4×10^{-5} M^{-1} sec^{-1}, with *higher* rates at *lower* acidities. Stranks' data (ref 6a, Table I) lead to R_{ex} values in all cases less than 1% of this value and show the opposite acid dependence.

(24) The b values used are those tabulated by Stranks (ref 6a, Table 1) which are claimed to be "equilibrium values." However, his observation that the fraction of aquation was between 4 and 9% must be in error, as pointed out in ref 23 relative to his Figure 1. The b values of Table 1 probably all need correction to higher values, depending on the concentration of carbonato complex, a. For this reason no attempt is made to deal with the data of Stranks' Table 1, other than the last five entries of Table 1 and that of Figure 1, for all of which $a = 0.0392$ and $b = 0.0189$.

(25) Using the quoted k_4 and k_6 values, eq 12, and the (H^+) values corresponding to the recorded pH's for the same data as used to obtain the R_{ex}/b (obsd) figures.

(26) C. Faurholt, quoted in I. Levin, L. A. Pohoryles, S. Sarel, and V. Usieli, *J. Chem. Soc.*, 3949 (1963).