Kinetic Study of the Hydrolysis of $(NH_3)_5CoCO_3^+$

D. J. Francis and Robert B. Jordan

Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada. *Received April 4, 1967*

Abstract: The hydrolysis of $(NH_3)_5CoCO_3^+$ was found to follow the rate law $-d \ln [\text{complex}]/dt = k_1'[OH^-]^{-1} + k_2[OH^-]$ at 0.02 to 1.00 M NaOH and $\mu = 1.0$ ($NaNO_3$) between 45 and 55°. The $k_2[OH^-]$ path has been attributed to the normal alkaline hydrolysis of $(NH_3)_5CoCO_3^+$ with $\Delta H^{\ddagger} = 30.0$ kcal mole^{-1}, $\Delta S^{\ddagger} = 18$ eu, and $k_2 = 3.3 \times 10^{-6}\ M^{-1}\ \text{sec}^{-1}$ at 25° (by extrapolation). The $k_1'[OH^-]^{-1}$ term is consistent with the uncatalyzed hydrolysis of $(NH_3)_5CoCO_3H^{2+}$, in which case $k_1' = k_1K_w/K_I$ where K_I is the acid dissociation constant of the bicarbonato complex. By extrapolation to 25°, $k_1/K_I = 4.2 \times 10^6\ M^{-1}\ \text{sec}^{-1}$, $\Delta H^{\ddagger} = 17.1$ kcal mole^{-1}, and $\Delta S^{\ddagger} = 30$ eu. Further kinetic studies at 25°, $\mu = 1.0$ ($NaClO_4$), and pH 8.5 to 9.5 in carbonate buffers have permitted a determination of $K_I = 5.9 \times 10^{-9}\ M$ and $k_1 = 2.3 \times 10^{-2}\ \text{sec}^{-1}$. The equilibrium constant K_f for the reaction $(NH_3)_5CoOH^{2+} + HCO_3^- \leftrightarrows (NH_3)_5CoCO_3H^{2+} + OH^-$ has been determined as 3×10^{-4} at 25°, $\mu = 1.0$ ($NaClO_4$).

The hydrolysis rate constant and pK_a of bicarbonatopentaamminecobalt(III) have been derived from analysis of the variation of rate of carbonate exchange with pH.[1,2] The present study reports a direct measurement of these values as well as the formation constant of the complex. The values found have led to a reinterpretation of the previous carbonate exchange data.

Also the rate constant for the hydroxide ion catalyzed hydrolysis of carbonatopentaamminecobalt(III) has been determined. The activation parameters for this process compared to those for hydrolysis of the bicarbonato complex indicate the differences to be expected for Co–O and O–C bond breaking.

Experimental Section

Preparation and Analysis of Complex Salt. Carbonatopentaamminecobalt(III) nitrate was prepared according to the method of Lamb and Mysels[3] and stored over calcium sulfate. The analysis of the complex for cobalt[4] and ammonia[5] agreed with the formula $((NH_3)_5CoCO_3)(NO_3)\cdot 1.5H_2O$ reported by Lamb and Mysels. *Anal.* Calcd for $((NH_3)_5CoCO_3)(NO_3)\cdot 1.5H_2O$: Co, 20.1; NH_3, 29.07. Found: Co, 20.9; NH_3, 29.1. The purity was also checked by comparing the spectrum of the acid hydrolysis product of the carbonato complex to the known spectrum of $(NH_3)_5CoOH_2^{3+}$. The results gave a calculated molecular weight of 287 ± 3 compared to the predicted value of 292. This deviation and the slight discrepancy in the other analysis are probably due to partial dehydration of the compound.

Base-Hydrolysis Kinetics. Solutions containing sodium hydroxide and sodium nitrate (to adjust the ionic strength to 1.0 M) of known concentration were brought to temperature equilibrium. A weighed quantity of the carbonato complex was added to the reaction solution. Aliquots were taken at various times, filtered through a 0.45-μ Millipore filter (Millipore Filter Corp., Bedford, Mass.) to remove any cobalt oxide formed, and diluted to volume. Optical densities of the diluted filtrate were determined at 328 mμ on a Bausch and Lomb Spectronic 505 spectrophotometer.

Solutions for the kinetic measurements at 25° and low pH were prepared by adding varying volumes of a solution of carbonato complex in sodium hydroxide to a known volume of sodium bicarbonate solution in a 5-cm cell. All solutions were adjusted to 1.0 M ionic strength with sodium perchlorate before mixing. The solution containing the complex ion was added from a syringe, and the change in optical density (295 mμ) with time was recorded as soon as possible (usually about 15 sec) after mixing. Infinite time optical densities were determined after at least eight half-times. These data gave good linear first-order plots for at least 95% reaction. The carbonate buffer concentration (about 0.020 M) was sufficiently high relative to the carbonato complex concentration (about 10^{-4} M) so that the pH will remain constant during the hydrolysis reaction.

The pH of the buffered reaction medium was measured with a Beckman Expandomatic pH meter with a 1 pH unit scale expansion. The measured pH was corrected for sodium ion error. This correction was negligible below pH 9 and was 0.024 pH unit at the highest pH used. From the known amounts of total carbonate and hydroxide added to the buffer solutions and the measured pH it is possible to calculate the acid dissociation constant of HCO_3^- in 1 M $NaClO_4$. Our calculated value of $2.75 \pm 0.10 \times 10^{-10}$ is in good agreement with the value of 2.7×10^{-10} also in 1 M $NaClO_4$ determined by Frydman, *et al.*[6]

Results

The variation of the rate of hydrolysis of $(NH_3)_5CoCO_3^+$ with hydroxide ion concentration at 45–55° is consistent with the rate law

$$
\begin{aligned}
-\frac{d[T]}{dt} &= k_1[(NH_3)_5CoCO_3H^{2+}] + k_2[(NH_3)_5CoCO_3^+][OH^-] \\
&= \left(\frac{k_1K_w}{K_I[OH^-]} + k_2[OH^-]\right)[(NH_3)_5CoCO_3^+] \\
&= \left(\frac{k_1K_w}{K_I[OH^-]} + k_2[OH^-]\right)\left(\frac{K_I}{K_I + [H^+]}\right)[T] \qquad (1)
\end{aligned}
$$

where [T] represents the concentration of total carbonato complex $(NH_3)_5CoCO_3^+$ plus $(NH_3)_5CoCO_3H^{2+}$; K_I is the acid dissociation constant of $(NH_3)_5CoCO_3H^{2+}$ and K_w is the ion product of water.

Under the conditions of our experiment the hydroxide ion concentration was always in large excess over the complex and $K_I >> [H^+]$; therefore the rate law may be represented by

$$
-\frac{d[T]}{dt} = k_{obsd}[T] = \left(\frac{k_1'}{[OH^-]} + k_2[OH^-]\right)[T] \qquad (2)
$$

The expression for k_1' can be found by comparison with eq 1. The values of k_{obsd} determined experi-

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(1) D. R. Stranks, *Trans. Faraday Soc.*, **51**, 505 (1955).

(2) G. Lapidus and G. M. Harris, *J. Am. Chem. Soc.*, **85**, 1223 (1963).

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

(4) R. E. Kitsen, *Anal. Chem.*, **22**, 664 (1950).

(5) H. A. Horan and H. J. Eppig, *J. Am. Chem. Soc.*, **71**, 581 (1949).

(6) M. Frydman, G. Nilsson, T. Rengemo, and L. G. Sillén, *Acta Chem. Scand.*, **12**, 878 (1958).

mentally at 50° and the values calculated from the best fit values of k_1' and k_2 are given in Table I. These data are typical of the fitting obtained at 45 and 55°. The values of k_1' and k_2 at the three temperatures are given in Table II along with values of k_1/K_1. The latter were calculated from k_1' using values of K_w at the appropriate temperature estimated from the data of Harned and Hamer.[7] Values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for k_1/K_1 and k_2 were determined in the standard way from transition-state theory.

Table I. Variation in the Rate of Hydrolysis of $(NH_3)_5CoCO_3^+$ with $[OH^-]$ at 50°, μ = 1.0 ($NaNO_3$)

$[OH^-]$	$k_{obsd} \times 10^5$ sec^{-1} Found	$k_{obsd} \times 10^5$ sec^{-1} Calcd[a]
0.020	22.3	22.3
0.040	12.2	11.6
0.060	9.00	8.26
0.100	5.97	6.01
0.200	5.37	5.42
0.500	9.00	8.93
0.800	12.6	13.4
0.900	14.8	14.9
1.00	16.7	16.5

[a] Calculated from $k_{obsd} = (0.44/[OH^-] + 16.1[OH^-]) \times 10^{-5}$.

Table II. Hydrolysis Rates of $(NH_3)_5CoCO_3^+$

Temp, °C	$k_1' \times 10^5$ M sec^{-1}	k_1/K_1[a] $\times 10^{-8}$ M^{-1} sec^{-1}	$k_2 \times 10^5$ M^{-1} sec^{-1}
45	0.19	0.27	8.1
50	0.44	0.45	16.1
55	0.82	0.62	35.2
$\Delta H^{\ddagger}$, kcal mole^{-1}		17.1	30.0
$\Delta S^{\ddagger}$, cal mole^{-1} deg^{-1}		18	30

[a] $k_1' = k_1K_w/K_1$. Values of K_w used are for 1.01 M KCl as calculated from ref 7. [b] Ionic strength 1.0 adjusted with $NaNO_3$.

The results of the experiments at low pH and 25° are presented in Table III. The value ϵ_0 is the optical density at zero time (obtained by extrapolation) divided by the total cobalt(III) complex concentration, ϵ_∞ is the optical density at infinite time also divided by the total complex concentration. The observed rate constants k_{obsd} were determined from plots of log ($\epsilon_t - \epsilon_\infty$) against time.

Extrapolation of the high-temperature results to 25° shows that only the first term in the rate law will be important in the pH range 8.5 to 9.5 studied here. Therefore the rate data have been interpreted in terms of the reaction

$$(NH_3)_5CoCO_3H^{2+} + \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (NH_3)_5CoOH_2^{3+} + HCO_3^- \qquad (3)$$

The rate of decomposition is given by

$$-\frac{d[T]}{dt} = k_1[(NH_3)_5CoCO_3H^{2+}] - k_{-1}[(NH_3)_5CoOH_2^{3+}][HCO_3] = k_1[(NH_3)_5CoCO_3H^{2+}] - \frac{k_{-1}}{K_2[OH^-]}[(NH_3)_5CoOH^{2+}][HCO_3^-] \qquad (4)$$

where $K_2 = [(NH_3)_5CoOH^{2+}]/[(NH_3)_5CoOH_2^{3+}][OH^-]$. Let the total concentration of carbonato complex at zero time be $[T]_0$, at any time be [T], and at equilibrium be $[T]_e$. Then applying the equilibrium and stoichiometry conditions

$$[(NH_3)_5CoCO_3H^{2+}] = \frac{[H^+]}{K_1 + [H^+]}[T] \qquad (5)$$

where K_1 is the acid dissociation constant of the bicarbonato complex as defined previously.

Table III. Hydrolysis of $(NH_3)_5CoCO_3^+$ at 25°, μ = 1.0 ($NaClO_4$)

pH[a]	$\epsilon_0 \times 10^{-3}$	$\epsilon_\infty \times 10^{-3}$	$k_{obsd} \times 10^3$ sec^{-1} Found	$k_{obsd} \times 10^3$ sec^{-1} Calcd[b]
8.492	2.32	1.630	26.2	26.7
8.648	2.44	1.645	19.5	19.1
8.695	2.32	1.581	18.0	18.0
8.763	2.40	1.575	15.9	15.0
8.855	2.38	1.590	11.8	13.1
8.960	2.57	1.515	10.5	16.2
9.013	2.39	1.575	9.62	9.46
9.148	2.41	1.445	5.87	6.04
9.237	2.39	1.420	4.68	4.94
9.294	2.22	1.390	4.68	4.87
9.338	2.28	1.355	4.22	3.91

[a] Corrected for sodium ion error. [b] Calculated from eq 7 using $k_1 = 2.26 \times 10^{-2}$ sec^{-1} and $K_1 = 5.94 \times 10^{-9}$ M.

At equilibrium the forward and reverse rates are equal, so that

$$\frac{k_{-1}}{K_2}\left(\frac{[HCO_3^-]}{[OH^-]}\right) = \frac{k_1[H^+]}{K_1 + [H^+]}\left(\frac{[T]_e}{[T]_0 - [T]_e}\right) \qquad (6)$$

Substituting from (5) and (6) into (4) and collecting terms gives the observed rate constant

$$k_{obsd} = \frac{k_1[H^+]}{K_1 + [H^+]}\left(\frac{[T]_0}{[T]_0 - [T]_e}\right)$$

The concentration ratio $[T]_0/([T]_0 - [T]_e)$ can easily be expressed in terms of the apparent extinction coefficients (ϵ) defined previously. Then

$$k_{obsd} = \frac{k_1[H^+]}{K_1 + [H^+]}\left(\frac{\epsilon_0}{\epsilon_0 - \epsilon_\infty}\right) \qquad (7)$$

The optical density due to $(NH_3)_5CoOH^{2+}$ was neglected because its measured extinction coefficient was only 1% of that of the carbonato complexes. Rearrangement of (7) gives

$$\frac{1}{[H^+]} + \frac{1}{K_1} = \frac{k_1}{K_1}\left(\frac{\epsilon_0}{\epsilon_0 - \epsilon_\infty}\right)\frac{1}{k_{obsd}} \qquad (8)$$

Using the data in Table III a plot of $\epsilon_0/[k_{obsd}(\epsilon_0 - \epsilon_\infty)]$ against $[H^+]^{-1}$ was found to be linear as shown in Figure 1. Values of k_1^{-1} and k_1/K_1 were derived from a least-squares fit of the data to a straight line. From this treatment $K_1 = 5.94 \times 10^{-9}$ M and $k_1 = 2.26 \times 10^{-2}$ sec^{-1} at 25° in 1 M $NaClO_4$. These results give $k_1/K_1 = 3.9 \times 10^6$ M^{-1} sec^{-1} at 25° in good agreement

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(7) H. S. Harned and W. J. Hamer, *J. Am. Chem. Soc.*, **55**, 2194 (1933).

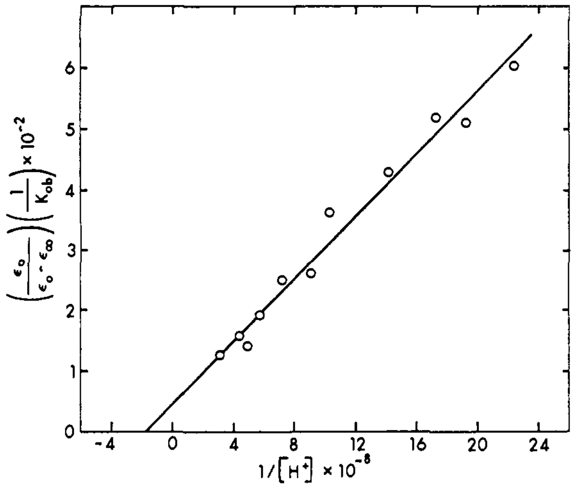

Figure 1. Plot of $\epsilon_0\{(\epsilon_0 - \epsilon_\infty)k_{obsd}]\}^{-1}$ *vs.* $[H^+]^{-1}$. The intercept gives K_1^{-1} and the slope equals k_1/K_1.

with the value 4.2×10^6 obtained by extrapolation of the high-temperature results.

It is also possible to calculate the formation constant K_f for the bicarbonato complex

$$K_f = \frac{[(NH_3)_5CoCO_3H^{2+}][OH^-]}{[(NH_3)_5CoOH^{2+}][HCO_3^-]} \tag{9}$$

It can be shown that

$$K_f = \frac{\epsilon_\infty K_w}{K_1(\epsilon_1 - \epsilon_\infty) + [H^+](\epsilon_2 - \epsilon_\infty)}\left(\frac{1}{[HCO_3^-]}\right) \tag{10}$$

where K_1 is the acid dissociation constant of $(NH_3)_5CoCO_3H^{2+}$ defined previously, and ϵ_1 and ϵ_2 are the molar extinction coefficients of the carbonato and bicarbonato complexes, respectively. The value of K_1 was determined as described and ϵ_1 was measured at various hydroxide ion concentrations greater than 0.05 M where hydrolysis is slow and the only species present is $(NH_3)_5CoCO_3^+$. However the value of ϵ_2 could not be measured directly because the hydrolysis is too fast at low pH where $(NH_3)_5CoCO_3H^{2+}$ would be the predominant species. In principle, knowing ϵ_1 and K_1 it should be possible to calculate ϵ_2 from the ϵ_0 values, since at zero time the only absorbing species are the carbonato and bicarbonato complexes. However the ϵ_0 values in Table III do not show a smooth trend with pH. This randomness is most probably due to the error in extrapolating back to the zero time of mixing. In fact, as shown in the subsequent treatment where a value of ϵ_2 is derived, very little variation is expected in ϵ_0, and the observed values are generally within 10% of the expected value.

The values of ϵ_2 and K_f have been obtained by fitting the ϵ_∞ values to a rearranged form of eq 10

$$\frac{K_1\epsilon_1 - \epsilon_\infty(K_1 + [H^+])}{[H^+]} = \frac{1}{K_f}\left(\frac{K_w\epsilon_\infty}{[H^+][HCO_3^-]}\right) - \epsilon_2 \tag{11}$$

The values used for ϵ_1, K_1, and K_w are 2180, 5.94×10^{-9}, and 1.7×10^{-14},[8] respectively. The bicarbonate ion concentration was calculated from the pH and bicarbonate acid dissociation constant, 2.75×10^{-10}, calculated from the pH of various carbonate buffers in 1 M NaClO$_4$. The resulting plot was found to be linear as shown in Figure 2. A least-squares fit of the data to a straight line gave $K_f = 2.97 \times 10^{-4}$ and $\epsilon_2 = 2134$.

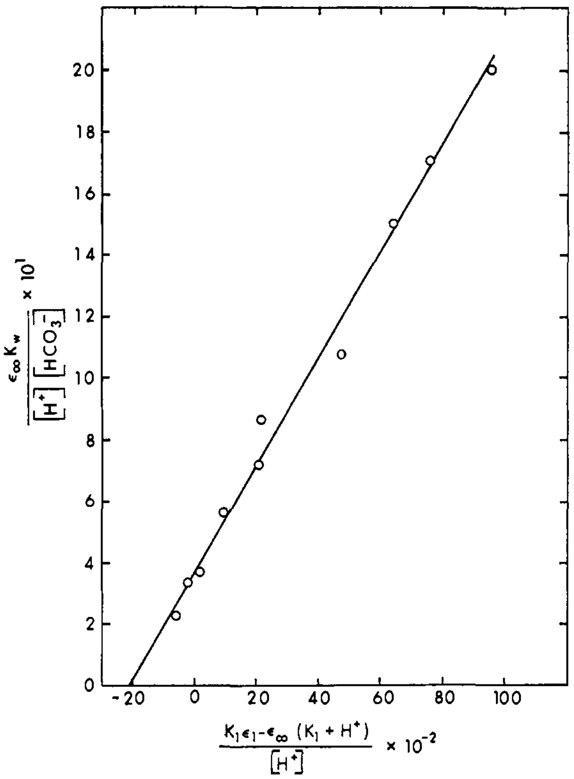

Figure 2. Plot of $\{K_1\epsilon_1 - \epsilon_\infty(K_1 + H^+)\}[H^+]^{-1}$ *vs.* $\epsilon_\infty K\omega([H^+]\cdot[HCO_3^-])^{-1}$. The intercept equals ϵ_2, the extinction coefficient of $Co(NH_3)_5CO_3H^{2+}$, and the slope equals K_f^{-1}.

Conclusions

The rate law for the hydrolysis of $(NH_3)_5CoCO_3^+$ is $-d \ln [\text{complex}]/dt = k_1'[OH^-]^{-1} + k_2[OH^-]$. The second term is consistent with the normal hydroxide ion catalyzed hydrolysis of pentaamminecobalt(III) complexes. Other evidence[10] indicates that these reactions proceed by an SN1CB mechanism. The present results are consistent with such a mechanism but do not substantiate it further.

The first term, $k_1'[OH^-]^{-1}$, in the rate law has been interpreted as due to the aquation of $(NH_3)_5CoCO_3H^{2+}$. Previous tracer studies[11] have shown that this aquation proceeds with O–C bond breaking. The hydrolyses of the analogous protonated oxalate[12] and phosphate[13] complexes indicate that the activation enthalpy for the hydrolysis of the protonated species is close to that

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(8) R. Näsänen and P. Meriläinen, *Suomen Kemistilehti*, 33B, 149 (1960), as quoted in ref 9.

(9) "Stability Constants," Special Publication No. 17, The Chemical Society, London, 1964.

(10) C. H. Langford and H. B. Gray, "Ligand Substitution Process," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 67.

(11) J. P. Hunt, A. C. Rutenberg, and H. Taube, *J. Am. Chem. Soc.*, 74, 268 (1952).

(12) C. Andrade and H. Taube, *Inorg. Chem.*, 5, 1087 (1966).

(13) W. Schmidt and H. Taube, *ibid.*, 2, 698 (1963).

for the unprotonated form. Therefore the difference of 13 kcal mole^{-1} in this case is consistent with the breaking of a different bond in the hydrolysis of $(NH_3)_5CO_3H^{2+}$. The value of 13 kcal mole^{-1} is based on the assumption that the ΔH for K_1 is small compared to the $\Delta H^{\ddagger}$ for k_1. The temperature dependence of the acid dissociation constant of the bicarbonate ion and of oxalatopentaamminecobalt(III)[12] are consistent with this assumption.

It is possible that the rate law could contain a third term which would be independent of acid and might correspond to either uncatalyzed aquation of $(NH_3)_5CoCO_3^+$ or the hydroxide ion catalyzed hydrolysis of $(NH_3)_5CoCO_3H^{2+}$. The results are consistent with such a term, but if such a term exists it must have an apparent rate constant not larger than the value for k_1' and it never contributes more than 10% to the over-all rate. Therefore it cannot be determined accurately and inclusion of such a term does not improve the fit between experimental and calculated observed rate constants.

The acid dissociation constant of $(NH_3)_5CoCO_3H^{2+}$ is approximately 20 times greater than that of the free bicarbonate ion, both in 1 M $NaClO_4$. Previous results on complexed $HO_2C_2O_2^-$ [12] and $H_2PO_4^-$ [13] indicate that the complexed ligand has a K_a about 40 and 100 times larger, respectively, than that of the free ion. Thus the acid dissociation constant is in agreement with estimates which can be made from values for other ligands complexed to cobalt(III).

Previous work on the rate of $^{14}CO_3^{2-}$ exchange on carbonatopentaamminecobalt(III) has given a value of 3.8×10^{-9} M for K_1 and 7.8×10^{-4} sec^{-1} for k_1. The K_1 value is in reasonable agreement with that reported here; however, our hydrolysis rate constant is about a factor of 30 larger (Table IV).

Table IV. Hydrolysis and $^{14}CO_3^{2-}$ Exchange Rates of $(NH_3)_5CoCO_3^+$ at 25°

pH[a]	Exchange rate[b] $\times 10^{-6}$ M sec^{-1}	Hydrolysis rate[c] $\times 10^{-6}$ M sec^{-1}
9.31	5.3	5.5
8.75	10.6	11.3
9.10	8.8	8.9
8.80	16.8	15.8

[a] The pH, complex concentration, and carbonate ion concentrations used are those given in Table 2 of ref 1. [b] Calculated from the rate law of Lapidus and Harris[2] using concentrations as noted in footnote *a*. [c] Calculated from eq 12 assuming only a hydrolysis mechanism.

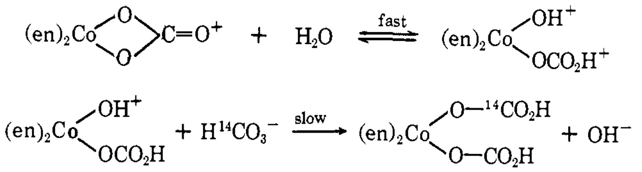
In attempting to determine the reason for the discrepancy in the values of the hydrolysis rate constant, we have tried to fit the exchange rate data to a simple hydrolysis mechanism, using the value of K_1 determined in the present work. The exchange rates were calculated for solution concentrations given by Stranks (Table 2 of ref 1), taking these concentrations as representative experimental conditions. The rates were calculated from the rate law of Harris and Lapidus. These rates are compared to those calculated from eq 12, which assumes only a hydrolysis mechanism for exchange.

$$\text{rate} = \frac{(1.9 \times 10^{-3})[H^+]}{(6 \times 10^{-9}) + [H^+]}[(NH_3)_5CoCO_3^+]_{\text{total}} \quad (12)$$

The fact that the rates calculated from eq 12 agree within ±6% with the exchange rates implies that the carbonate ion exchange rate can be explained adequately by a hydrolysis mechanism without involving carbonate ion attack on the carbonato complex.

However the k_1 value is still about a factor of 10 smaller than the directly measured value. At least part of the difference can be attributed to the differences in ionic strength, which was about 0.08 M for the exchange and 1.00 M in this work. Based on studies of analogous complexes[14,15] the activity coefficient is expected to decrease by about a factor of 5 with an increase in ionic strength from 0.08 to 1.0 M. It is not possible to predict quantitatively the effect of carbonate ion pairing but it is expected to be small because of the large size and low charge of the ions involved.

The above analysis, indicating that there may not be a carbonate ion dependent term in the exchange rate of $(NH_3)_5CoCO_3^+$, might be questioned on the basis that there is such a term in the rate law for carbonate exchange of chelated carbonatoamminecobalt(III) complexes.[2] This term is too significant in the rate law for the latter complexes to be eliminated by a simple juggling of rate and equilibrium constants. However, the results of Scheidegger and Schwarzenbach[16] on carbonatobisethylenediaminecobalt(III) indicate that the chelate CO_3^{2-} ring opens rapidly and the complex exists largely in the monodendate form below pH 10. If this result is assumed to apply generally to other carbonato chelates, then these complexes may undergo carbonate exchange through a dicarbonato complex as outlined for $(en)_2CoCO_3^+$.



This mechanism is only open to the chelated carbonate complexes, and a carbonate ion dependent exchange rate is to be expected for these complexes but not for $(NH_3)_5CoCO_3^+$. It should also be noted that the formation of the dicarbonato complex may proceed with O–C bond making since the aquation of these complexes is known to involve O–C bond breaking.[11,17] This possibility is consistent with the fact that the carbonate ion dependent exchange rate has the same activation energy for all the chelate systems studied[2] except the trimethylenediamine, where steric factors may be important. Oxygen-18 tracer experiments currently in progress should establish if this mechanism is correct.

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[14] W. L. Masterson and J. A. Scola, *J. Phys. Chem.*, **68**, 14 (1964).

[15] C. H. Brubaker and T. E. Haass, *ibid.*, **65**, 866 (1961), and references quoted therein.

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

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