Kinetic Study of the Carbonate Chelate Ring Opening of $(en)_2CoCO_3^+$ in Alkaline Solution[1]

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Abstract: A study has been made of the rate of carbonate chelate ring opening and closing in alkaline solution, over the concentration range 1.19×10^{-3} to 0.90 M NaOH and ionic strength (μ) 1.0 M ($NaClO_4$), between 26 and 44°. The results are interpreted in terms of the reactions $(en)_2CoCO_3^+ + OH^- \rightleftarrows (en)_2CoOHCO_3$ k^1, k_{-1} (3) and $(en)_2CoCO_3^+ + H_2O \rightleftarrows (en)_2CoOHCO_3H^+$ k_2, k_{-2} (4). If the system described by (3) and (4) is approaching equilibrium, under conditions in which $[OH^-]$ is in large excess and therefore constant, then the observed rate constant $k_{obsd} = k_1[OH^-] + k_{-1} + k_2[H_2O] + k_{-2}K_w/K_3[OH^-]$, where K_3 is the acid dissociation constant of $(en_2)CoOHCO_3H^+$. The individual rate constants were determined by fitting k_{obsd} to this equation. The values for the rate constants (at 26°), activation enthalpies (kcal mole^{-1}), and entropies (eu) are: k_1, 3.17×10^{-3} M^{-1} sec^{-1}, 22.0, 3.6; k_{-1}, 6.52×10^{-5} sec^{-1}, 28.2, 16.6; k_2 $[H_2O]$, 5.4×10^{-5} sec^{-1}, 21.4, −6.6; $k_{-2}K_w/K_3$, 1.11×10^{-1} M sec^{-1}, 27.4, 10.6. The equilibrium constant for the first reaction (K_1) was determined spectrophotometrically as 48.5 ± 2.5 at 26°, $\mu = 1.0$ ($NaClO_4$), with a $\Delta H°$ and $\Delta S°$ of −6.46 kcal mole^{-1} and −13.19 eu, respectively. An ^{18}O tracer study has shown that the k_1 path proceeds with Co–O bond cleavage. The results are compared to previous studies on the acid hydrolysis and carbonate exchange of $(en_2)CoCO_3^+$, and to work on phosphate, sulfate, and oxalate chelates.

The alkaline hydrolysis of monodendate ligand cobalt(III) ammine complexes seems to be best explained by the SN1CB mechanism.[2,3] However, prior to the recently published study[4] on $(en)_2CoPO_4$, relatively little was known about the factors controlling rates of chelate ring opening and closing in simple oxyanion chelate complexes. A study of the oxalato complex[5] $(en)_2CoC_2O_4^+$ indicated that oxalate chelate ring opening was the rate-controlling step in the hydrolysis of the complex in alkaline solution to give $(en)_2Co(OH)_2^+$. Taube and Andrade[6] have shown that the oxalate ring opening in alkaline solution proceeds with C–O bond breaking. The chelate ring opening in $(en)_2CoSO_4^+$ was found to be too fast to measure by standard techniques.[7]

The present study was undertaken to try to determine the ligand factors controlling chelate ring-opening rates. In addition, previous studies on $^{14}CO_3^{2-}$[8] and $H_2{}^{18}O$[9] exchange rates have indicated that chelate ring opening is a rate-controlling step in these reactions. A knowledge of the ring-opening rates can be used to evaluate the proposed mechanisms for the exchange reactions.

Experimental Section

Preparation and Analysis of Complex Salt. Carbonatobis(ethylenediamine)cobalt(III) chloride was prepared as described by Schlessinger.[10] The corresponding perchlorate salt precipitates directly on mixing a warm saturated solution of $[(en)_2CoCO_3]Cl$ with a solution of sodium perchlorate. The $[(en)_2CoCO_3]ClO_4$ was recrystallized from hot water, washed with methanol, and stored in a vacuum desiccator over calcium sulfate. The spectra of $[(en)_2CoCO_3]ClO_4$ and its acid hydrolysis product, *cis*-$(en)_2Co(OH_2)_2^{3+}$, compared well with the known spectra.[11,12]

Anal. Calcd for $[(en)_2CoCO_3]ClO_4$: N, 16.6; H, 4.7; C, 17.4. Found: N, 16.8; H, 5.2; C, 17.9.

Base Hydrolysis Kinetics

Solutions containing sodium hydroxide and sodium perchlorate (to adjust the ionic strength to 1.0 M) were added to a thermostated spectrophotometer cell and allowed to come to temperature equilibrium. A stock solution of $[(en)_2CoCO_3]ClO_4$ and $NaClO_4$ was allowed to come to temperature equilibrium and then added to the cell with a syringe surrounded by a water jacket connected to the constant-temperature bath. The complex concentration was varied between 5×10^{-4} and 5×10^{-3} M, depending on the hydroxide ion concentration. The change in absorbance with time at 300 mμ was followed continuously on a Bausch and Lomb Spectronic 505 spectrophotometer. The value of $[OH^-]$ at low concentrations was determined by titration of the reaction solution to pH 7 using a Beckman Expandomatic pH meter equipped with an Expandomatic range selector. The hydroxide ion concentration was always at least ten times greater than the complex concentration. The experimental error in $[OH^-]$ varied greatly owing to the use of different methods of adding the NaOH solution. The experimental error in k_{obsd} was also quite varied because of the different total changes in absorbance at different hydroxide ion concentrations. The absolute error in absorbance was taken to be ±0.010 absorbance unit, the relative error in the time was ±1.7%, and the relative error in complex

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[1] Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

[2] C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter 3.

[3] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1967, Chapter 3.

[4] S. F. Lincoln and D. R. Stranks, *Aust. J. Chem.*, **21**, 57, 1745 (1968).

[5] S. Sheel, D. T. Meloon, and G. M. Harris, *Inorg. Chem.*, **1**, 170 (1962).

[6] C. A. Andrade and H. Taube, *J. Am. Chem. Soc.*, **86**, 1328 (1964).

[7] C. G. Barraclough and R. S. Murray, *J. Chem. Soc.*, 7047 (1965).

[8] G. Lapidus and G. M. Harris, *J. Am. Chem. Soc.*, **85**, 1223 (1963); see also ref 25.

[9] D. McKenzie, C. O'Connor, and A. L. Odell, *J. Chem. Soc., A*, 184 (1966).

[10] G. S. Schlessinger, "Inorganic Laboratory Preparations," Chemical Publishing Co., Inc., New York, N. Y., 1962, p 230.

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

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

concentration was ±3%. The absolute error in the temperature measurements was ±0.1°.

The kinetic runs, at 24.5°, in which ionic strength was not controlled and sodium hydroxide concentration varied from 1.00 to 3.71 *M*, were followed on a Bausch and Lomb Precision spectrophotometer using the same procedure as in the runs with sodium hydroxide concentration less than 1.00 *M*. The temperature of the thermostated cell holder was controlled using a Colora (Papst) constant-temperature bath equipped with a Thermistemp temperature controller (Model 71). During these runs the reaction was followed past 90% completion, during which time the absorbance had quickly risen to a maximum value and then had decreased slowly to a constant value.

Sodium hydroxide solutions were prepared by dilution of ampoules of concentrated reagent (Fisher Certified Reagent). The sodium perchlorate solutions were prepared either by neutralizing sodium carbonate with perchloric acid or by dissolving anhydrous sodium perchlorate (G. Fredrick Smith Chemical Co.). The sodium perchlorate solutions were standardized by elution through a Dowex 50-X12 cation-exchange resin in the hydrogen ion form, and the resultant acid eluent solution titrated with standard sodium hydroxide. All reagents were prepared in water redistilled from alkaline permanganate in an all-glass apparatus.

The reaction product was analyzed for possible geometrical isomerization during the reaction by hydrolyzing aliquots from the reaction solution at various times with 1 *M* $HClO_4$, at 10°, under which conditions no isomerization occurs.[13] The visible spectrum of this product was compared with the known spectra[12] of *cis*- and *trans*-$(en)_2Co(OH_2)_2{}^{3+}$. This comparison was done on reaction solutions which were initially 0.79 and 0.90 *M* in sodium hydroxide.

Oxygen-18 Tracer Study. A solution of ^{18}O-enriched sodium hydroxide was prepared by diluting a concentrated sodium hydroxide solution with 1.7% ^{18}O-enriched water. The molarity of the solution was determined by titration with standard 0.7320 *M* HCl to a phenolphthalein end point. A stock solution containing $[(en)_2CoCO_3]ClO_4$ and $NaClO_4$, in water of normal isotopic abundance, was prepared. The reaction was started by mixing about 4 ml of the stock solution with about 21 ml of the ^{18}O-enriched sodium hydroxide solution. During these runs the complex was about 1×10^{-2} *M*, NaOH varied from 0.50 to 1.00 *M*, μ was 1.0 *M*, and the temperature was 26°. At various times, 2-ml samples of the solution were withdrawn with a syringe and injected into a gas bubbler containing 0.5 ml of concentrated perchloric acid. The CO_2 evolved was carried in a nitrogen stream through a Dry Ice–acetone cooled trap filled with magnesium chips to remove water and then trapped in a U trap with liquid nitrogen. This trap was closed off from the gas stream, the nitrogen removed under vacuum, and the CO_2 transferred to a sample tube by distillation from the U tube which was cooled by a Dry Ice–acetone bath.

The sample was analyzed for $C^{16}O^{16}O$ and $C^{16}O^{18}O$ on a C.E.C. Model 21-614 low-resolution mass spectrometer equipped with a Penning-type pressure gauge on the inlet system (No. EW230a, Atlas MAT and Analysentechnik, Bremen, Germany) and a Honeywell Electronik 15 recorder. The average intensity ratio of the 44–46 mass peaks from three scans was used to determine the ratio $R = C^{16}O^{18}O/C^{16}O^{16}O$. The maximum experimental error for values of *R* was found to be ±2%. The value of *R* for carbon dioxide of normal isotopic abundance was found to be 0.00401 with a standard deviation of 0.00005.

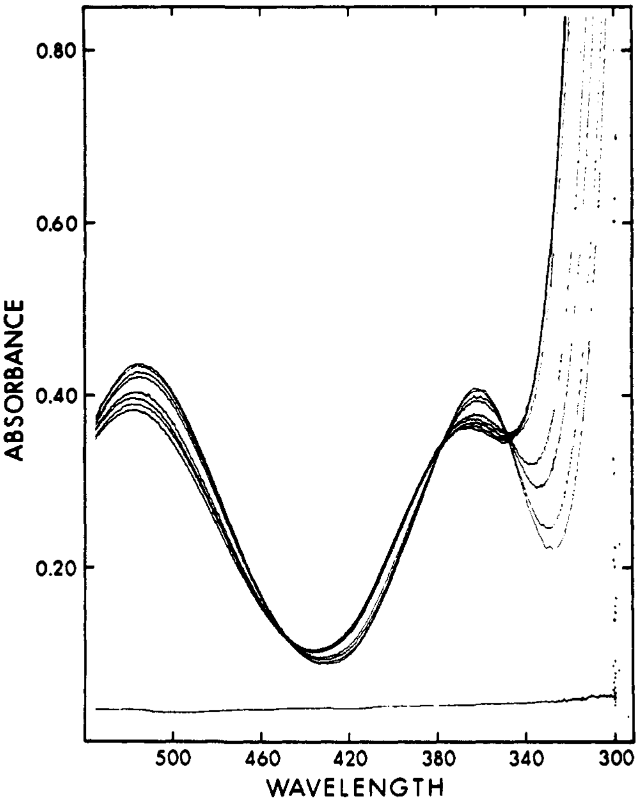

Figure 1. Change in absorbance with time of a solution of $Co(en)_2CO_3{}^+$ (3.05×10^{-3} *M*) and NaOH (0.100 *M*) at 26° over a time period of 115 min after mixing. The absorbance is increasing at 320 mμ and decreasing at 360 and 515 mμ.

Results

It was found that a solution of $[(en)_2CoCO_3]ClO_4$ in water was stable and that no spectral change occurred for periods of at least 1 week. Figure 1 shows the spectral change which occurred when sodium hydroxide was added to the neutral stock solution of complex. From a comparison of the spectra in Figure 2, it is obvious that the first species being produced cannot be *cis*-$(en)_2Co(OH)_2{}^+$. A similar comparison to the spectra of Bjerrum and Rasmussen[12] shows that the product cannot be *trans*-$(en)_2Co(OH)_2{}^+$. The initial rise in absorbance at 300 mμ as shown in Figure 3 has been interpreted as being caused by the production of *cis*-$(en)_2CoOHCO_3$. The slow decrease in absorbance then corresponds to the production of *cis*-$(en)_2Co(OH)_2{}^+$.

Figure 3 also indicates that the second reaction cannot be ignored when determining the observed rate constant for the first reaction. A_t and A_∞ are the absorbancies of the reaction solution at some time *t* and at complete reaction, respectively. If A_{max} is the value of the maximum observed absorbance, then plots of log $(A_{max} - A_t)$ *vs.* time become nonlinear after approximately

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[13] F. P. Dwyer, A. M. Sargeson, and I. K. Reid, *J. Am. Chem. Soc.*, **85**, 1215 (1963).

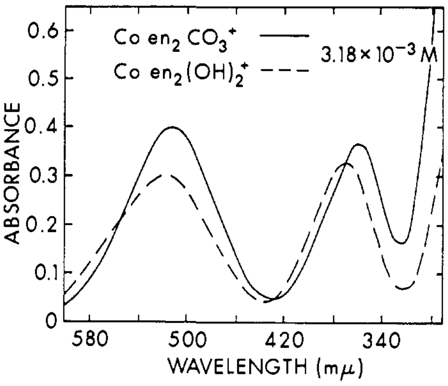

Figure 2. Visible absorption spectra of Co(en)$_2$CO$_3^+$ (———) and *cis*-Co(en)$_2$(OH)$_2^+$ (- - -). Both solutions are 3.18 × 10^{-3} *M*.

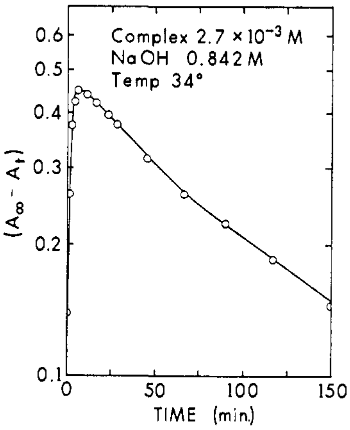

Figure 3. Variation of log (A_t − A_∞) with time of a solution of Co(en)$_2$CO$_3^+$ (2.7 × 10^{-3} *M*) and NaOH (0.842 *M*) at 34°, recorded at 300 mμ. A_∞ is the calculated absorbance of an equimolar solution of *cis*-Co(en)$_2$(OH)$_2^+$.

one half-time of the first reaction as seen in Figure 4, plot A. Provided the rate constants of consecutive, first-order reactions are different by at least a factor of 10, it is possible to separate the concentration–time dependence data into components corresponding to each of the consecutive reactions.[14] For the present case, this separation was done by extrapolating the log (A_t − A_∞) *vs.* time plot to zero time to obtain a value for log (A'_{max} − A_∞). A'_{max} is the absorbance which the reaction solution would have shown at the completion of the first reaction had the second reaction not occurred. As seen in Figure 4, plot B, a plot of log (A'_{max} − A_t) *vs.* time is linear and has a different observed rate constant from the log (A_{max} − A_t) *vs.* time plot. This "extrapolation" method was used to analyze the kinetic data at 24.5° and resulted in the rate constants used for Figure 8. It was found that increasing A_{max} to some A'_{max} where A'_{max} was sufficiently large to cause linearity in a plot of log (A'_{max} − A_t) *vs.* time was equivalent to obtaining A'_{max} by extrapolation. Since sufficient data for the extrapolation had not been obtained, this second method of obtaining A'_{max} was used to evaluate the kinetic data at 26.0 (Table I) and also at 34.0 and 44.0°. As the sodium hydroxide concentration decreased from 3.71 to 0.817 *M*, the corrections in k_{obsd} decreased from −32 to −16%, respectively, and became negligible below 0.50 *M*.

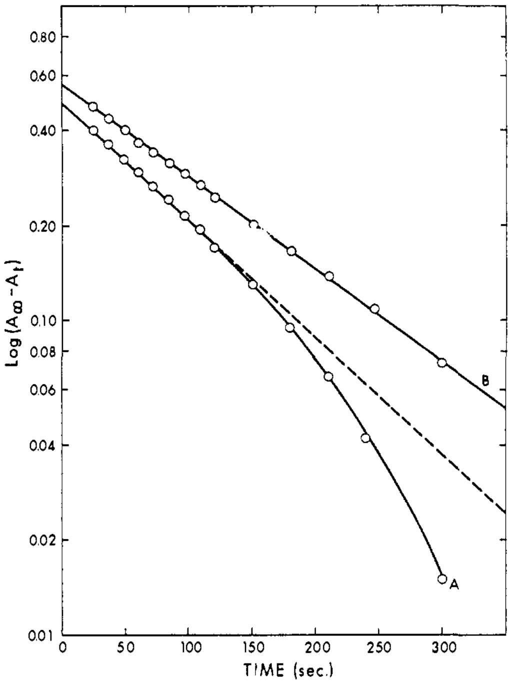

Figure 4. Plot of log (A_{max} − A_t) (curve A) and log (A'_{max} − A_t) (curve B) *vs.* time. A_{max} is the maximum absorbance observed; A'_{max} is obtained by extrapolation to zero time of a plot similar to Figure 3. Co(en)$_2$CO$_3^+$, 1.475 × 10^{-4} *M*; NaOH, 3.00 *M*; 24.5°; μ = 3.0.

The spectrophotometric determination of the geometrical configuration of the product, as described in the Experimental Section, showed that the first reaction produces greater than 95% *cis*-(en)$_2$CoOHCO$_3$ for 0.79 *M* < [OH$^-$] < 0.90 *M*. With respect to the second

Table I. Variation in k_{obsd} with Hydroxide Ion Concentration at 26°, μ = 1.0 *M* (NaClO$_4$)

	$k_{\text{obsd}} \times 10^3$ sec^{-1}	
[OH$^-$], *M*	Calcd[a]	Exptl
0.00119	1.05	1.31
0.00179	0.745	0.729
0.00232	0.605	0.607
0.00246	0.577	0.577
0.00342	0.455	0.525
0.00681	0.304	0.285
0.01363	0.243	0.244
0.01705	0.238	0.229
0.02042	0.238	0.230
0.02720	0.246	0.214
0.04080	0.276	0.252
0.04080	0.276	0.259
0.06810	0.351	0.324
0.1302	0.557	0.490
0.2040	0.771	0.745
0.2725	0.987	1.00
0.3410	1.20	1.26
0.3550	1.25	1.26
0.3810	1.32	1.32
0.4450	1.53	1.72
0.5080	1.73	1.87
0.5720	1.93	2.04
0.6030	2.03	2.15
0.6130	2.23	2.37
0.6800	2.37	2.64
0.7480	2.80	2.86
0.8170	3.24	3.12
0.8860	3.32	3.53

[a] Calculated from eq 7 and the fitted rate constants, Table III.

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[14] C. G. Swain, *J. Am. Chem. Soc.*, 66, 1696 (1944).

reaction, the curvature in the plot of log $(A_t - A_\infty)$ *vs.* time (Figure 3) which appears after one half-time has been attributed to the *cis* ⇄ *trans* isomerization of $\mathrm{(en)_2Co(OH)_2^+}$ because the *trans*-dihydroxy isomer has a slightly higher extinction coefficient at 300mμ[12] than the *cis* isomer and because the half-times of the second reaction and the isomerization are comparable, being 1.49×10^4 sec ($[\mathrm{OH^-}] = 1.00\ M$) and 18.7×10^4 sec, respectively, at 25°.[15] At $[\mathrm{OH^-}] > 1.00\ M$, no curvature appears in the log $(A_t - A_\infty)$ *vs.* time plots even after two half-times of the second reaction indicating that the second reaction is essentially complete before appreciable isomerization can occur.

It was observed that the corrected value of the absorbance of the reaction solution after completion of the first reaction (*i.e.*, $A'_{\max}$) varied both with temperature and hydroxide ion concentration. Both these effects indicated that the first step in the reaction is an equilibrium process. An equilibrium constant, K_1, is defined by

$$K_1 = [\mathrm{(en)_2CoOHCO_3}]/[\mathrm{(en)_2CoCO_3^+}][\mathrm{OH^-}]$$

It can be shown that K_1 and $[\mathrm{OH^-}]$ are related by the equation

$$\frac{1}{[\mathrm{OH^-}]} = K_1(\epsilon_\mathrm{B} - \epsilon_\mathrm{A})\left(\frac{la_0}{A'_{\max} - A_0}\right) - K_1 \qquad (1)$$

where ϵ_B and ϵ_A are the extinction coefficients of $\mathrm{(en)_2CoCO_3^+}$ and $\mathrm{(en)_2CoOHCO_3}$, respectively, a_0 is the total complex concentration, l is the cell length in centimeters, A_0 is the zero-time absorbance of the solution derived from the zero-time extrapolated value of the log $(A'_{\max} - A_t)$ *vs.* time plot, and A_t and $A'_{\max}$ have been defined previously. Equation 1 shows that a plot of $[\mathrm{OH^-}]^{-1}$ *vs.* $la_0/(A'_{\max} - A_0)$, Figure 5, should be linear. The best fit of the data to eq 1 was obtained by an IBM 360-65 computer using a least-squares fit to a polynomial. A weighting factor of $1/[\mathrm{OH^-}]$ was used to compensate for the large order of magnitude changes in the data. Table II shows the values of K_1 obtained at various temperatures, the standard error of the fit on the parameter, and the values of $\Delta H°$ and $\Delta S°$ obtained from a plot of log K_1 *vs.* $1/T$.

Table II. Variation in K_1 with Temperature ($\mu = 1.0\ M$ ($\mathrm{NaClO_4}$))

Temp, °C	K_1, M^{-1}
26	48.5 ± 2.5
34	36.7 ± 1.4
44	26.4 ± 2.1
$\Delta H°$, kcal mole^{-1}	−6.46 (−7.78 → −5.03)
$\Delta S°$, cal mole^{-1} deg^{-1}	−13.9 (−18.2 → −9.1)

Over the range of hydroxide ion concentrations, 1.19×10^{-3} to 0.899 M, the dependence of the rate of approach to equilibrium on hydroxide ion is represented by

$$\frac{-\mathrm{d}\ln[\mathrm{(en)_2CoCO_3^+}]}{\mathrm{d}t} = k'[\mathrm{OH^-}] + k'' + k'''[\mathrm{OH^-}]^{-1} = k_{\mathrm{obsd}} \qquad (2)$$

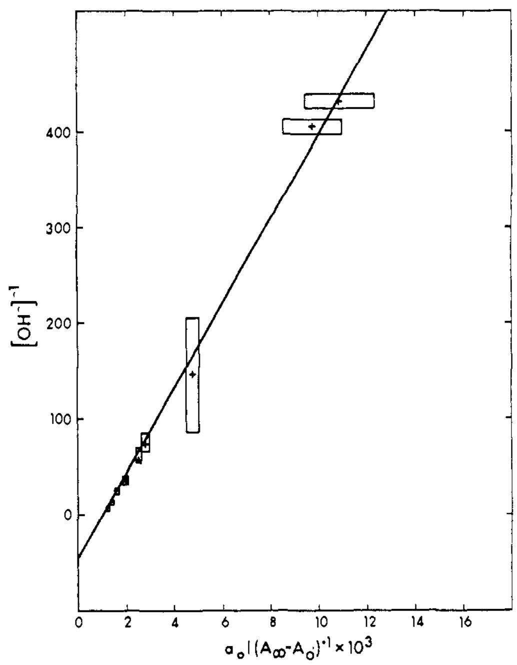

Figure 5. Plot of $[\mathrm{OH^-}]^{-1}$ *vs.* $a_0l/(A'_{\max} - A_0)$. The boxes indicate the experimental error; the line is obtained from a least-squares analysis.

If reactions 3 and 4 are the processes involved in the rate of equilibrium attainment, then the rate law is given by eq 5. K_w is the ion product of water. K_1 is related to the various rate constants by

$$\mathrm{(en)_2CoCO_3^+ + OH^-} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{(en)_2CoOHCO_3} \qquad (3)$$

$$\mathrm{(en)_2CoCO_3^+ + H_2O} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{(en)_2CoOHCO_3H^+} \overset{K_3}{\rightleftarrows} \mathrm{(en)_2CoOHCO_3 + H^+} \qquad (4)$$

$$\frac{-\mathrm{d}\ln[\mathrm{(en)_2CoCO_3^+}]}{\mathrm{d}t} = k_1[\mathrm{OH^-}] + k_{-1} + k_2[\mathrm{H_2O}] + \frac{k_{-2}K_\mathrm{w}}{K_3[\mathrm{OH^-}]} \qquad (5)$$

$$K_1 = \frac{k_1}{k_{-1}} = \frac{k_2[\mathrm{H_2O}]K_3}{k_{-2}K_\mathrm{w}} \qquad (6)$$

Substitution for k_{-1} and $k_2[\mathrm{H_2O}]$ in eq 5 results in

$$k_{\mathrm{obsd}} = k_1[\mathrm{OH^-}] + k_1/K_1 + k_{-2}K_\mathrm{w}K_1/K_3 + k_{-2}K_\mathrm{w}/(K_3[\mathrm{OH^-}]) \qquad (7)$$

It can be seen by comparison of (2) and (7) that the rate law developed from reactions 3 and 4 is consistent with the experimental rate law. The values of the specific rate constants were obtained by fitting the experimental k_{obsd} values to eq 7 and using the previously determined value of K_1. The program[16] was modified to minimize the sum of the squares of the relative residuals, in the least-squares analysis, instead of the normal minimization of the sum of the squares of the absolute residuals. The standard errors[17] of the fit at 26.0, 34.0, and 44.0° were 0.0814, 0.1569, and 0.0769, respectively.

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[15] W. Kruse and H. Taube, *J. Am. Chem. Soc.*, **83**, 1280 (1961).

[16] Share No. SDA 3094, IBM 360-65.

[17] The standard error (SE) of the fit is defined by SE = $\sqrt{\hat{\Phi}/n - k}$ where n is the total number of data points, k is the total number of parameters, $\hat{\Phi} = \Sigma_{i=1}{}^{n}[Y_i - \hat{Y}_i]^2$, $\hat{\Phi}$ is the minimum Φ, Y_i is the experimental value of Y, and $\hat{Y}_i$ is the calculated value of Y.

Table III. Specific Rate Constants for Base Hydrolysis of $(en)_2CoCO_3^{+a}$

Temp, °C	$k_1 \times 10^3$, M^{-1} sec^{-1}	$k_{-1} \times 10^5$, sec^{-1}	$k_2[H_2O] \times 10^5$, sec^{-1}	$k_{-2}K_w/K_3 \times 10^6$, M sec^{-1}
26.0	3.17 ± 0.18	6.52 ± 0.71	5.40 ± 0.81	1.11 ± 0.11
34.0	8.69 ± 0.74	23.7 ± 2.9	13.4 ± 3.2	3.65 ± 0.73
44.0	27.4 ± 1.7	104 ± 15	43.1 ± 8.7	16.3 ± 2.0
$\Delta H^{\ddagger}$, kcal/mole	22.0 (23.3–20.8)	28.2 (31.0–25.6)	21.4 (23.3–17.3)	27.4 (29.6–25.0)
$\Delta S^{\ddagger}$, eu	+3.6 (+7.9 → −0.5)	+16.6 (+25.9–+8.1)	−6.6 (−0.3–−20.5)	+10.6 (+13.0–+2.1)

[a] The errors in k_1 and $k_{-2}K_w/K_3$ are determined from the least-squares fit and approximate 95% confidence limits. k_1 and $k_2[H_2O]$ were calculated from k_1 and $k_{-2}K_w/K_3$, respectively, and K_1. Errors in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are calculated from lines of maximum and minimum slope on a plot of k/T vs. $1/T$.

From the standard error of the fit, the program also computed upper and lower boundaries on the parameters which approximate their 95% confidence limits. Using these values, the 95% confidence regions for the fitted lines were calculated, and these were seen to overlap with the experimental error on the data points for each temperature. Equation 7 was found to fit the observed data within the experimental error, as shown in Figures 6 and 7 for the 26.0° data. Calculated and observed values are compared in Table I. Table III gives the specific rate constants at each temperature and their activation parameters determined from a plot of log (k/T) vs. $1/T$.

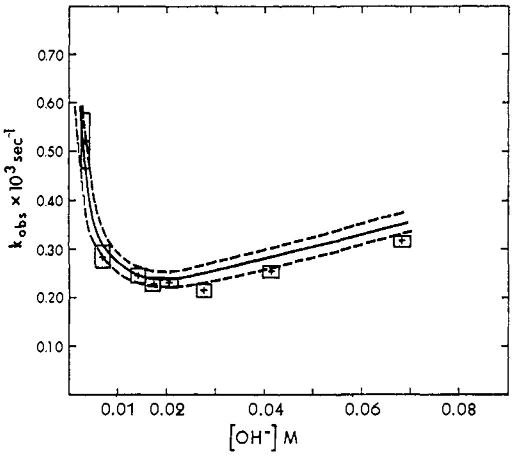
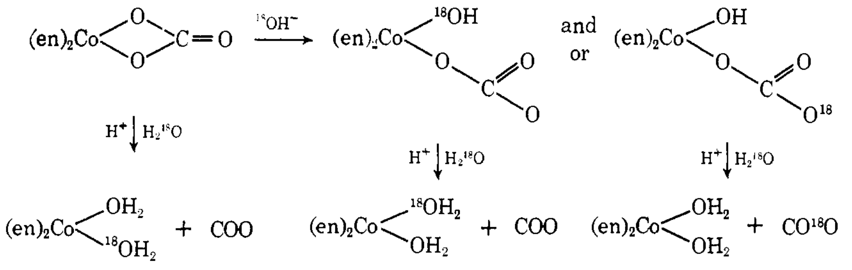


Figure 6. Plot of k_{obsd} vs. $[OH^-]$ at 26°, μ = 1.0 M. The boxes indicate the experimental error. The solid line is the best fit of the data to eq 5; the dashed line indicates the limits of the 95% confidence region.



(8)

The oxygen-18 tracer study was carried out by acidifying the strongly alkaline reaction solution and collecting the carbon dioxide evolved as described in the Experimental Section. Equation 8 shows the possible isotope distributions in the CO_2 product. It is known for the analogous tetraammine and pentaammine species that acid hydrolysis goes without incorporation of solvent oxygen into the CO_2.[18,19] Therefore ^{18}O enrichment of the CO_2 would be consistent only with carbon–oxygen bond cleavage in the ring-opening step. At 26.0° and over a hydroxide ion concentration range of 0.50–1.00 M, no enrichment of CO_2 was observed. Table IV shows the results of a typical run. The difference in R values for the reaction mixture and CO_2 of normal isotopic composition was found to be entirely due to dissolved carbonates in the concentrated sodium hydroxide solutions.

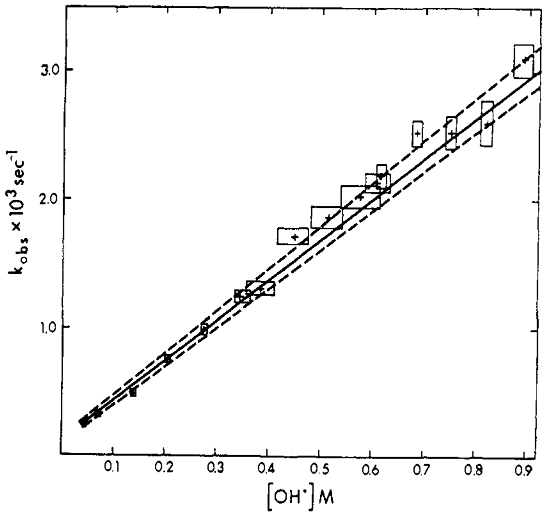


Figure 7. Plot of k_{obsd} vs. $[OH^-]$ at 26° at the higher hydroxide ion concentrations. The symbols have the same meaning as in Figure 6.

It has not been possible to reproduce the rate constants obtained by Farago[20] for the hydrolysis of $(en)_2$-

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

(19) F. A. Posey and H. Taube, *ibid.*, **75**, 4099 (1953).

(20) M. E. Farago, *Coord. Chem. Rev.*, **1**, 66 (1966).

Table IV. Tracer Results on the Hydrolysis of $(en)_2CoCO_3^+$ (0.50 M $[OH^-]$; 26°, μ = 1.0 M $(NaClO_4)$)[a]

Time, min	$R^a \times 10^3$
5.5	5.68
27.5	6.50
59	5.95
214	6.69
1043	6.62
1127	6.31
2495	5.62

[a] R is the intensity ratio of mass 46 to mass 44 peaks in the mass spectrum of CO_2. R of CO_2 of normal isotopic composition was found to be 0.00384. R of CO_2 equilibrated for 24 hr at 80° with ^{18}O enriched water (vacuum distilled from reaction solution) was 0.02970. If the base-catalyzed ring opening occurs by C–O bond cleavage, a value of R of 0.0168 is predicted.

$CoCO_3^+$ at high hydroxide ion concentrations. The results are compared in Figure 8, where it can be seen that no large leveling effect was observed. The values of k_{obsd} have been corrected for the change in activity of sodium hydroxide by the factor N, the ratio of the activity coefficient of 1 M NaOH to the activity coefficient of NaOH at the concentration used. The k_{obsd} values, in the range 0.4–0.9 M NaOH, were calculated from the values of the specific rate constants at 24.5° and eq 5. The curves in Figure 8 might be explained by ion pairing between hydroxide ion and $(en)_2CoCO_3^+$ as suggested by Farago. However, the results from our study show no distinct leveling, and the curvature may be due to a change in the activity coefficient of the complex as the total ionic strength changes. Without a reliable independent measure of the ion-pair formation constant, it is not possible to decide between these alternatives.

Discussion

It has been found that the hydrolysis of $(en)_2CoCO_3^+$ in the pH range 1–5 may be described by the reactions[21]

$$(en)_2CoCO_3^+ + H_3O^+ \xrightarrow{k_1'} (en)_2CoOH_2CO_3H \xrightarrow{\text{fast}} (en)_2Co(OH_2)_2 + CO_2 \qquad (9)$$

$$(en)_2CoCO_3^+ + H_2O \xrightarrow{k_2} (en)_2CoOH_2CO_3 \xrightarrow{\text{fast}} (en)_2Co(OH_2)_2 + CO_2 \qquad (10)$$

The value of 4.9×10^{-5} sec^{-1} for $k_2[H_2O]$ found in this study is in only fair agreement with the value of 2.04×10^{-4} sec^{-1} [22] determined from the data of Sastri and Harris. The acid hydrolysis study of the analogous tetraammine complex $(NH_3)_4CoCO_3^+$ yields a value for $k_2[H_2O]$ of 1.3×10^{-4} sec^{-1}.[21] The values of the activation parameters for $k_2[H_2O]$ for the tetraammine complex, $\Delta H^\ddagger = 20$ kcal mole^{-1} and $\Delta S^\ddagger = -15$ eu, are similar to the corresponding values for the bis(ethylenediamine) complex of $\Delta H^\ddagger = 21.4$ kcal mole^{-1} and $\Delta S^\ddagger = -6.6$ eu.

Odell[9] has studied the rate of exchange of ^{18}O-enriched water with the $(NH_3)_4CoCO_3^+$ ion in the pH region 8–10 at 25°. He found that all three carbonate oxygens exchanged and that the rate of exchange of three solvent oxygens for three coordinated oxygens was slower than the analogous rate of exchange for uncoordinated carbonate. Exchange of all three oxygens requires fast exchange after the ring has opened but before ring closure. Ring opening by cobalt–oxygen bond cleavage requires only water–carbonate exchange of oxygens while carbon–oxygen bond cleavage requires both water–carbonate and water–water exchange of oxygens. These two mechanisms are indistinguishable in the exchange study. Derivation of the rate law for both paths shows that the experimental rate constant for the exchange of one water molecule is equal to the specific rate constant for ring opening, *i.e.*

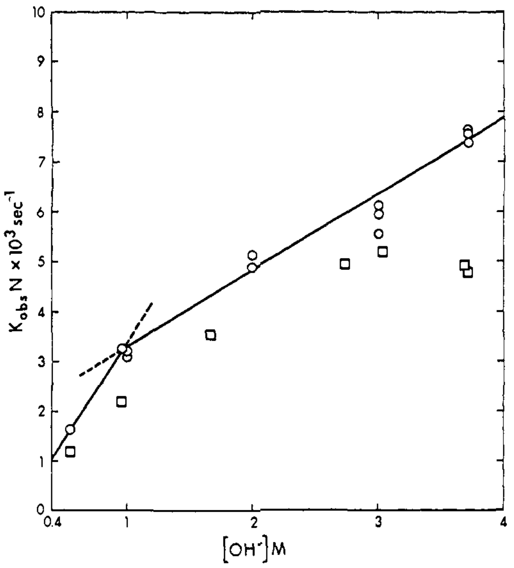

Figure 8. Plot of k_{obsd} N *vs.* $[OH^-]$ at high hydroxide ion concentrations with no ionic strength control. The results from this work (○) are compared to those of Farago (□). N is the activity coefficient of sodium hydroxide divided by the activity coefficient in 1.0 M sodium hydroxide (temperature 24.5°).

$$\frac{3 \times 0.693}{(t_{1/2})_{\text{exchange}}} = k_2[H_2O]$$

At 25°, Odell's value of $k_2[H_2O]$, 2.20×10^{-5} sec^{-1}, ($\Delta H^\ddagger = 24.3$ kcal mole^{-1}, $\Delta S^\ddagger = +2.1$ eu) compares well with our value of 4.94×10^{-5} sec^{-1} ($\Delta H^\ddagger = 21.4$ kcal mole^{-1}, $\Delta S^\ddagger = 6.6$ eu) considering the different ammine ligands. In general then, the value of $k_2[H_2O]$ determined in our base hydrolysis study is consistent with independent measurements of the same parameter.

It should also be noted that, in a previous study[24] of the hydrolysis of $(en)_2CoCO_3^+$ at $[OH^-] > 0.1$ M, values were obtained for $k_1 = 3.2 \times 10^{-3}$ M^{-1} sec^{-1}, $\Delta H_1^\ddagger =$ 21.6 kcal mole^{-1}, and $\Delta S_1^\ddagger = 0.6$ eu. These values are in excellent agreement with those found in the present study.

It is also possible to compare the rate of chelate ring opening for various ligands. The available rate constants are summarized in Table V. In addition it has been observed that the rate of ring opening in $(en)_2CoSO_4^+$ is too fast to measure by conventional techniques.[7] The lack of any activation enthalpies and entropies for the sulfato, oxalato, and phosphato systems prevents any meaningful rationalization of these rate trends in terms of factors such as chelate ring strain, ligand solvation, and mechanism changes.

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[21] K. V. Krishnamurty, G. M. Harris, and V. S. Sastri, *Chem. Rev.*, in press.

[22] This value of $k_2[H_2O]$ at 25° was determined by fitting the data of Sastri and Harris calculated from their fitted equation to the rate law developed from eq 9 and 10 and does not quite agree with the value of 1.3×10^{-4} sec^{-1} reported by Harris.[23]

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

[24] G. Hargis, Ph.D. Dissertation, Ohio University, 1966.

Table V. Comparison of Parameters for $(en)_2CoC_2O_4^+$, $(en)_2CoCO_3^+$, and $(en)_2CoPO_4$ at 22.5°

Complex	$k_1 \times 10^4$, M^{-1} sec^{-1}	$k_{-1} \times 10^3$, sec^{-1}	$k_2(H_2O) \times 10^3$, sec^{-1}	$k_{-2} \times 10^2$, sec^{-1}	K_1, M^{-1}	Co–O cleavage in base hydrolysis, %
$(en)_2CoC_2O_4^+$	0.056[a]	...	...	...	...	0[b]
$(en)_2CoCO_3^+$	2.2	0.0042	0.034	7.1	52.8	100
$(en)_2CoPO_4$	17.5	2.4	0.025	0.083	764	65[c]

[a] Calculated from the measured value at 71° and the activation energy of 34 kcal mole^{-1} reported by S. Sheel, *et al.*, *Inorg. Chem.*, **1**, 170 (1962). [b] C. A. Andrade and H. Taube, *J. Am. Chem. Soc.*, **86**, 1328 (1964). [c] S. F. Lincoln and D. R. Stranks, *Aust. J. Chem.*, **21**, 1745 (1968).

It is also noted in Table V that the position of bond cleavage is different for the phosphate, carbonate, and oxalate complexes. The relative importance of cobalt–oxygen or oxygen–ligand central atom bond breaking will depend on the relative strengths of these two bonds and also on the susceptibility of the ligand atom to nucleophilic attack by hydroxide ion. It is not possible as yet to anticipate the bond-breaking pattern with different oxyanion ligands. It is unfortunate that in the phosphate system, where both bond-breaking paths are contributing, no kinetic parameters for the two paths are available.

It is generally observed that the ratio of the rate constants for hydroxide-catalyzed and uncatalyzed hydrolysis for cobalt(III) ammine complexes is of the order of 10^5 to 10^8 M^{-1}. The ratio $k_1/k_2[H_2O]$ for $(en)_2CoPO_4$ is 7×10^4 and seems reasonably normal; however, for $(en)_2CoCO_3^+$ the ratio is only 6.5. This strongly suggests a change of mechanism in the carbonate system and it seems likely that the $k_2[H_2O]$ path proceeds with C–O bond breaking.

It is also interesting to compare the rate constants for the ring-closing reaction (k_{-1}) in Table V for the phosphato and carbonato complexes. If this reaction is analogous to an anation reaction, then the rate would be controlled by the rate of hydroxide ion exchange from the ring-opened complex for an SN1 mechanism. The fact that k_{-1} for $(en)_2CoPO_4OH^-$ is 500 times faster than for $(en)_2CoCO_3OH$ may be due to the charge difference but is also in the direction expected for an SN2 mechanism for chelate ring closure. Studies of the $^{18}OH^-$ exchange with the ring-opened species and rate of ring closure for other ligands would be most helpful in determining the mechanism for the chelation reaction.

Acknowledgments. The authors wish to acknowledge the financial support of the National Research Council of Canada under Contract No. NRC A-2950. D. J. F. wishes to express thanks for a bursary from the National Research Council of Canada.

Synthesis and Characterization of Some Cobalt(III) Complexes of Ethylenediaminetriacetic Acid

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Abstract: A series of complex compounds of cobalt(III) involving pentadentate ethylenediaminetriacetic acid, ED3A, as the chelating agent have been prepared. These compounds have the general formula K[Co(ED3A)X] where X^- is Cl^-, NO_2^-, or ONO^-. The structures of these complexes are inferred from their chemistries and spectral data. The infrared spectra of the compounds have been measured and interpreted. The absorption spectra of the complexes are compared with those for the related series of complexes $Co(EDTA)X^{2-}$, $Co(HEDTA)X^-$, and $Co(MEDTA)X^-$. The proton nmr spectra indicate that ED3A acts as a pentadentate ligand exhibiting three different AB acetate patterns occurring in the region 4.3 to 3.2 ppm (*vs.* sodium 3-(trimethylsilyl)-1-propanesulfonate). The spectrum in acid solution confirms the existence of the ED3A ligand by the amine proton absorption and its coupling with the low-field acetate protons. Partial resolution was achieved by use of a cellulose ion-exchange column.

Numerous examples of cobalt(III) complexes that employ pentadentate chelating agents of the aminopolycarboxylic acid variety have been prepared and are rather well characterized. Schwarzenbach[1] prepared the first pentadentate cobalt(III) complexes using ethylenediaminetetraacetic acid. He reported compounds of the general formula $Co(HY)X^-$ where HY is the singly protonated form of ethylenediaminetetraacetic acid and X^- is Br^- and NO_2^-. Recently Van Saun and Douglas[2] have prepared and resolved a series of cobalt(III) complexes of MEDTA, $Co(MEDTA)X^-$, where MEDTA is the anion of N-methylethylenedi-

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[1] G. Schwarzenbach, *Helv. Chim. Acta*, **32**, 839 (1949).

[2] C. W. Van Saun and B. E. Douglas, *Inorg. Chem.*, **7**, 1393 (1968).