The Mechanism of the Base Catalysed Carbonato Ring Opening of *cis*-[Co(cyclen)CO_3]$^+$

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The kinetics of carbonato ring opening of cis-*[Co(cyclen)CO_3]$^+$ (cyclen = 1,4,7,10-tetraazacyclododecane) in basic solution has been studied in detail over a temperature range. The reaction shows a complex dependence on the hydroxide ion concentration with both first and second order terms in [OH^-] occurring. The observed first order rate constant k_{obs} is given by the equation*

$$k_{obs} = \frac{k_1K_1[OH^-] + k_2K_1K_2[OH^-]^2}{1 + K_1[OH^-] + K_1K_2[OH^-]^2}$$

Values of k_1K_1 and $k_2K_1K_2$ have been obtained and the apparent activation parameters determined. A mechanism is developed which can rationalise all the kinetic data.

Introduction

The acid catalysed decarboxylation of carbonato complexes of cobalt(III) has been thoroughly studied and the mechanism of the reaction is now well understood [1, 2]. Ring opening of *cis*-[Co(en)$_2$-CO_3]$^+$ occurs in basic solution and the reaction has been studied kinetically [3], but the kinetics are complicated by subsequent *cis* ⇌ *trans* isomerisation. Base hydrolysis of *cis*-[Co(tren)CO_3]$^+$ gives [Co(tren)(OH)(CO_3)] which has been characterised in solution [4]. In acidic solution this latter complex is protonated to give [Co(tren)(OH_2)(HCO_3)]$^{2+}$, which undergoes rapid decarboxylation (k = 1.19 s^{-1} at 25 °C) by a mechanism completely analogous to that of acid-catalysed decarboxylation of related pentaaminecobalt(III) complex ions.

The present study was undertaken to gain information about the mechanism of ring opening of carbonato complexes in basic solution. The ligand cyclen gives only *cis*-complexes with cobalt(III) [5] and the kinetics of ring opening are not complicated by subsequent *cis* ⇌ *trans* isomerisation.

Experimental

The ligand cyclen was prepared as previously described [6] and *cis*-[$CoCl_2$(cyclen)]Cl as described by Hay and Jeragh [2]. *Cis*-[Co(cyclen)CO_3]Cl·$2H_2O$ was synthesised essentially as described by Collman and Schneider [5] by reacting the dichloro complex with Li_2CO_3. The complex was recrystallised from H_2O:EtOH. *Anal.* Calc. for $C_9H_{24}ClCoN_4O_4$, C, 29.8; H, 6.7; N, 15.4. Found: C, 29.4; H, 6.4; N, 15.1%. In aqueous solution the complex has λ_{max} 522 nm (ϵ = 279 M^{-1} cm^{-1}) and 362 nm (ϵ = 208 M^{-1} cm^{-1}). Collman and Schneider [5] report 530 nm (ϵ = 280) and 368 nm (ϵ = 210 M^{-1} cm^{-1}).

Ring opening of the carbonato complex was monitored using the decrease in absorbance at 300 nm. Absorbance data were collected using a Gilford 2400S spectrophotometer and logged on an Apple II computing system. Values of k_{obs} were evaluated by a least squares treatment of plots of $\ln(A_\infty - A_t)$ *versus* time. Each rate constant is the mean of some four to five kinetic runs. All kinetic measurements were carried out using an ionic strength of 0.5 *M* ($NaClO_4$). Routine and interval scan visible spectra were measured using a Perkin-Elmer 402 instrument.

Results and Discussion

Values of k_{obs} (the observed first order rate constant) at constant hydroxide ion concentration were obtained from the decrease in the absorbance of the carbonato complex at 300 nm as a function of time. The rate constants at three different temperatures are summarised in Table I. Plots of k_{obs} versus the hydroxide ion concentration are not linear, Fig. 1, indicating that a simple first order dependence of k_{obs} on the hydroxide ion concentration does not occur. The observed kinetic behaviour is indicative of a second order dependence on [OH^-]. The data

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TABLE I. Rate Constants k_{obs} for Ring Opening of *cis*-[Co(cyclen)CO$_3$]$^+$ in Basic Solution at I = 0.5 *M* (NaClO$_4$).

Temp. (°C)	[OH$^-$] (*M*)	10^3 k_{obs} (s^{-1})	10^3 k_{obs}/[OH$^-$] (M^{-1} s^{-1})
18.6	0.04	0.36	9.0
	0.06	0.80	13.3
	0.10	1.89	18.9
	0.15	3.88	25.9
	0.20	6.38	31.9
	0.25	8.81	35.2
	0.35	13.70	39.1
24.8	0.02	0.36	18.0
	0.04	0.77	19.25
	0.06	1.35	22.5
	0.10	3.90	39.0
	0.12	4.87	40.6
	0.15	7.35	49.0
	0.20	11.55	57.75
	0.25	15.17	60.70
29.8	0.03	1.19	39.7
	0.06	2.93	48.8
	0.08	4.33	54.1
	0.12	8.01	66.75
	0.15	11.95	79.7
	0.20	17.10	85.5
	0.25	22.68	90.7

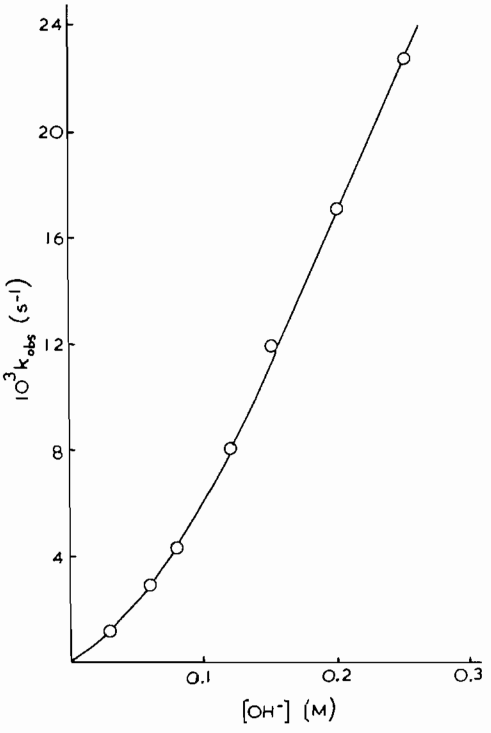


Fig. 1. Ring opening of *cis*-[Co(cyclen)CO$_3$]$^+$ in basic solution at 29.8 °C and I = 0.5 *M* (NaClO$_4$).

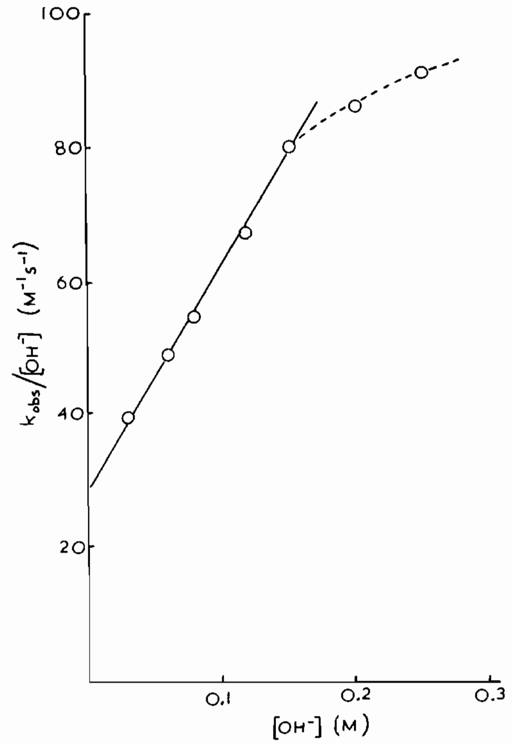


Fig. 2. Plot of k_{obs}/[OH$^-$] *versus* [OH$^-$] for the ring opening of *cis*-[Co(cyclen)CO$_3$]$^+$ at 29.8 °C and I = 0.5 *M* (NaCLO$_4$).

were analysed by plotting k_{obs}/[OH$^-$] *versus* [OH$^-$]. Such plots will be linear, passing through the origin if only a second order dependence on the hydroxide ion concentration occurs, and the second order rate constant can be obtained from the slope of such plots as

$$k_{obs} = k[OH^-]^2$$

and

$$k_{obs}/[OH^-] = k[OH^-]$$

A mixture of first order and second order dependence on the hydroxide ion concentration gives

$$k_{obs} = k_a[OH^-] + k_b[OH]^2$$

and

$$\frac{k_{obs}}{[OH^-]} = k_a + k_b[OH^-]$$

In this case a linear plot will be observed with a positive intercept k_a and slope k_b, and both the first order and second order rate constants can be derived. Figure 2 shows a plot of k_{obs}/[OH$^-$] *versus* [OH$^-$] at 29.8 °C. The plot is linear with a positive intercept

TABLE II. Comparison of Observed and Calculated Values of k_{obs} at 29.8 °C.[a]

$[OH^-]$ (M)	10^3 k_{obs} (s^{-1})	10^3 k_{obs} (calc) (s^{-1})
0.03	1.19	1.17
0.06	2.93	2.93
0.08	4.33	4.43
0.12	8.01	8.23
0.15	11.95	11.78

[a] Values of k_{obs} calculated from the equation: $k_{obs} = 2.9 \times 10^{-2}\,[OH^-] + 3.3 \times 10^{-1}\,[OH^-]^2$.

TABLE III. Summary of the Kinetic Data and Observed Activation Parameters.[a]

Temp. (°C)	10^3 k_1K_1 (M^{-1} s^{-1})	10^1 $k_2K_1K_2$ (M^{-2} s^{-1})
18.6	5.6	1.25
24.8	11.4	2.4
29.8	29.0	3.3

[a] For k_1K_1, $\Delta H^{\ddagger} = 104$ kJ mol^{-1} and $\Delta S^{\ddagger}_{298} = 69$ J K^{-1} mol^{-1}. For $k_2K_1K_2$, $\Delta H^{\ddagger} = 62$ kJ mol^{-1} and $\Delta S^{\ddagger}_{298} = -48$ J K^{-1} mol^{-1}. Note $k_a = k_1K_1$ and $k_b = k_2K_1K_2$.

indicating that both a first and second order dependence on $[OH^-]$ occurs in this reaction. Above *ca.* 0.15 M hydroxide the plot shows a marked divergence from linearity. At 29.8 °C the values of k_a and k_b are 2.9×10^{-2} M^{-1} s^{-1} and 3.3×10^{-1} M^{-2} s^{-1} at $I = 0.5$ M respectively. Below 0.15 M hydroxide at this temperature,

$$k_{obs} = 2.9 \times 10^{-2}[OH^-] + 3.3 \times 10^{-1}\,[OH^-]^2.$$

Table II lists calculated values of k_{obs} obtained using this expression. Good agreement with the experimentally determined k_{obs} rate constants is observed.

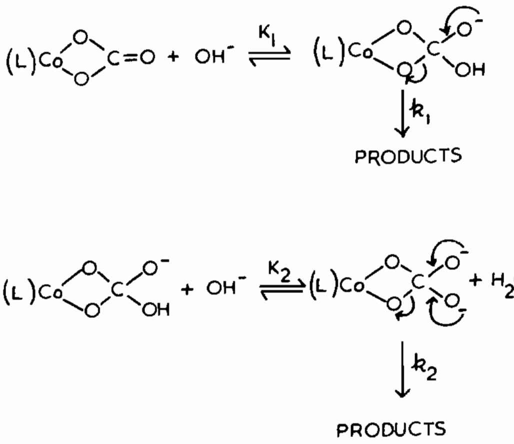
Values of k_a and k_b were calculated similarly at the other temperatures, Table III.

Mechanisms

The results obtained can be rationalised in terms of the mechanism shown in the Scheme. For this Scheme it can readily be shown that,

$$k_{obs} = \frac{k_1K_1[OH^-] + k_2K_1K_2[OH^-]^2}{1 + K_1[OH^-] + K_1K_2[OH^-]^2}$$

At low $[OH^-]$, $(K_1[OH^-] + K_1K_2[OH^-]^2)$ is $\ll 1$ so that



Scheme. Ring opening of *cis*-$[Co(cyclen)CO_3]^+$ in basic solution with carbon–oxygen bond cleavage.

$$k_{obs} = k_1K_1[OH^-] + k_2K_1K_2[OH^-]^2$$

with $k_a = k_1K_1$ and $k_b = k_2K_1K_2$. At higher values of $[OH^-]$, the expression $(K_1[OH^-] + K_1K_2[OH^-]^2)$ is not negligible with respect to unity, thus accounting for the divergence observed at high $[OH^-]$ in Fig. 2.

The base hydrolysis of $[Co(NH_3)_5OOCCF_3]^{2+}$ with carbon–oxygen bond cleavage shows a second order dependence on $[OH^-]$ [7]. The $[Co(NH_3)_5O]^{2+}$ group is one of the poorest leaving groups known. It appears to be a quite general phenomenon that the hydrolysis of compounds with poor leaving groups occurs via a process which is second order with respect to hydroxide ion. A single hydroxide ion does not have sufficient driving force to expel the leaving group, but this process becomes easier when deprotonation of the hydroxyl group occurs in the presence of additional base.

Activation parameters were determined for $k_a = k_1K_1$ and $k_b = k_2K_1K_2$. In the case of k_a, $\Delta H^{\ddagger} = 104$ kJ mol^{-1} and $\Delta S^{\ddagger}_{298} = 69$ J K^{-1} mol^{-1} while for k_b, $\Delta H^{\ddagger} = 62$ kJ mol^{-1} and $\Delta S^{\ddagger}_{298} = -48$ J K^{-1} mol^{-1}, Table III. These activation parameters involve both rate and equilibrium terms, making their interpretation somewhat difficult. However, it is significant that the k_2 pathway has a lower enthalpy of activation compared with the k_1 pathway and a much less favourable entropy of activation.

The present work clarifies the mechanism of dechelation of carbonato complexes in basic solution. Comparable kinetic behaviour is expected with oxalato and malonato complexes where a mechanism involving a tetrahedral intermediate and carbon–oxygen bond cleavage is also expected to occur. There have been a number of previous observations of a second order dependence on $[OH^-]$ in base catalysed dechelation reactions [8]. Wilkins states [8] that 'this is believed to arise from a concerted attack on the cobalt complex by two OH^-, an event not easy to visualize'. The mechanism defined is the Scheme can account for this second order dependence, and rationalise the kinetic data.

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