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Kinetics and Mechanism of the Base Hydrolysis of $[Co(tren)CO_3]^+$ (tren = 2,2′,2″-triaminotriethylamine)

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The reactions of $[Co(tren)CO_3]^+$ *in basic solution have been studied in detail. For opening of the carbonato ring, values of* k_{obs} *(the observed first order rate constant at constant hydroxide ion concentration) correspond to the expression,* $k_{obs} = k_o + k_{OH}[OH^-]$*, where* k_o *relates to the aquation pathway and* k_{OH} *to base hydrolysis. At 30 °C,* $k_o = 7.0 \times 10^{-4}$ s^{-1} *and* $k_{OH} = 4.7 \times 10^{-3}$ M^{-1} s^{-1} *at* $I = 1.0$ M *(*KNO_3*). The corresponding activation parameters are* $\Delta H^\ddagger = 22.7$ *kcal* mol^{-1} *and* $\Delta S^\ddagger_{298} = +2.2$ *cal* K^{-1} mol^{-1} *(for* k_o*) and* $\Delta H^\ddagger = 34.1$ *kcal* mol^{-1} *and* $\Delta S^\ddagger_{298} = +43.5$ *cal* K^{-1} mol^{-1} *(for* k_{OH}*).*

The monodentate carbonato complex $[Co(tren)(OH)OCO_2]$ *has been prepared in solution and its base hydrolysis studied in isolation. Only a base hydrolysis pathway was observed with* $k_{OH} = 2.8 \times 10^{-4}$ M^{-1} s^{-1} *at 50.2 °C and* $I = 1.0$ M *(*$NaClO_4$*). The requisite activation parameters are* $\Delta H^\ddagger = 27.8$ *kcal* mol^{-1} *and* $\Delta S^\ddagger{}_{298} = 10.9$ *cal* K^{-1} mol^{-1}*. Literature data on this latter reaction are considered in detail.*

Introduction

Although extensive kinetic and mechanistic studies of the acid-catalysed decarboxylation of carbonato complexes of cobalt(III) have been carried out [1–7], there have been few investigations of the base hydrolysis of such complexes. Francis and Jordan [8] have studied the base hydrolysis of *cis*-$[Co(en)_2CO_3]^+$ and have shown that the ring-opened intermediate $[Co(en)_2(OH)(OCO_2)]$ is relatively stable. This behaviour contrasts markedly with the acid-catalysed decarboxylations. In these reactions, chelate ring opening is the rate-determining step, except at high acidities where the rate of ring-opening can effectively 'catch up' with [1, 9], or even substantially exceed, the rate of CO_2 release [10].

When this work was initiated, detailed studies of the kinetics of base hydrolysis of a chelated carbonato complex were reported only for the *cis*-$[Co(en)_2CO_3]^+$ species [8, 11], for which an S_N1CB was proposed. These studies are subject to some uncertainties of interpretation as *cis* ⇌ *trans* isomerism can occur in the case of both the intermediate and the final products, $[Co(en)_2(OH)(OCO_2)]$ and $[Co(en)_2(OH)_2]^+$. As a result, an investigation of the geometrically rigid complexes *cis*-$[Co(tren)CO_3]^+$ and *cis*-$[Co(cyclen)CO_3]^+$ [12] seemed worthwhile. Dasgupta and Harris [13] have recently studied the base hydrolysis of *cis*-$[Co(tren)CO_3]^+$ in some detail, however a subsequent paper [14] questions some of the initial conclusions.

Experimental

The ligand 2,2′,2″-triaminotriethylamine (tren) was isolated from a commercial sample of triethylenetetramine as described in the literature [15]. The tren·3HCl so obtained had the two expected ^{13}C resonances at 39.095 δ and 52.399 δ in D_2O with NaTMS as reference. *Anal.* Calc. for $C_6H_{21}N_4Cl_3$; C, 28.19; H, 8.58; N, 21.92. Found: C, 28.14; H, 8.23; N, 21.63%.

The complexes $[Co(tren)(NO_2)_2]Cl$, $[Co(tren)Cl_2]Cl \cdot H_2O$ and $[Co(tren)CO_3]Cl \cdot 2.5H_2O$ were prepared as described by Young [16]. A solid sample of $[Co(tren)(OH)_2]Cl$ was prepared as described by Barclay and Barnard [17]. The ion $[Co(tren)(OH_2)_2]^{3+}$ was also generated in solution by treating the carbonato complex with 0.1 *M* $HClO_4$ followed by N_2 sparging to remove any dissolved CO_2. The ion $[Co(tren)(OH)_2]^+$ was generated in 0.1 *M* NaOH solution. The monodentate carbonato complex $[Co(tren)(OH)(OCO_2)]$ was prepared in solution as previously described [13] and stored

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at pH 10 in a refrigerator to eliminate the possibility of ring closure.

Kinetics

The kinetic measurements were carried out using a Gilford 2400S spectrophotometer interfaced with an Apple II computing system. The observed first order rate constants at constant hydroxide ion concentration (k_{obs}) were determined directly from the absorbance *versus* time data. All kinetic runs were carried out in triplicate, and were monitored to at least 90% completion. The ionic strength was maintained at 1.0 *M* using KNO_3 in the ring opening reaction, and $NaClO_4$ in the studies of decarboxylation of the monodentate species $[Co(tren)(OH)(OCO_2)]$. Ring opening was monitored at 320 nm and decarboxylation at 325 nm.

Routine i.r. and u.v. spectra were determined using Perkin Elmer 457 and 402 spectrophotometers respectively. All i.r. spectra were determined as discs in KBr. Proton and ^{13}C n.m.r. spectra were determined using a Bruker W.P. 80 instrument with D_2O as solvent and NaTMS as reference. The absorption spectra of the products of decarboxylation were checked using authentic samples of the compounds.

Results and Discussion

Neutral aqueous solutions of $[Co(tren)CO_3]^+$ are stable over a period of several days showing no observable spectral change. In sodium hydroxide solutions a fairly rapid spectral change occurs to give the $[Co(tren)(OH)(OCO_2)]$ species which is sufficiently stable to be characterised [13, 18]. The ring-opened product has λ_{max} 518 nm (ϵ = 150 M^{-1} cm^{-1}) with a shoulder at *ca.* 355 nm (ϵ = 125 M^{-1} cm^{-1}), λ_{min} is 430 nm (ϵ = 20 M^{-1} cm^{-1}), agreeing well with the literature data [13, 18]. Long standing in basic solution (pH > 12) gives the final product $[Co(tren)(OH)_2]^+$.

Ring opening was monitored using the absorbance increase at 320 nm and values of k_{obs} were derived from plots of $\log(A_\infty - A_t)$ *versus* time. As the second step is quite slow, it was possible to obtain quite constant values of A_∞. The rate constants obtained are summarised in Table I. Plots of k_{obs} *versus* $[OH^-]$ are linear with a positive intercept, so that $k_{obs} = k_o + k_{OH}[OH^-]$. Values of k_o and k_{OH} were evaluated from the least squares intercept and slope of such plots, Fig. 1. The k_o pathway can be assigned to aquation of the carbonato complex and k_{OH} to the base hydrolysis pathway. At 30 °C, $k_o = 7.3 \times 10^{-4}$ s^{-1} and $k_{OH} = 4.70 \times 10^{-3}$ M^{-1} s^{-1} at I = 1.0 *M*, Table II. These values may be compared with $k_o = 5.55 \times 10^{-4}$ s^{-1} and $k_{OH} = 5.45 \times 10^{-3}$ M^{-1} s^{-1} quoted by Dasgupta and Harris [13] at 30 °C and I = 1.0 *M*. These authors also quote $\Delta H^\ddagger$ = 17.2 kcal mol^{-1} and $\Delta S^\ddagger$ = −12.6 cal K^{-1} mol^{-1} for the k_{OH} pathway. The present work gives very different activation data, Table II, with $\Delta H^\ddagger$ = 34.1 kcal mol^{-1} and $\Delta S^\ddagger$ = 43.5 cal K^{-1} mol^{-1}. In the latter case the Eyring plot has an excellent correlation coefficient of 0.998. Ring opening by an S_N1CB mechanism would be expected to involve a substantial positive entropy of activation, rather than a negative value.

TABLE I. Values of k_{obs} for Ring Opening of $[Co(tren)CO_3]^+$ in Basic Solution at Various Temperatures, I = 1.0 *M* (KNO_3).

Temp. (°C)	$[OH^-]$ (*M*)	10^3 k_{obs} (s^{-1})
30	0.05	0.93
	0.10	1.27
	0.20	1.60
	0.30	2.14
	0.40	2.64
	0.50	3.06
35	0.10	2.76
	0.20	4.64
	0.30	5.90
	0.40	7.11
	0.50	8.18
40	0.05	3.84
	0.07	4.69
	0.10	5.47
	0.15	7.14
	0.20	8.30

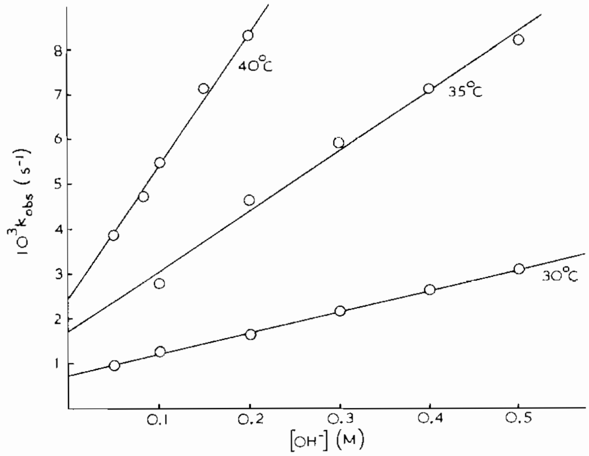


Fig. 1. Plots of k_{obs} versus the hydroxide ion concentration for ring opening of $[Co(tren)CO_3]^+$ at various temperatures and I = 1.0 *M* (KNO_3).

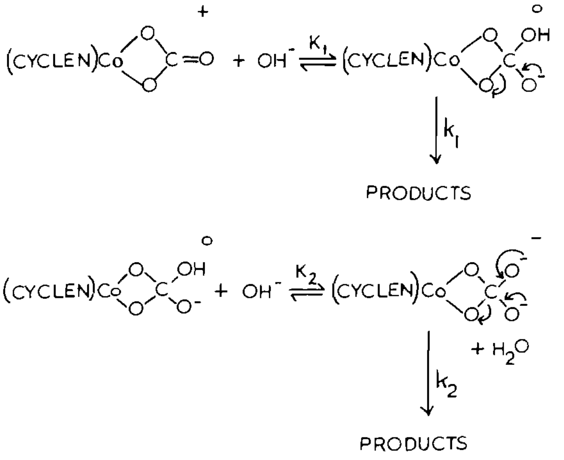
Ring opening of $[Co(tren)CO_3]^+$ in basic solution does not show the mixed first and second order

TABLE II. Values of k_o and k_{OH} at Various Temperatures[a] and I = 1.0 *M* (KNO_3) for Ring Opening of $[Co(tren)CO_3]^+$.

Temp. (°C)	10^3 k_o (s^{-1})	10^3 k_{OH} (M^{-1} s^{-1})	Corr. Coeff.
30	0.73	4.70	0.998
35	1.73	13.31	0.994
40	2.51	29.63	0.997

[a] For k_o, $\Delta H^{\ddagger}$ = 22.7 kcal mol^{-1} and $\Delta S^{\ddagger}$ = 2.2 cal K^{-1} mol^{-1} (corr. coeff. = 0.975). For k_{OH}, $\Delta H^{\ddagger}$ = 34.1 kcal mol^{-1} and $\Delta S^{\ddagger}$ = 43.5 cal K^{-1} mol^{-1} (corr. coeff. = 0.998).

dependence on the hydroxide ion concentration observed with $[Co(cyclen)CO_3]^+$ [12]. This observation may be indicative of different mechanisms for ring opening in the two complexes. Ring opening of $[Co(cyclen)CO_3]^+$ appears to involve carbon-oxygen bond cleavage by the reactions shown in Scheme 1. Ring opening of $[Co(tren)CO_3]^+$ may occur solely by an S_N1CB mechanism. The acid-catalysed ring opening of carbonato complexes derived from open chain polyamines with cobalt(III) is very much faster than that of macrocyclic carbonato complexes [4] and the difficulty of ring opening may also be reflected in base hydrolysis.



Scheme 1. Mechanism of ring-opening of $[Co(cyclen)CO_3]^+$ in basic solution.

The value of k_o = 7.3 × 10^{-4} s^{-1} at 30 °C and I = 1.0 *M* must be assigned to the reaction,

$$[Co(tren)CO_3]^+ + H_2O \xrightarrow{k_o} [Co(tren)(OH_2)(OCO_3)]^+$$

Previous studies of the acid-catalysed reaction [1] have given k_o = 1.7 × 10^{-4} s^{-1} at 25 °C and I = 0.5 *M* with E_a = 15.6 kcal mol^{-1}. These constants give a value of k_o = 2.6 × 10^{-4} s^{-1} at 30 °C. Considering the differences in ionic strength the agreement is quite reasonable. Approximate values of the activation parameters for k_o, derived from the base hydrolysis data, are given in Table II. These values must be regarded as approximate, due to the experimental difficulties of measuring k_o with any degree of precision.

TABLE III. Base Hydrolysis of $[Co(tren)(OH)(OCO_2)]$ at Various Temperatures and Concentrations of Sodium Hydroxide at I = 1.0 *M* ($NaClO_4$).[a]

Temp. (°C)	$[OH^-]$ (*M*)	10^5 k_{obs} (s^{-1})	10^5 k_{OH} (M^{-1} s^{-1})
35.1	0.8	2.64	3.30
	0.9	2.95	3.27
	1.0	3.19	3.19
43	0.6	5.86	9.77
	0.6	5.96	9.93
	0.8	7.99	9.99
50.2	0.5	13.56	27.12
	0.6	17.93	29.89
	0.7	19.83	28.33

[a] Using the values k_{OH} = 3.26 × 10^{-5} M^{-1} s^{-1} (35.1 °C), k_{OH} = 9.90 × 10^{-5} M^{-1} s^{-1} (43 °C) and k_{OH} = 28.45 M^{-1} s^{-1} (50.2 °C) gives $\Delta H^{\ddagger}$ = 27.8 kcal mol^{-1} and $\Delta S^{\ddagger}$ = 10.9 cal K^{-1} mol^{-1} with a correlation coefficient of 0.9997.

Base Hydrolysis of $[Co(tren)(OH)(OCO_2)]$

The base hydrolysis of the monodentate carbonato complex $[Co(tren)(OH)(OCO_2)]$ was monitored using the absorbance decrease at 325 nm. Values of k_{obs} were obtained from plots of $\log(A_t - A_\infty)$ *versus* time at constant hydroxide ion concentration and I = 1.0 *M* ($NaClO_4$). The observed rate constants, k_{obs}, are listed in Table III at various hydroxide ion concentrations and three temperatures. Over this range of hydroxide ion concentrations, values of k_{OH} = $k_{obs}/[OH^-]$ are effectively constant, with k_{OH} = 3.26 × 10^{-5} M^{-1} s^{-1} at 35.1 °C and I = 1.0 *M*. This value is in very close agreement with the rate constant k_{OH} = 3.17 × 10^{-5} M^{-1} s^{-1} at 35 °C quoted by Dasgupta and Harris [13] at the same ionic strength. The $[OH^-]$ dependence of the reaction was not studied by these investigators and a first-order dependence on $[OH^-]$ was assumed. The data in Table III give $\Delta H^{\ddagger}$ =27.76 kcal mol^{-1} and $\Delta S^{\ddagger}_{298}$ = 10.90 cal K^{-1} mol^{-1} with a correlation coefficient of 0.9997 for the Eyring plot. The literature data [13] is $\Delta H^{\ddagger}$ = 24.7 kcal mol^{-1} and $\Delta S^{\ddagger}$ = –0.96 cal K^{-1}

mol^{-1}. However, the literature data has been miscalculated and a recalculation gives $\Delta H^{\ddagger} = 27.0$ kcal mol^{-1} and $\Delta S^{\ddagger} = 9.4$ cal K^{-1} mol^{-1} (correlation coefficient = 0.994). The recalculated data is in good agreement with the present results.

Van Eldik and Harris [14] have studied the hydrolysis of [Co(tren)(OH)(OCO$_2$)] at pH 13 during an investigation of the anation of [Co(tren)(OH$_2$)]$^+$ by carbonate ion in the pH range 10.5 to 13. The formation of carbonato complexes was studied at 304 nm and the carbonate dependence over the entire pH range can be described by the equation

$$k_{obs} = k_a + k_b\,[\text{Total carbonate}]$$

At pH ~ 12 no ring closure of the [Co(tren)(OH)(OCO$_2$)] species occurs. A discontinuity in the k_a values is observed at higher pH with initially a decrease in k_a followed by a steady increase with increasing [OH$^-$]. The discontinuity in the k_a values is suggested to be due to a change in rate-determining step from a non-catalysed ring opening reaction to base hydrolysis of the ring opened species. The k_a data at [OH$^-$] > 5 × 10^{-3} *M* is assigned to the reaction

$$[\text{Co(tren)(OH)(OCO}_2)] + \text{OH}^- \xrightarrow{k_{OH}} [\text{Co(tren)(OH)}_2]^+ + \text{CO}_3^{2-}$$

At these hydroxide ion concentrations, plots of k_a *versus* [OH$^-$] are linear with positive intercepts, *i.e.* $k_a = k_1 + k_{OH}[\text{OH}^-]$ with $k_{OH} = 2.4 \times 10^{-3}$ M^{-1} s^{-1} at 50 °C. The present results and those of Dasgupta and Harris [13] indicate that at 50 °C, k_{OH} is 2.8 × 10^{-4} M^{-1} s^{-1}. The large discrepancy suggests that the literature analysis [14] is probably incorrect, presumably as a result of attempts to extrapolate data through a pH region where a change in rate-determining step occurs.

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