Inorganica Chimica Acta, 78 (1983) L173–L175

Kinetics and Mechanism of Base Hydrolysis of Carbonato(1,4,8,11-tetraazacyclotetradecane)cobalt(III) Cations. Evidence for the 'Kinetic Nephelauxetic Effect'

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Received October 22, 1982

Introduction

A great deal of work has been done on the factors controlling chelate ring opening and closing in simple oxyanion chelate complexes of cobalt(III) ion [1–6] in acidic and basic aqueous solutions. Among the simple oxyanion ligands the carbonate ligand seems to occupy a special place. The rate constant for acid-catalysed ring-opening of Co(en)$_2$CO$_3^+$ and Co-(cyclam)CO$_3^+$ (where cyclam = 1,4,8,11-tetraazacyclotetradecane) differ [7] by a factor of 3000 at 25 °C whereas the rates of ring-closure [3] of the species *cis*-Co(en)$_2$(OH)(HCO$_3$)$^+$ and *cis*-Co(cyclam)(OH)-(HCO$_3$)$^+$ differ by a factor of only two, indicating different mechanisms for the two types of reaction. A kinetic study [8] of the hydrolysis of oxalate complex, Co(en)$_2$C$_2$O$_4^+$, indicated that oxalate chelate ring opening was the rate controlling step in alkaline solution and proceeds with C–O bond breaking [9]. A detailed investigation [4, 5] on base hydrolysis of Co(en)$_2$CO$_3^+$ and Co(tren)CO$_3^+$ revealed that both de-chelation and formation of the dihydroxo product occur by the Dcb mechanism. Since acid hydrolysis of Co(cyclam)CO$_3^+$ indicates considerable contrast in rate constants for the de-chelation step, we have studied the kinetics of hydrolysis of Co(cyclam)CO$_3^+$ in strongly basic solution. We now report here the results of the kinetic study and the mechanism proposed by us in the light of very different electronic effect of the macrocyclic ligand.

Experimental Section

Preparation of Compounds

1,4,8,11-Tetraazacyclotetradecane (cyclam) was prepared starting from commercially available 1,3-bis(2′-aminoethylamino)propane and 1,3-dibromopropane, following the method of Bosnich *et al.* [10]. Sodium triscarbonatocobalt(III) trihydrate was prepared by the method of Bauer and Drikard [11].

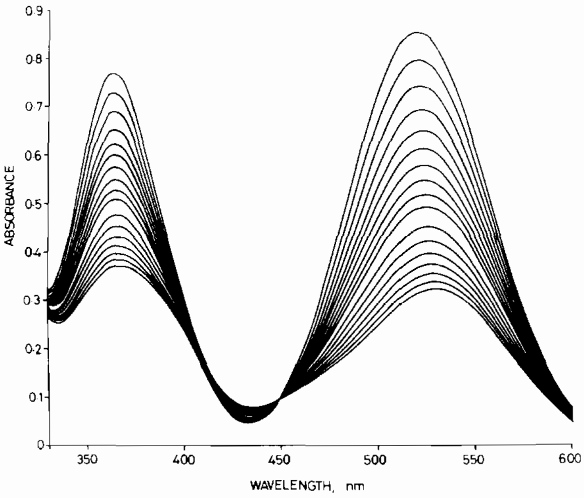

Fig. 1. Spectral change during base-catalysed hydrolysis of Co(cyclam)CO$_3^+$ ion.

cis-Carbonato(cyclam)cobalt(III) chloride was synthesised by the method described earlier [7]. The purity was checked by microanalysis [12]. Calcd. for C$_{11}$H$_{24}$ClCoN$_4$O$_3$: C, 37.3; H, 6.8; N, 15.8%. Found: C, 37.0; H, 6.6; N, 15.9%.

cis-Dichloro(cyclam)cobalt(III) chloride was made as described in the literature [13] and the purity was checked by visible spectroscopy. *cis*- and *trans*-dihydroxo(cyclam)cobalt(III) complex ions were generated *in situ* as described previously [3].

Materials

All the chemicals used were reagent grade. Distilled water, made from a Corning distillation unit, was further purified by passing through a Milli-Q ion-exchange train and was used for making up all solutions for physical measurements.

The visible and ultraviolet spectra were obtained with a Unicam SP8-100 recording spectrophotometer. The kinetic runs were followed at 520 nm which offers the largest absorbance difference between reactant and product (Fig. 1) utilising the time-drive chart mechanism of the spectrophotometer. Temperature control of the solution inside the optical cell was maintained to within ±0.1 °C by circulating water through the cell compartment. Standard lithium hydroxide solution was used to maintain the hydroxide ion concentration. The ionic strength (1.0 *M*) was established by adding the requisite amount of standard lithium perchlorate

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0020-1693/83/0000-0000/$03.00

solution. Pseudo-first-order rate constants were derived from Guggenheim plots [14].

Results and Discussion

It was found that an aqueous solution of [Co(cyclam)CO_3^+]Cl was stable and no appreciable spectral change was observed for periods of at least one week. However, a spectral change occurred when lithium hydroxide was added to the neutral solution of the complex and this is presented in Fig. 1. It is obvious from the spectral change in Fig. 1 that Co(cyclam)CO_3^+ is gradually being converted to *cis*-Co(cyclam)$(OH)_2^+$ without any appreciable formation of the intermediate Co(cyclam)(OH)(CO_3). This is in complete contradiction to the observation made on the base hydrolysis of $Co(en)_2CO_3^+$ and Co(tren)CO_3^+ where the production of dihydroxo complexes occur by two completely distinguishable steps as follows:

$$Co(N_4)CO_3^+ + OH^- \xrightarrow{k_1} Co(N_4)(OH)(CO_3)$$

$$Co(N_4)(OH)(CO_3) + OH^- \xrightarrow{k_2} Co(N_4)(OH)_2^+ + CO_3^{2-}$$

(N_4 = $(en)_2$ or tren; en = ethylenediamine and tren = 2-2′-2″-triaminotriethylamine).

Since k_1 is about 25 times [15] greater than k_2 for en and tren complexes, both rate constants were measured independently. However, in case of Co(cyclam)CO_3^+ we think k_2 is much greater than k_1 which is indicated by the formation of an isosbestic point in Fig. 1. There is only a slight loss of isosbestic point near the end of the reaction and at low hydroxyl ion concentration, which is probably due to the *cis–trans* isomerisation [16] of Co(cyclam)$(OH)_2^+$.

The kinetics of base hydrolysis of Co(cyclam)CO_3^+ has been studied in alkaline solution in the concentration range 0.29 $M \leqslant OH^- \leqslant$ 0.95 M. The pseudo-first-order constants, k_{obs}, are listed in Table I. Plots of k_{obs} *vs.* OH^- are linear and the data can be interpreted in terms of the following processes:

$$cis\text{-}Co(cyclam)CO_3^+ + OH^- \xrightarrow{k_1} cis\text{-}Co(cyclam)(OH)(CO_3)$$

$$cis\text{-}Co(cyclam)(OH)(CO_3) + OH^- \xrightarrow{Fast} cis\text{-}Co(cyclam)(OH)_2^+ + CO_3^{2-}$$

$$cis\text{-}Co(cyclam)(OH)_2^+ \xrightarrow{k_2} trans\text{-}Co(cyclam)(OH)_2^+$$

TABLE I. Observed First-order Rate Constants for the Base Hydrolysis of Co(cyclam)(CO_3^+. Complex, 1 × 10^{-3} M. I, 1.0 M ($LiClO_4$).

$[OH^-]/M$	10^4 k_{obs}/s^{-1}	Temp/°C
0.29	2.24	31.2
0.44	4.93	
0.58	6.29	
0.65	6.70	
0.73	8.50	
0.87	10.35	
0.95	11.24	
0.44	14.90	41.1
0.50	16.40	
0.58	18.50	
0.66	22.80	
0.73	26.80	
0.35	22.70	46.3
0.50	32.90	
0.55	38.80	
0.73	47.50	
0.80	52.10	

This mechanism conforms to the rate law $k_{obs} = k_1[OH^-]$ where $k_2 > k_1$.

A least squares analysis of the data of Table I on this basis yields values of k_1 with their standard deviations at three temperatures, and these constants along with their activation parameters are listed in Table II. It is of interest to compare the rate parameters for the similar types of complexes which appear in Table III. As is evident from the Table III the rate of ring opening by base is about 5 times slower than the corresponding ethylenediamine and tren-complexes, which suggests a stronger Co–O bond for the complex Co(cyclam)CO_3^+. This is in keeping with the hydrolytic cleavage of this complex in acid [7]. It is curious to notice in Table III that the activation parameters for $Co(en)_2CO_3^+$ are somewhat different from that of Co(tren)CO_3^+ and Co(cyclam)CO_3^+, although one would tend to invoke similar ring-opening mechanisms for all these complexes.

Finally, the most interesting aspect is the unusually fast base hydrolysis of Co(cyclam)(OH)(CO_3) in comparison to the hydrolytic behaviour of the corresponding en- and tren-complexes. We strongly believe that this is due, at least partly, to the influence [16] of a 'Nephelauxetic effect' on the kinetic stability of the intermediate Co(cyclam)(OH)(CO_3). It is quite evident from earlier investigations [17] that the base hydrolysis of $Co(N_4)XY^+$, where N_4 stands for non-labile amine ligand and X and Y are substitutionally labile groups, occur by Dcb mechanism and the rate of hydrolysis increases in the nephelauxetic series: Cyclen > cyclam > tren > en > pn > NH_3. Or course, it is important to realise

TABLE II. Rate Parameters for the Base Catalysed Ring-opening of Co(cyclam)CO_3^+.

Temp./°C	10^3 k_1/M^{-1} s^{-1}	ΔH^+/kcal mol^{-1}	ΔS^+/cal deg^{-1} mol^{-1}
31.2	1.34 + 0.06		
41.1	4.09 + 0.44	19.6 + 0.93	−7.3 + 3.1
46.3	6.42 + 0.42		

TABLE III. Comparison of Rate Parameters for the Ring-opening Process of Various Carbonato Complexes of Cobalt(III) Ion.

Complex	$10^3k/M^{-1}$ s^{-1}	$\Delta H^{\#}$/kcal mol^{-1}	$\Delta S^{\#}$/cal deg^{-1} mol^{-1}.
Co$(en)_2CO_3^+$	3.0[a]	22.0	3.0
Co(trne)CO_3^+	3.6[a]	17.2	−12.0
Co(cyclam)CO_3^+	0.67	19.6	−7.3

[a]Ref. 15.

that the nephelauxetic effect is not the only effect which accounts for such a large difference in base hydrolysis rates [18]. It is not possible for us to assess the rate of carbonate substitution by water in our experimental condition, but for Co(cyclam)(A)Cl^+ where A is a non-labile group the rate of aquation has been found to be very slow. This indicates that the influence of steric effects is not important in this case. Nevertheless, we believe that there is some other effect which adds to the nephelauxetic effect in enhancing the rate of base hydrolysis of Co(cyclam)(OH)(CO_3).

Acknowledgements

This work was supported by grants provided by the Research and Publications Fund Committee and by the Board for Postgraduate Studies, University of the West Indies. The authors are also grateful to Dr. W. K. Wan for making Cyclam during his tenure at the State University of New York at Buffalo, N.Y., U.S.A.

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18 Ref. 15; the rate constants for the base hydrolysis of Co$(en)_2$(OH)(CO_3) and Co(tren)(OH)(CO_3) are 10^{-3} M^{-1} s^{-1} and 2 × 10^{-4} M^{-1} s^{-1} respectively at 47.5 °C. The rate constant for the base hydrolysis of Co(cyclam)(OH)(CO_3) is definitely much faster than the en and tren analogues and is probably in the range of 10^{-1} to 10^{-2} M^{-2} s^{-1} at the same temperature.