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# Kinetics and Mechanism of Acid-catalyzed Aquation of Carbonato-(1,4,8,11-Tetra-Azacyclotetradecane)cobalt(III) Ion

T. P. DASGUPTA
*Department of Chemistry, University of the West Indies, Kingston 7, Jamaica, W.I.*

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*The acid-catalyzed aquation of the title compound has been studied over the range of* $0.05<[H^+]<0.5\,M$ *and* $40°<T<50°$ *C at* $I=0.5\,M$. *The pseudo-first-order rate constants are directly proportional to* $[H^+]$ *for the range of acidity studied. The results have been interpreted in terms of mechanism involving acid-catalyzed dechelation followed by a rapid decarboxylation of the monodentate intermediate. At 25° C, the acid-catalyzed ring-opening rate constant,* $k_1$, *is* $1.3 \times 10^{-3} M^{-1} sec^{-1}$ *and the temperature variations describing this constant are* $\Delta H^*$, $20.6 \pm 0.4$ *kcal/mol and* $\Delta S^* = -2.6 \pm 1.3$ *cal/deg mol. The results are compared with those obtained for similar carbonato (tetramine)cobalt(III) complexes.*

## Introduction

In our earlier papers we have established[1,2] that both cationic and anionic carbonato complexes of cobalt(III) undergo aquation *via* a common mechanism consisting of ring opening of the chelated carbonato group both by water and by hydronium ion followed by a rapid decarboxylation of the monodentate intermediate. The rate law which describes the variation of rate constant, k, with the acidity can be expressed as

$$k_{obs} = k_0 + k_1 [H^+]$$

where $k_0$ and $k_1$ are the parellel rate determining ring opening processes catalyzed by water and hydronium ion respectively. The most interesting aspect which has emerged from these studies is the large variation of the magnitude of the rate constant of acid-catalyzed aquation with the variation of amine ligand around the cobalt ion. We showed previously that the higher value of $k_1$ could be attributed largely to the greater strain in the carbonato rings which is produced by the amine chelate ring coplanar with the carbonato ring and the ligand offering more stereochemical hindrance would lower the magnitude of $k_1$. However, Francis and Jordan[3] predicted from the correlation between ligand basicity and $k_1$ that the variations in electron donor ability of the amines were more important than steric effects.

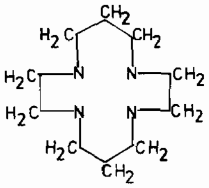

Figure 1. Cyclam (1,4,8,11-tetra-azacyclotetradecane).

In order to gain further insight into the above factors which control the reactivities we have studied the aquation reaction of *cis*-carbonato(cyclam)cobalt(III) ion where cyclam is 1, 4, 8, 11-tetra-azacyclotetradecane (Figure 1). Cyclam is an interesting ligand for two reasons. First, the methylene groups of the cyclic ligand would result in much greater congestion in its folded arrangement. Secondly, the average $pK_a$ of the amine is considerably lower than the simple tetramines.

This paper now reports in detail the kinetic results of the acid-catalyzed aquation studies which substantiate both the steric requirement and the basicity correlation.

## Experimental

1,4,8,11-tetra-azacyclotetradecane was prepared[4] by the method of Bosnich, Poon and Tobe[5]. Sodium triscarbonatocobaltate(III) trihydrate was prepared by the method of Bauer and Drinkard[6]. *cis*-Carbonato (cyclam)cobalt(III) chloride was prepared essentially by following the method of Poon and Tobe[7]. 4 g of cyclam·3.5 HCl (prepared by adding conc. HCl to a methanolic solution of cyclam) was dissolved in 25 ml of water and 5 g of sodium triscarbonatocobaltate(III) was gradually added with stirring. The resultant solution was heated on a steam bath for 15 minutes. The red solution was cooled and filtered. Ethanol and acetone were then added in excess and the solution was left in the refrigerator for 12 hours. The crude product was then filtered off, washed with alcohol and ether and recrystallised several times by adding acetone to a methanolic solution. The purity of the compound was then checked by microanalysis.

*Anal.* Calcd. for $C_{11}H_{24}ClCoN_4O_3$; C, 37.3; H, 6.8; N, 15.8%. Found: C, 37.0; H, 6.6; N, 15.9%.

*cis*-Diaquo(cyclam)cobalt(III) perchlorate was prepared according to the published method[7]. The spectrum of the diaquo complex agreed quite well with the spectrum of the aquation product of carbonato complex.

The electronic spectra of the carbonato and diaquo species were determined on a Cary model 118 recording spectrophotometer[8]. The kinetic runs were carried out as described previously[1]. The runs were followed at 520 nm which offers the largest absorbance difference between reactant and product utilizing the time-drive chart mechanism of the Cary spectrophotometer. Temperature control of the solution inside the optical cell was maintained to within ±0.1° by circulating water through a metal block cell holder. The ionic strength ($0.5M$) was established by adding requisite amounts of standard sodium perchlorate solution. Pseudo-first-order rate constants were derived in the conventional manner from semilogarithmic plots of ($A_t - A_\infty$) as a function of time where $A_t$ and $A_\infty$ are the solution absorbances at time t and after complete reaction respectively.

## Results and Discussion

A clean first order dependency of the aquation rate on $[H^+]$ is demonstrated in Figure 2 where the pseudo-first-order rate constants, $k_{obs}$, are plotted against $[H^+]$ at three different temperatures. The results can be interpreted very satisfactorily in terms of the mechanism proposed in the earlier studies[1,2] and can be written as follows:

$$\mathrm{Co(cyclam)CO_3^+ + H_2O \rightarrow Co(cyclam)(OH)(CO_3H)^+} \qquad k_0$$

$$\mathrm{Co(cyclam)CO_3^+ + H_3O^+ \rightarrow Co(cyclam)(OH_2)(CO_3H)^{2+}} \qquad k_1$$

$$\mathrm{Co(cyclam)(OH_2)(CO_3H)^{2+} + H_2O \rightleftharpoons Co(cyclam)(OH)(CO_3H)^+ + H_3O^+} \qquad K_1$$

$$\mathrm{Co(cyclam)(OH_2)(CO_3H)^{2+} \rightarrow Co(cyclam)(OH_2)(OH)^{2+} + CO_2} \qquad k_3$$

$$\mathrm{Co(cyclam)(OH_2)_2^{3+} + H_2O \rightleftharpoons Co(cyclam)(OH)(OH_2)^+ + H_3O^+} \qquad K_2$$

According to the above reaction scheme the data should fit the expected rate expression $k_{obs} = k_0 + k_1[H^+]$ but $k_0$ values are too small to observe in the plot of $k_{obs}$ *vs.* $[H^+]$. However, the least squares treatment of the data at each temperature reveals that there is a residual rate for each set of data. $k_0$ and $k_1$ values obtained from such treatment are listed in Table I along with the temperature parameters for the acid-catalyzed path. It is apparent from the Table that the uncertainties of $k_0$ values are too large to justify any further critical discussion. Nevertheless, one should be able to get more reliable $k_0$ values by studying the aquation rate at lower $H^+$ concentration where the contribution of the water-catalyzed path is

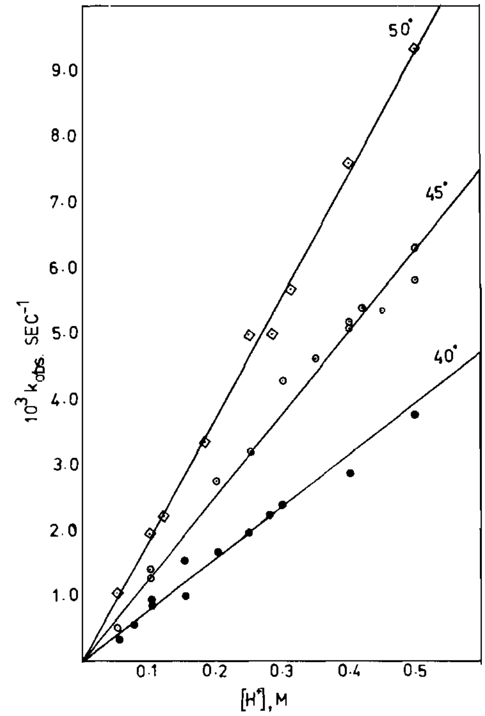

Figure 2. Plot of $k_{obs}$ *vs.* $[H^+]$ at different temperatures and $I = 0.5M$.

TABLE I. Rate Parameters for the Acid-Catalyzed Aquation Reaction of $Co(cyclam)CO_3^+$, $I = 0.5M$.

| Temp., °C | $10^4k_0$, sec$^{-1}$ | $10^3k_1$, $M^{-1}$ sec$^{-1}$ |
|---|---|---|
| 40 | 2.5 ± 0.1 | 7.1 ± 0.3 |
| 45 | 2.1 ± 2.0 | 11.9 ± 0.5 |
| 50 | 0.3 ± 1 | 18.5 ± 0.4 |

$\Delta H^{\ne}_1$, 20.6 ± 0.43 kcal/mol
$\Delta S^{\ne}_1$, −2.6 ± 1.3 cal/deg mol

expected to be higher. In fact some runs were carried out at higher pH's, but the reactions were found to be complicated by concurrent isomerization of diaquo and aquo carbonato species. This is quite understandable when one considers the lower pK values[9] of *cis*-Co(cyclam)$(OH_2)_2^{3+}$ and the rapid rates of isomerization of *cis*-hydroxoaquo species.

It is of interest now to consider the similarities and contrasts in the rate parameters for the acid-catalyzed ring opening process of the various $CoN_4CO_3^+$ complexes ($N_4$ = tetraamine) for which results are available.

The rate constant data are collected in Table II together with the activation parameters. One sees that the rate constant for the cyclam complex is nearly $10^3$ times slower than the $(NH_3)_4$ complex but only 8 times faster than the *trans*-[14] diene. One also notes that the $\Delta H^\#$ and $\Delta S^\#$ values of cyclam complex are very similar to phen, bipy, py and *trans*-[14] diene complexes, but differ considerably from the simple tetraamines ($(NH_3)_4$, $(en)_2$, $(pn)_2$ *etc.*) whose rates are much faster; thus the activation parameter data clearly reflects the contrasts in the rate constants.

Francis and Jordan proposed a correlation between the rate constant $k_1$ and the values of average $pK_a$ of the amine ligands for $CoN_4CO_3^+$ complexes where the average $pK_a$ of the amine ligand is a measure of the basicity and hence the electron-donating capability of the nitrogen. Obviously the more acidic the ligands are the stronger will be the Co–O bond. This correlation can now be extended to cyclam complex. It is clear from Table II that the average $pK_a$ value of cyclam fits between trien and dmtr and so does the rate constant value. The $pK_a$ values of *trans*-[14] diene are not known, but it is expected that the average $pK_a$ value is the same as the cyclam which would justify its position between trien and cyclam as shown in Table II. However, it is obvious from the data available that the $pK_a$ values are not systematically related to the rate constant, $k_1$. The py complex undergoes hydrolysis at a much slower rate than phen- and bipy-complexes though the basicity of pyridine is higher than the ligands phen and bipy. This suggests that the ring opening reactivity is not entirely dependent on the electron-donating capability of nitrogens of the ligand. This is also obvious in the studies of anionic carbonato complexes of cobalt(III)[2].

Steric hindrance as suggested earlier[1] is undoubtedly an important factor to consider also for the retarding influence on the acid-catalyzed ring opening process. The X-ray structure determination of Co(cyclam)$CO_3^+$ has not been done yet, but one can visualize from the

TABLE II. Rate Parameters for the Acid-Catalyzed Aquation Reactions of Various $CoN_4CO_3^+$ Complex Ions at 25° C.

| $N_4$[a,b] | $k_1, M^{-1}\ sec^{-1}$ | $\Delta H^\#$, kcal/mol | $\Delta S^\#$, e.u. | Av. $pK_a$ of Amine Ligand |
|---|---|---|---|---|
| $(NH_3)_4$ | 1.5 | 15.3 | –6.3 | 9.3 |
| $(en)_2$ | 0.6 | 13.8 | –7.4 | 8.6 |
| $(pn)_2$ | 0.5 | 14.0 | –13.0 | 8.5 |
| $(tn)_2$ | 0.8 | 12.0 | –19.0 | 9.7 |
| tren | 2.0 | 11.1 | –20.0 | – |
| *trans*-(en)$(NH_3)_2$ | 8.9 | 10.0 | –20.0 | – |
| *cis*-(en)$(NH_3)_2$ | 0.9 | 16.0 | –4.0 | – |
| α-trien | 5.2 | 15.0 | –5.0 | 7.3 |
| β-trien | 0.2 | 17.0 | –5.0 | 7.3 |
| *trans*-[14]-diene[c] | $8 \times 10^{-3}$ | 24.0 | – | – |
| cyclam[d] | $(1.3 \times 10^{-3})$[e] | 20.6 | –2.6 | 6.7[f] |
| α-dmtr[g] | $1.8 \times 10^{-2}$ | – | – | 6.4 |
| β-dmtr[g] | $5.6 \times 10^{-4}$ | – | – | 6.4 |
| py[h] | $8.9 \times 10^{-6}$ | 24.0 | –1.0 | 5.3[i] |
| phen[j] | $1.5 \times 10^{-4}$ | 20.4 | –8.6 | 5.0 |
| bpy[j] | $2.2 \times 10^{-4}$ | 22.3 | –2.0 | 4.5 |

[a] en = ethylenediamine; pn = 1,2-diaminopropane; tn = 1,3-diaminopropane; tren = 2-2′-2″-triaminotri-ethylamine; trien = triethylenetetramine; *trans*-[14]-diene = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene; cyclam = 1,4,8,11-tetra-azacyclotetradecane; dmtr = 4,7-dimethyl-triethylenetetramine; phen = *o*-phenanthroline; bpy = bipyridine; py = pyridine. [b] References to previous work are given in Ref. 1. [c] A.J. Kaernohan and J.F. Endicott, *J. Am. Chem. Soc., 91,* 6977 (1969). [d] This work. [e] Estimated by the use of temperature parameters given in this Table. [f] Average of four successive pK values (10.76, 10.18, 3.54 and 2.67), D.K. Cabbiness, *Ph. D. Dissertation,* Purdue University, 1970. [g] D.J. Francis and G.H. Searle, *Aust. J. Chem. 27,* 269(1974). [h] K. Hyde and G.M. Harris, Unpublished work. [i] Handbook of Chemistry and Physics, ed. R. C. Weast, The Chemical Rubber Co., Cleveland, Ohio, U.S.A. (1968). [j] Ref. 3.

model that considerable twisting of this cyclic ligand in the *cis*-configuration occurs and thus one achieves a greater protection of carbonate ion from protonation.

One should perhaps also consider solvation properties which differ considerably from one ligand to the other. Indeed, the contrasts in $k_1$ values between dmtr and trien complexes or between tren and NTA complexes clearly demonstrate this possibility.

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