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Kinetics and Mechanism of the Decomposition of μ-Amido-μ-hydroxo(tetraamminecobalt(III))(tetraaquacobalt(III)) Ion in Acidic Aqueous Solution

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Abstract

The title complex undergoes decomposition in acidic aqueous solution resulting in equimolar concentration of aquapentaamminecobalt(III) and hexaaquacobalt(II). The kinetic studies over the ranges of $0.048\ \mathrm{M} \leqslant [\mathrm{H}^+] \leqslant 0.385\ \mathrm{M}$, $25 \leqslant \theta_c \leqslant 41.5\ ^\circ\mathrm{C}$ and at $I = 0.5$ M reveals that the intricate mechanism involves protonation equilibrium of the title complex, followed by a rate determining bridge cleavage. The further follow-up reaction is a fast electron transfer process to form products. The rate expression derived from the mechanism is $k_{\mathrm{obs}} = k_1K_1[\mathrm{H}^+]/(1 + K_1[\mathrm{H}^+])$ where the values of k, and K, are found to be $8.9 \times 10^{-4}\ \mathrm{s}^{-1}$ and $3.5\ \mathrm{M}^{-1}$ respectively at 25 °C. The results are compared with that obtained for the decomposition reactions of mononuclear aquaammine complexes of cobalt(III).

Introduction

The complex $[(\mathrm{NH_3})_4\mathrm{Co}(\mu\text{-}\mathrm{NH_2})(\mu\text{-}\mathrm{OH})\mathrm{Co}(\mathrm{CO_3})_2]$ (**1**) is perhaps the most fascinating unsymmetrical molecule amongst the dinuclear complexes of cobalt(III). Since its synthesis and complete characterization by X-ray diffraction study [1], the mechanism of formation of complex **1** from the complex ion $[(\mathrm{NH_3})_4\mathrm{Co}(\mu\text{-}\mathrm{NH_2})(\mu\text{-}\mathrm{OH})\mathrm{Co}(\mathrm{NH_3})_4]^{2+}$ (**2**) has been reported [2] and some novel unsymmetrical dinuclear complexes by substitution of the terminal carbonate groups have been synthesized [3]. We have also shown previously [1, 3] that the terminal carbonate groups in complex **1** behave similar to the bidentate carbonate of mononuclear complexes of cobalt(III) and hence undergo acid catalysed decarboxylation. Once the two terminal carbonate groups in complex **1** are hydrolyzed by acid, the complex ion $[(\mathrm{NH_3})_4\mathrm{Co}(\mu\text{-}\mathrm{NH_2})(\mu\text{-}\mathrm{OH})\mathrm{Co}(\mathrm{H_2O})_4]^{4+}$ (**3**) becomes very sensitive to the acid concentration in solution. In excess acid complex ion **3** spontaneously decomposes into mononuclear complexes of Co(II) and Co(III). We now report here a detailed kinetic study of this decomposition process and a probable mechanistic scheme.

Experimental

Materials

All the reagents were of reagent grade. Distilled water was used for preparative work while ultrapure water, obtained by deionizing distilled water using a Milli-Q Reagent Grade water system, was used to make up solutions for physical measurements.

Preparation of Compounds

μ-Amido-μ-hydroxo-(tetraamminecobalt(III))-(bis(carbonato)cobalt(III))

This compound was prepared from μ-amido-μ-hydroxo-bis(tetraamminecobalt(III)) as described in the literature [1]. The purity of the compound was checked by microanalysis**. *Anal.* Calc. for $\mathrm{Co_2N_5H_{25}O_{12}C_2}$: C, 5.59; H, 5.83; N, 16.31; Co, 27.50. Found: C, 5.53; H, 5.72; N, 16.63; Co, 27.20%. The composition of this complex was established unambiguously by a single crystal X-ray diffraction study [1].

μ-Amido-μ-hydroxo-(tetraamminecobalt(III))-(tetraaquacobalt(III))perchlorate

This compound was prepared and characterized in solution only as described previously [3].

Spectra

The absorption spectra in the UV–Vis region were obtained by use of a Pye Unican SP8-100 or Cary 219 recording spectrophotometer. The infrared spectrum

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**Microanalysis was performed by Mikroanalytisches Labor Pascher, An der Pulvermuhle 3, D-5480 Remagen 8, F.R.G.

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of complex **1** was measured with a Pye Unicam SP3-300 auto scanning spectrophotometer using the KBr disc technique. The dicarbonato complex (**1**) shows two strong peaks at 1585 and 1265 cm^{-1}. These peaks are comparable to the strong peaks at 1593 cm^{-1} (γ(C–O)) and 1265 cm^{-1} (γ(C–O) + γ(O–C–)) obtained [4] for $[Co(NH_3)_4CO_3]Cl$.

Kinetic Studies

A stock solution of complex **3** was prepared for kinetic studies by dissolving the required weight of complex **1** in the appropriate volume of acidic aqueous solution which contained four times its molar concentration of $HClO_4$. The resulting dark brown solution (pH 5) showed no change in its UV-Vis spectra for at least four hours. The required amount of standard $HClO_4$ and standard $LiClO_4$ solution were added to a 10 ml volumetric flask to give the desired hydrogen ion concentration and ionic strength (0.5 M) respectively. The solution was thermostatted at the desired temperature and thermostatted deionized distilled water plus 1 ml of the thermostatted stock complex solution (5×10^{-3} M) added to give a final volume of 10 ml.

The cuvette filled with the solution was then quickly placed in the cell compartment of the spectrophotometer and the change in absorbance *versus* time was recorded at 340 nm. The pseudo-first order rate constants, k_{obs}, were computed from the slope of the $\ln(A_t - A_\infty)$ *versus* time plot by least-squares treatment of the data.

Results and Discussion

When complex **3** is allowed to react in dilute solution of $HClO_4$, a gradual decrease in absorbance was observed in the wavelength range of 250–400 nm. A family of spectra (Fig. 1) collected during the course of the reaction of complex **3** with 0.025 M $HClO_4$ reveals the overall sequence of the reaction. The peak at 310 nm corresponding to the complex ion **3** slowly disappears and the final spectrum corresponds to that of equimolar quantities of $Co(H_2O)_6^{2+}$ and $[Co(NH_3)_5H_2O]^{3+}$. This was confirmed by comparing the final spectrum obtained with that of a synthetic mixture.

The pseudo-first order rate constants for the decomposition of complex **3** at different acid concentrations and at various temperatures are presented in Table I. It is clear that the k_{obs} values are dependent on $[H^+]$ and such dependency can be explained satisfactorily by the mechanism proposed in Scheme 1. This mechanism leads to the rate expression

$$k_{obs} = \frac{k_1 K_1 [H^+]}{1 + K_1 [H^+]} \qquad (1)$$

By rearranging eqn. (1) one can get

$$\frac{1}{k_{obs}} = \frac{1}{k_1 K_1 [H^+]} + \frac{1}{k_1} \qquad (2)$$

This treatment is illustrated in Fig. 2, where data at four temperatures from Table I are shown as $1/k_{obs}$ *versus* $1/[H^+]$ plot. The values of k_1 and K_1 obtained by least-square fitting of the data along with the

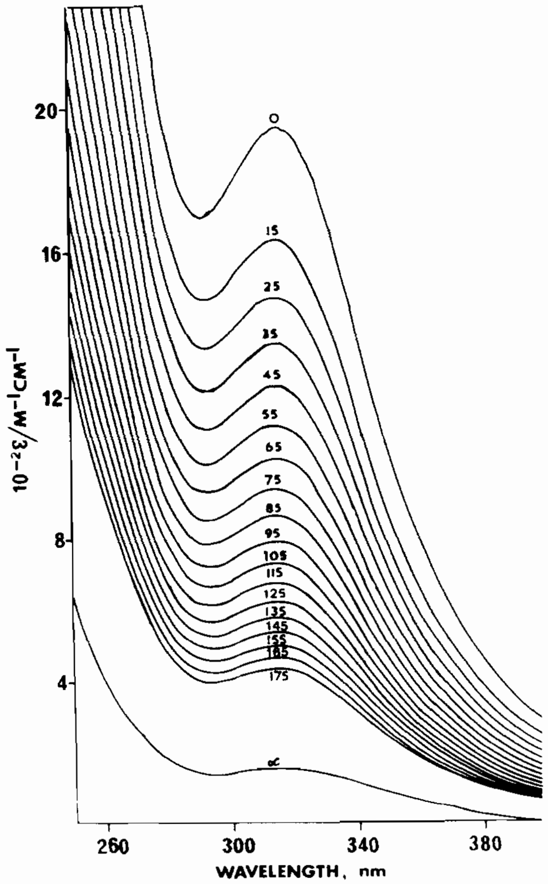
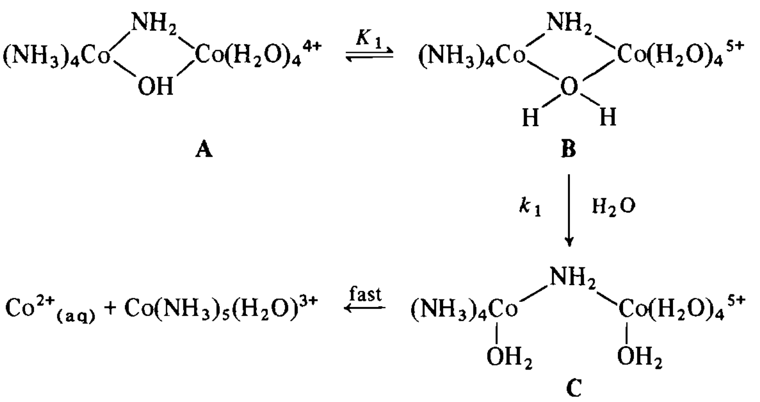


Fig. 1. Spectral change during decomposition of the complex ion **3**. Numbers in the spectra indicate times in minutes at which spectra were run.

TABLE I. Observed Rate Constants for the Decomposition Reaction of Complex **3** in Aqueous Perchloric Acid Solution[a]

$[H^+]$ (M)	$10^4 \times k_{obs}$ (s^{-1})			
	25.0 °C	30.0 °C	35.2 °C	41.5 °C
0.048	1.29	2.20	3.23	5.27
0.096	2.38	3.70	5.28	8.70
0.144	2.86		6.80	11.33
0.193	3.62	5.41	7.76	12.27
0.241	4.14		8.60	13.10
0.289	4.53	6.71	9.65	13.80
0.337	4.82	6.86	10.05	14.30
0.385	5.24	6.97	10.30	

[a] [Complex], 5×10^{-4} M; I, 0.5 M ($LiClO_4$).



Scheme 1.

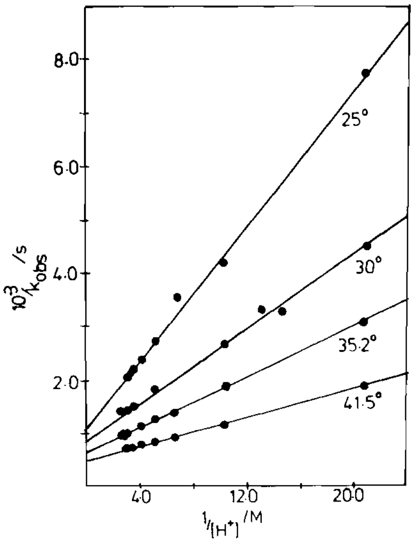


Fig. 2. Plot of $1/k_{obs}$ vs. $1/[H^+]$.

TABLE II. Kinetic Parameters for the Decomposition Reaction of Complex 3 in Aqueous Perchloric Acid Solution

Temperature (°C)	$10^3 \times k_1$ (s^{-1})	K_1 (M^{-1})
25.0	0.89 + 0.06	3.54 + 0.24
30.0	1.06 + 0.03	4.45 + 0.14
35.2	1.52 + 0.02	5.61 + 0.10
41.5	2.13 + 0.02	6.93 + 0.20

$\Delta H_1^{\neq} = 9.56 \pm 0.10$ kcal mol^{-1} $\Delta H_1^{\circ} = 6.9 \pm 1.6$ kcal mol^{-1}

$\Delta S_1^{\neq} = -40.41 \pm 17.2$ cal K^{-1} mol^{-1} $\Delta S_1^{\circ} = 25.8 \pm 6.2$ cal K^{-1} mol^{-1}

corresponding temperature parameters are summarized in Table II.

It is obvious from Scheme 1 that the cleavage of the amido bridge in I as a first step has not been considered. This is justifiable since the process is expected to be independent of hydrogen ion concentration [5]. This mechanism also proposes that the cleavage of the amido bridge in **C** of Scheme 1 to give the final product is relatively fast compared to the cleavage of amido bridges in other dinuclear complexes. For example the decomposition [6, 7] of the μ-amido-bis(pentaamminecobalt(III)) ion occurs at a slow rate of 1.35×10^{-4} s^{-1} at 64.6 °C being independent of $[H^+]$. So it is highly unlikely that the k_1 path is accompanied by Co–N bond breaking.

The kinetic data for the hydroxo bridge cleavage of complex 3 cannot be compared with the data for other hydroxo bridge dinuclear complexes, since complex 3 is very unique in its asymmetric composition. The only complex which is somewhat comparable is its parent compound 2. The direct kinetic study for the conversion of complex 2 to the corresponding diaqua complex, $[(NH_3)_4(H_2O)Co(\mu\text{-}NH_2)\text{-}Co(H_2O)(NH_3)_4]^{5+}$ has not been studied directly because of lack of spectral change between the reactant and product. However, the rate of bridge cleavage for complex 2 has been measured [8] indirectly by the help of reducing agents like Cr^{2+} and V^{2+} which act as scavengers for the aqua complex. The reaction involves protonation followed by bridge cleavage resulting in the formation of the diaqua complex which then undergoes rapid electron transfer reaction with Cr^{2+} or V^{2+}. The mechanism for the formation of the diaqua complex is very similar to the one displayed in Scheme 1. The kK for complex 2 is 1.6×10^{-4} M^{-1} s^{-1} at 35 °C. This value is comparable to our value, 5.8×10^{-3} M^{-1} s^{-1}, for complex 3. In the absence of the individual values for the constants k and K for complex 2 it is very difficult to comment on the values of kK.

It is quite possible that the rate constants for the cleavages of complexes 2 and 3 are similar and hence, any difference in the values of kK must lie on the protonation constant K.

The unusual stability of the species **A** needs some comments at this point. It is well known [9] that the mononuclear cobalt(III) complexes with more than

TABLE III. Rate Parameters [9] for the Decomposition Reactions of $[CoR_n(H_2O)_{6-n}]^{3+}$ Complexes in Aqueous Perchloric Acid[a]

Complex (R_n)	Rate determining step	kK (M^{-1} s^{-1})
$(NH_3)_5$	loss of NH_3	1.0×10^{-9}
cis-$(NH_3)_4$	loss of NH_3	6.5×10^{-8}
fac-$(NH_3)_3$	redox	1.1×10^{-6}
cis-$(NH_3)_2$	redox	1.7×10^{-5}
cis-$(py)_2$	redox	1.2×10^{-2}
Zero	redox	10^{-1}

[a] *I*, 1.0 M; temperature, 70 °C.

three water molecules attached to the metal centre tend to undergo spontaneous decomposition. The kinetics of the reactions involving the loss of NH_3 from a number of aquaamminecobalt(III) complexes of the type $[Co(NH_3)_n(H_2O)_{6-n}]^{3+}$ have been investigated in detail [10]. The plausible mechanism proposed for the spontaneous decomposition of these ammine complexes is

$$[Co(NH_3)_n(H_2O)_{6-n}]^{3+} \overset{K}{\rightleftharpoons} [Co(NH_3)_n(H_2O)_{5-n}(OH)]^{2+} + H^+$$

$$[Co(NH_3)_n(H_2O)_{5-n}(OH)]^{2+} \xrightarrow{k} Co^{2+}_{aq} + nNH_3 + \tfrac{1}{4}O_2$$

The corresponding rate expression is

$$k_{obs} = \frac{kK}{K + [H^+]}$$

If $K \ll [H^+]$, $k_{obs} = kK/[H^+]$.

The values of kK obtained for a number of ammine complexes of cobalt(III) are listed in Table III. The values of the equilibrium constants, K, are not obtainable independently, but those values are estimated to be considerably less than unity. There is an unresolved disagreement [9] concerning the rate of spontaneous reduction of $Co(H_2O)_6^{3+}$ and much controversy concerning its rate law and mechanism. However, from the available data, the value of kK has been found to be nearly 10^{-1} M^{-1} s^{-1}. It is, therefore, believed that the lability of the mononuclear cobalt(III) complex is dependent on the acidity of the water molecule attached to the metal centre and the acidity increases as the number of water molecules attached to the metal centre increases. The increase in acidity will facilitate the formation of the hydroxo complex which is believed to take part in an electron transfer reaction leading to the complete decomposition of the complex molecule.

The rate of decomposition of **A** is, however, entirely controlled by the rate of hydroxo bridge cleavage. This is surprising since, as one of the cobalt(III) centres in the dinuclear complex possesses four water molecules, it was expected that the complex would undergo electron transfer reaction much faster than the rate of hydroxo bridge cleavage observed. One could possibly explain this unusual stability in terms of the electron releasing resonance effect of the bridging $-NH_2$ and $-OH$ groups resulting in increased electron density on the oxygen atoms of the water molecules attached to the cobalt. This will reduce the acidity of the water molecules considerably and hence give extra stability to complex **A**. After cleavage of the hydroxide bridge occurs to form **C**, subsequent cleavage of the amido bridge will naturally be facilitated once the electron transfer process is completed resulting in the formation of a labile cobalt(II) centre in **C**. Work on similar redox process involving dinuclear complexes of cobalt(III) is now in progress in our laboratory.

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References

1 M. R. Churchill, G. M. Harris, R. A. Lashewycz, T. P. Dasgupta and K. Koshy, *Inorg. Chem., 18,* 2290 (1979).

2 K. Koshy and T. P. Dasgupta, *Inorg. Chim. Acta, 117,* 111 (1986).

3 G. G. Sadler and T. P. Dasgupta, *Inorg. Chim. Acta, 103,* 57 (1985).

4 A. M. Greenaway, T. P. Dasgupta, K. C. Koshy and G. G. Sadler, *Spectrochim. Acta, Part A, 42,* 949 (1986).

5 R. D. Mast and A. G. Sykes, *J. Chem. Soc. A,* 1031 (1968).

6 J. Doyle and A. G. Sykes, *J. Chem. Soc. A,* 2836 (1968).

7 J. Doyle and A. G. Sykes, *J. Chem. Soc. A,* 794 (1967).

8 R. S. Taylor and A. G. Sykes, *J. Chem. Soc. A,* 1991 (1970).

9 G. Davies and B. Warnquist, *Coord. Chem. Rev., 5,* 349 (1970).

10 K. E. Hyde and G. M. Harris, *J. Phys. Chem., 83,* 2204 (1978).