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THERMAL STUDIES ON OXALATE COMPLEXES. VI. HEXAMMINECOBALT(III) OXALATE TETRAHYDRATE

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ABSTRACT

The thermal decomposition of $[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4\ H_2O$ has been studied using TG and DTG. Infrared analysis and chemical tests were carried out to identify the products of decomposition from among three possible mechanisms. The first step involves a complete dehydration and has an activation energy of 234 kJ mole^{-1}. Continued heating of the anhydrous complex causes loss of $H_2C_2O_4$, NH_3, N_2H_4, and CO in two steps to give CoO as the final product. Kinetic and thermal parameters for these reactions are presented.

INTRODUCTION

Metal oxalate complexes have been studied by several workers and thermal studies on the dissociation of numerous transition metal ammine complexes have been reviewed in the monograph by Wendlandt and Smith [1]. However, a few complexes of this type have not been studied to determine their thermal behavior. In this report, we describe the thermal decomposition of one of those complexes, $[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4\ H_2O$.

According to the published work on the dissociation of hexamminecobalt(III) complexes, the nature of the final products depends on the anion of the complex and/or the atmosphere employed [1]. For example, complexes with halide anions, $[Co(NH_3)_6]X_3$ (where X = Cl or Br), give CoX_2 as the end product in an inert atmosphere while Co_3O_4 is obtained as the final product in a static air atmosphere. However, regardless of the atmosphere, compounds like $[Co(NH_3)_6](NO_3)_3$ and $[Co(NH_3)_6]_2(SO_4)_3$ give Co_3O_4 and $CoSO_4$, respectively, as the terminal residues [2,3]. In the present study, we have investigated the thermal behavior of hexamminecobalt(III) with the oxalate anion.

EXPERIMENTAL

The preparation of $[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4\ H_2O$ was carried out by the method described by Fernelius [4]. Thermogravimetric analysis was per-

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formed using a Perkin-Elmer thermogravimetric system Model TGS-2. The complex was heated in a dynamic nitrogen atmosphere and the procedures employed were similar to those previously described [5]. Infrared spectra were obtained using a Perkin-Elmer Model 621 grating IR spectrophotometer. Samples were studied as mulls in oil between plates of cesium bromide.

Kinetic parameters were obtained by analyzing the TG data using both the Coats and Redfern equations [6] and the Reich and Stivala method [7]. In applying the Coats and Redfern method, the equations used were

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]=\ln\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)-\frac{E}{RT} \qquad (1)$$

and for the case where $n = 1$

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]=\ln\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)-\frac{E}{RT} \qquad (2)$$

where α is the fraction of the reaction completed, E is the activation energy, β is the heating rate, T is the temperature (K), A is the frequency factor, and R is the molar gas constant. Calculations for the Coats and Redfern method and the iterative Reich and Stivala method were carried out by computer using programs written in FORTRAN.

RESULTS AND DISCUSSION

The TG and DTG curves for the thermal decomposition of $[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4\ H_2O$ are shown in Fig. 1. According to the TG

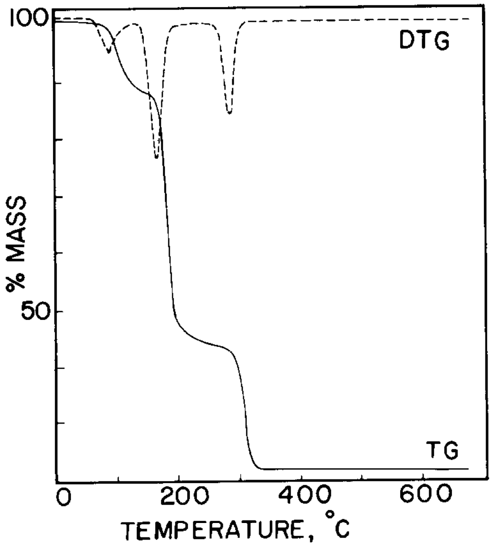

Fig. 1. TG and DTG curves for the decomposition of $[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4\ H_2O$.

curve, the decomposition of this complex takes place in three distinct steps. As would be expected, the first step of this decomposition process is the dehydration reaction. The decomposition pattern of this complex can be represented by three possible mechanisms all of which agree satisfactorily with the observed mass losses. These possible mechanisms are:

Mechanism 1

$$[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4\,H_2O(s) \rightarrow [Co(NH_3)_6]_2(C_2O_4)_3(s) + 4\,H_2O(g) \quad (3)$$

$$[Co(NH_3)_6]_2(C_2O_4)_3(s) \rightarrow [Co_2(NH_3)_2(NH_2)_4]C_2O_4(s) + 2\,H_2C_2O_4(g) + 6\,NH_3(g) \quad (4)$$

$$[Co_2(NH_3)_2(NH_2)_4]C_2O_4 \rightarrow 2\,CoO(s) + 2\,CO(g) + 2\,NH_3(g) + 2\,N_2H_4(g) \quad (5)$$

Mechanism 2

$$[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4\,H_2O(s) \rightarrow [Co(NH_3)_6]_2(C_2O_4)_3(s) + 4\,H_2O(g) \quad (6)$$

$$[Co(NH_3)_6]_2(C_2O_4)_3(s) \rightarrow [Co_2(NH_3)_5(NH_2)_6](s) + 3\,H_2C_2O_4(g) + NH_3(g) \quad (7)$$

$$[Co_2(NH_3)_5(NH_2)_6](s) \rightarrow 2\,CoNH(s) + 7\,NH_3(g) + N_2H_4(g) \quad (8)$$

Mechanism 3

$$[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4\,H_2O(s) \rightarrow [Co(NH_3)_6]_2(C_2O_4)_3(s) + 4\,H_2O(g) \quad (9)$$

$$[Co(NH_3)_6]_2(C_2O_4)_3(s) \rightarrow 2\,CoC_2O_4(s) + 10\,NH_3(g) + N_2H_4(g) + H_2C_2O_4(g) \quad (10)$$

TABLE 1

A comparison of calculated and observed mass losses

Transition	Temp. range (°C)	% Mass loss			
		Obsd. ave.	Calcd.		
			Mechanism 1	Mechanism 2	Mechanism 3
I[a]	92–147	11.3	10.9	10.9	10.9
II[b]	150–247	43.2	42.9	43.6	44.4
III[c]	265–328	22.6	23.4	22.9	21.9
Total	92–328	77.1	77.2	77.4	77.2

[a] Transition I represents eqn. (3), (6), or (9).
[b] Transition II represents eqn. (4), (7), or (10).
[c] Transition III represents eqn. (5), (8), or (11).

$$2\ CoC_2O_4(s) \rightarrow 2\ CoO(s) + 2\ CO_2(g) + 2\ CO(g) \qquad (11)$$

A comparison of the calculated percentage mass loss for each mechanism with the observed mass losses is given in Table 1. It is clear from the data shown in Table 1 that the calculated values of each transition are fairly close to each other and agree with the observed values. In addition, the total mass loss for each mechanism is almost identical to the observed value.

In all three mechanisms, the first step of the decomposition is the complete dehydration. According to Mechanism 1, in the second step of the decomposition partial loss of oxalate groups and ammine groups [eqn. (4)] takes place. But in Mechanisms 2 and 3, either a complete loss of oxalate groups [eqn. (7)] or a complete loss of ammine groups [eqn. (10)] takes place in the second step of the decomposition.

In order to identify the intermediate product after the second step of the decomposition, the product was isolated and analyzed by IR spectroscopy and by means of chemical tests. The IR analysis of the intermediate showed strong vibrations at 3370, 3280, and 1315 cm^{-1}, a medium band at 500 cm^{-1}, and a band with a shoulder in the region of 1700–1620 cm^{-1}. The strong vibrations at 3370 and 3280 and the medium band at 500 cm^{-1} can be assigned to the stretching vibrations of the NH_3 group and to the Co(III)–N stretching mode, respectively [8]. The presence of the NH_3 groups in the intermediate is further supported by the strong band at 1315 cm^{-1} and the broad band at 1620 cm^{-1}, which could be assigned to the NH_3 deformation. The shoulder at 1700 cm^{-1} is due to the C=O stretching vibration and it indicates the presence of oxalate groups in the intermediate.

Addition of calcium chloride solution to a clear solution of the intermediate compound gave a white precipitate of calcium oxalate which dissolved on the addition of hydrochloric acid. This again indicated that the oxalate group was present in the intermediate compound that is formed by the second step of the decomposition.

The information from the IR spectra and the chemical tests reveal that both the oxalate group and the ammine group are present in the intermediate compound. This information eliminates the possible Mechanisms 2 and 3. Therefore, on the basis of all the observations, it appears that the correct mechanism for the decomposition of $[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4\ H_2O$ is expressed by eqns. (3)–(5).

Several samples were analyzed separately and the linear regression analysis of the data was carried out using the Coats and Redfern equations [eqns. (1) and (2)] and the iterative method of Reich and Stivala. Table 2 shows the average thermal parameters obtained for the decomposition of $[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4\ H_2O$ by these methods.

The dehydration reaction begins near 90°C and is complete at about 150°C. According to the Reich and Stivala iterative analysis, this process follows a reaction with $n = 2.4$ and the energy of activation for this process is

TABLE 2

Thermal parameters for the decomposition of $[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4\ H_2O$

Eqn.	Temp. range (°C)	% Mass loss		Reich/Stivala		Coats/Redfern		
		Calcd.	Obsd.	n [a]	E_a [b]	n [a,c]	E_a [b]	r
3	92–147	10.9	11.3	2.4	234.3	2	227.3	0.9990
4	150–247	42.9	43.2	1.4	196.5	4/3	193.1	1.0000
5	265–328	77.2	77.1	0.8	324.5	2/3	323.4	0.9999

[a] The apparent order of the reaction.

[b] E_a given in kJ $mole^{-1}$.

[c] Determined only to the nearest 1/3 by the Coats and Redfern method.

234.3 kJ $mole^{-1}$. The analysis of the same data by the Coats and Redfern equations gave an activation energy of 227.3 kJ $mole^{-1}$ and an n value that varied between 2 and 8/3 for all samples. Thus, the dehydration process yields similar parameters by either method of analysis.

From the data shown in Table 2, it can be seen that the energy of activation and the order of reaction obtained by the two different methods for the second and third steps are also in good agreement with each other. The correlation coefficients obtained with the "best" n according to the Coats and Redfern method are quite close to unity. The decomposition of the anhydrous complex begins [eqn. (4)] with deprotonation of coordinated NH_3. Similar reactions have been observed for ammine complexes where the anion is also a complex [9]. Oxalic acid is volatile at the temperature where the second step is observed so deprotonation leads to its loss. It is likely that this behavior is the result of the oxalate ion being the conjugate base of a weak acid. Ammonia is also lost in this decomposition step and the product, $[Co_2(NH_3)_2(NH_2)_4]C_2O_4$, undoubtedly contains NH_2^- and/or $C_2O_4^{2-}$ bridges. This behavior is also similar to that of $[Co(NH_3)_5H_2O][M(CN)_6]$ where deaquation leads to the formation of amide bridges after loss of HCN [10].

The final step in the decomposition, that of the tetramidobisamminedicobalt(III) oxalate, leads to the reduction of Co(III) to Co(II) and complete loss of all the nitrogen containing ligands and CO. It appears that both NH_3 and N_2H_4 are lost in that step. Consequently, the decomposition of $[Co(NH_3)_6]_2(C_2O_4)_3$ is somewhat different to that of other hexamminecobalt(III) compounds.

REFERENCES

1 W.W. Wendlandt and J.P. Smith, The Thermal Properties of Transition-Metal Ammine Complexes, Elsevier, Amsterdam, 1967, Chap. 3.

2 M. Viltange, Microchim. Ichnoanal. Acta, (1964) 461.
3 W.W. Wendlandt, J. Inorg. Nucl. Chem., 25 (1963) 545.
4 W.C Fernelius, Inorg. Synth., 2 (1946) 217.
5 J.E House, Jr., G.L. Jepsen and J.C. Bailar, Jr., Inorg. Chem., 18 (1979) 1397.
6 A.W. Coats and J.P. Redfern, Nature (London), 201 (1964) 68.
7 L. Reich and S.S. Stivala, Thermochim. Acta, 36 (1980) 103.
8 K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley-Interscience, New York, 1970, p. 150.
9 J.E. House, Jr. and C.A. Jepsen, Thermochim. Acta, 37 (1980) 49.
10 C.A. Jepsen and J.E. House, Jr., J. Inorg. Nucl. Chem., 43 (1981) 953.