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KINETIC STUDIES ON THE DECOMPOSITION OF *trans*-DICHLOROTETRAMMINECOBALT(III) BISULFATE

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ABSTRACT

The decomposition of *trans*-$[Co(NH_3)_4Cl_2]HSO_4$ has been studied using TG. The first step in the decomposition involves the loss of NH_3 while the second step appears to involve the loss of NH_3 and $(NH_4)_2SO_4$. The final products appear to be $CoCl_2$ and $CoSO_4$. Kinetic parameters have been determined for these reactions and the mechanisms have been elucidated.

INTRODUCTION

It is well known that heating *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$ results in the loss of water and isomerization of the complex ion to give a *cis* product [1–5]. Recently, we have investigated the thermal characteristics of other complexes of this type in which the anions were BrO_3^-, NO_3^-, and NO_2^- [6]. However, none of these compounds gave any indication of being converted to the *cis* isomer, though the decomposition patterns were determined and kinetic parameters were evaluated. We have now investigated the thermal behavior of *trans*-$[Co(NH_3)_4Cl_2]HSO_4$, which is quite different from that of the complexes containing oxidizing anions like BrO_3^-, NO_3^-, or NO_2^-. Accordingly, this report presents the results of kinetic studies on the decomposition of *trans*-$[Co(NH_3)_4Cl_2]HSO_4$ and indicates the probable mechanisms of these reactions.

EXPERIMENTAL

Preparation of compounds

Trans-dichlorotetramminecobalt(III) bisulfate was prepared by the method of Schlessinger [7]. The crystals were separated by filtration and washed in

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turn with cold dilute HCl, 95% ethanol, and ether. The product was allowed to dry in air.

Thermal studies

The decomposition of *trans*-$[Co(NH_3)_4Cl_2HSO_4$ was studied using a Perkin-Elmer thermogravimetric system Model TGS-2. All studies were conducted in a dry nitrogen atmosphere and heating rates of 2.5, 5, 10, and 20 °C min^{-1} were used.

Kinetics and mechanism

Kinetic parameters were evaluated using the Reich and Stivala [8] and Coats and Redfern [9] methods. The Coats and Redfern method was applied using n values of 0, 1/3, 2/3,...,2. Calculations were carried out using a microcomputer with a program written in BASIC.

Mechanisms were determined using the procedure of Reich and Stivala [10]. In this method, the fraction of the reaction completed α is determined at the same temperatures when runs are made at different heating rates. Thus

$$(RH)_2 = g(\alpha_1) \tag{1a}$$

$$(RH)_1 = g(\alpha_2) \tag{1b}$$

where α_1 and α_2 are two different degrees of conversion, $(RH)_1$ and $(RH)_2$ are two heating rates, and

$$g(\alpha) = \frac{d\alpha}{f(\alpha)} \tag{2}$$

The method uses heating rates such that $(RH)_2/(RH)_1 = 2$ and tests fourteen $f(\alpha)$ functions from different mechanisms to determine which best represents the data by giving the smallest sum of squares of errors (SSE).

RESULTS AND DISCUSSION

A typical TG curve for the decomposition of *trans*-$[Co(NH_3)_4Cl_2]HSO_4$ is shown in Fig. 1. There are three reactions in the decomposition and the first corresponds to a 5.7 ± 0.6% mass loss which is 16.8 ± 0.8 mass units. Thus the loss of NH_3 is indicated with the anation reaction being

$$trans\text{-}[Co(NH_3)_4Cl_2]HSO_4(s) \rightarrow trans\text{-}[Co(NH_3)_3Cl_2HSO_4](s) + NH_3(g) \tag{3}$$

for which the calculated mass loss is 5.76%. This reaction has been studied

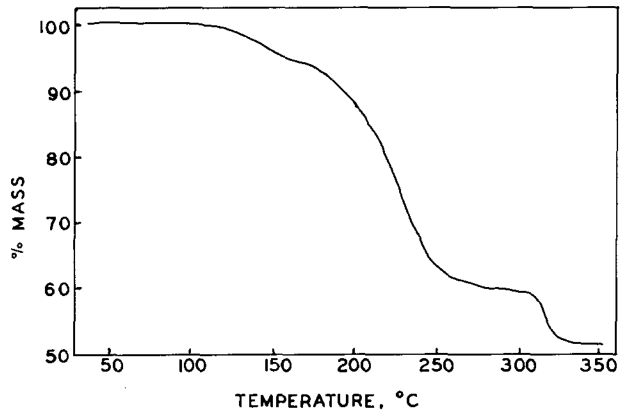

Fig. 1. TG curve for *trans*-$[Co(NH_3)_4Cl_2]HSO_4$.

over a wide range of heating rates, and the kinetic parameters are shown in Table 1.

The second reaction takes place in the range 170–260 °C and corresponds to a 34.0% mass loss which is 100 mass units. This mass loss corresponds well to the reaction

$$2\text{-}trans\text{-}[Co(NH_3)_3Cl_2HSO_4](s) \rightarrow Co_2Cl_4SO_4(s) + (NH_4)_2SO_4(g) + 4NH_3(g \quad (4)$$

TABLE 1

Kinetic parameters for the decomposition reactions of *trans*-$[Co(NH_3)_4Cl_2]HSO_4$

Reaction	Heating rate (°C min^{-1})	Coats and Redfern [9]		Reich and Stivala [8]	
		n	E (kJ $mole^{-1}$)	n	E (kJ $mole^{-1}$)
(3)	2.5	2	103.9	2.52	134.1
(3)	5.0 (A) [a]	4/3	108.6	1.40	111.3
(3)	5.0 (B) [a]	2	147.4	2.61	195.8
(3)	10.0 (A) [a]	4/3	88.5	1.03	67.9
(3)	10.0 (B) [a]	4/3	108.6	1.09	92.1
(3)	20.0	5/3	86.9	1.37	71.0
(4)	2.5	1	106.5	1.07	111.5
(4)	5.0 (A) [a]	2/3	82.8	0.64	75.8
(4)	5.0 (B) [a]	1	104.0	1.00	56.5
(4)	10.0(A) [a]	2/3	89.1	0.56	81.1
(4)	10.0(B) [a]	2/3	79.3	0.47	65.8
(5)	2.5	1	403.0	1.16	405.4
(5)	5.0 (A) [a]	2	457.0	1.87	392.0
(5)	5.0 (B) [a]	4/3	404.3	1.20	347.0
(5)	10.0 (A) [a]	1	304.0	1.20	326.2
(5)	10.0 (B) [a]	0	181.6	–	–

[a] Different runs at the same heating rate.

TABLE 2

Mechanisms indicated for the decomposition reactions

Reaction	Data used [a]	Mechanism
(3)	2.5 and 5 (A)	D3: $(1-(1-\alpha)\hat{}(1/3))\hat{}2$
(3)	2.5 and 5 (B)	D3: $(1-(1-\alpha)\hat{}(1/3))\hat{}2$
(3)	5 (A) and 10 (A)	D3: $(1-(1-\alpha)\hat{}(1/3))\hat{}2$
(3)	5 (A) and 10 (B)	D3: $(1-(1-\alpha)\hat{}(1/3))\hat{}2$
(3)	5 (B) and 10 (A)	F1: $-\ln(1-\alpha)$
(3)	5 (B) and 10 (B)	D3: $(1-(1-\alpha)\hat{}(1/3))\hat{}2$
(3)	10 (A) and 20	D3: $(1-(1-\alpha)\hat{}(1/3))\hat{}2$
(3)	10 (B) and 20	D3: $(1-(1-\alpha)\hat{}(1/3))\hat{}2$
(4)	2.5 and 5 (A)	D3: $(1-(1-\alpha)\hat{}(1/3))\hat{}2$
(4)	2.5 and 5 (B)	D3: $(1-(1-\alpha)\hat{}(1/3))\hat{}2$
(4)	5 (A) and 10 (A)	D3: $(1-(1-\alpha)\hat{}(1/3))\hat{}2$
(4)	5 (A) and 10 (B)	D3: $(1-(1-\alpha)\hat{}(1/3))\hat{}2$
(4)	5 (B) and 10 (A)	R2: $(1-(1-\alpha)\hat{}(1/2)$
(4)	5 (B) and 10 (B)	D3: $(1-(1-\alpha)\hat{}(1/3))\hat{}2$

[a] The α, T data are from the runs at these heating rates. A and B refer to different runs at the same heating rate.

For this reaction, the calculated mass loss is 33.9%. Kinetic parameters for this process are shown in Table 1.

The third step in the decomposition has a corresponding mass loss of 10.0% which indicates that the reaction is probably

$$Co_2Cl_4SO_4(s) \rightarrow CoCl_2(s) + CoSO_4(s) + Cl_2(g) \qquad (5)$$

for which a mass loss of 12.0% is expected. Table 1 also shows the kinetic parameters obtained for this reaction.

In general, the apparent activation energies for all three reactions show a decrease as the heating rate increases. Other studies of the effects of heating rate have shown that the dehydration of $CaC_2O_4 \cdot H_2O$ is similar [11]. It should be noted, however, that the sample-to-sample variations appear to be quite large, even when allowances are made for the effects of different heating rates. Such variations have been previously studied [12].

The procedure of Reich and Stivala [10] for determining the mechanism from nonisothermal TG has been applied to the data obtained in this work. In a recent study, we have shown that the mechanism indicated by the SSE criterion sometimes depends on which data are selected for inclusion [13]. In this work, several combinations are possible since heating rates of 2.5–20 °C min^{-1} were used. Accordingly, we have used data from all possible combinations of heating rates which differ by a factor of two. Table 2 shows the results of these calculations. Because of the requirement that α values be known at the same temperatures when different heating rates are used, the third reaction was not analyzed for mechanism. This is because the third reaction was somewhat erratic and was found to occur within narrow temperature ranges.

For reactions (3) and (4), every combination of data from different runs except one gave the smallest SSE with the D3, three-dimensional diffusion control, mechanism. In the case of reaction (3), one combination of data indicated a first order (F1) mechanism, whereas in the case of reaction (4), one combination of data resulted in the smallest SSE with the R2 (contracting-area) mechanism. These results are apparently spurious and both reactions probably should be considered as following the D3 mechanism. This result is not unexpected considering that both reactions involve the loss of gaseous NH_3 which could be controlled by diffusion rates.

Like the other *trans*-dichlorotetramminecobalt(III) complexes [6], preliminary studies show no evidence of a *trans* to *cis* isomerization for the bisulfate compound. Thus, while no additional examples of geometrical isomerization have been found, the decomposition reactions have been studied and two of the three decomposition reactions appear to have mechanisms that are of the three-dimensional diffusion-controlled type.

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