

## OXIDATION OF AMMONIA EVOLVED BY THERMAL DECOMPOSITION OF Co(III) AMMINE COMPLEXES

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### ABSTRACT

Thermal decomposition of various compounds containing Co(III) ammine complex cations was studied by use of a differential thermal analysis–thermogravimetry instrument. When heated in an air atmosphere, remarkable exothermic peaks corresponding to  $\text{NH}_3$  liberation were observed for the sulfato double complexes such as  $[\text{Co}(\text{NH}_3)_6][\text{Ln}(\text{SO}_4)_3] \cdot n\text{H}_2\text{O}$ , where Ln is a trivalent rare earth metal, whereas simple salts gave endothermic peaks in the same temperature range with liberation of the coordinated  $\text{NH}_3$  as a gaseous product. This exothermic effect was found to be due to oxidation of the liberated  $\text{NH}_3$  on the surface of the sample holders, but only if they are made of Pt or Pd. The thermal analytical data were examined to find the conditions under which the oxidation of  $\text{NH}_3$  takes place effectively after liberation from compounds of various compositions. In addition to the presence of oxygen and of Pt or Pd as catalysts, the temperature and rate of  $\text{NH}_3$  liberation seem to be important factors, but their involvement is quite complicated.

### INTRODUCTION

In previous papers [1,2], the author has reported thermal analytical studies of double complexes composed of  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and trisulfato lanthanide(III), such as  $[\text{Co}(\text{NH}_3)_6][\text{Nd}(\text{SO}_4)_3] \cdot n\text{H}_2\text{O}$  and  $[\text{Co}(\text{NH}_3)_6]-(\text{M}^1)_3[\text{Ln}(\text{SO}_4)_3]_2 \cdot n\text{H}_2\text{O}$ . When they are heated in an air atmosphere, packed in a platinum crucible, deamination is followed by remarkable heat evolution. By differential thermal analysis (DTA), thermogravimetry (TG) or evolved gas analysis (EGA) studies, this phenomenon was found to be caused by catalytic oxidation of the evolved  $\text{NH}_3$  by atmospheric oxygen on the surface of the Pt sample holder. Catalytic oxidation of  $\text{NH}_3$  has been studied extensively, because of its practical importance, since the beginning of this century [3]. The reaction on the surfaces of metals or transition metal oxides is characteristically fast and is assumed to be composed of several elementary processes [4]. Common to the various theories, is the assumption that the first step is the reaction between oxygen adsorbed on the catalyst and  $\text{NH}_3$  which strikes the surface. Factors such as temperature, the ratio of  $\text{NH}_3$  to air and the flow rate of the gaseous reactants have been extensively

studied to maximize the conversion of  $\text{NH}_3$  to nitric acid. Optimum conditions are a temperature of 900–1000 °C, a 2:1 ratio of  $\text{O}_2$  to  $\text{NH}_3$ , and a contact time for the gas mixture with Pt–Rh gauze catalyst of  $1 \times 10^{-4}$  to  $1 \times 10^{-3}$  s [3]. It is known that this catalytic oxidation can take place at temperatures as low as 200 °C [5]. Thus, the phenomena observed to be associated with deamination seem to be explained reasonably by this reaction on the surface of the sample holders. However, there remain a few questions unanswered. These include the issues of why oxidation does not take place for the  $\text{NH}_3$  evolved when simple salts such as  $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  are decomposed in the same circumstances; whether this kind of phenomenon is observed for other ammine complexes or for other sample holder materials; and how the evolved  $\text{NH}_3$  is oxidized so effectively at the surface of the sample holders, even though the structure is rather simple compared to that of a Pt–Rh gauze catalyst, for example.

The effect of counter anions of the Co(III) ammine complexes on the decomposition stoichiometry or on the temperature at which the reduction of Co(III) to Co(II) begins has been studied [6]. For most of the complexes, deamination begins at about 200 °C. However, another study has found that  $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$  liberates  $\text{NH}_3$  at about 300 °C, which is one of the highest values [7]. According to studies of separate rare earth or actinide ions by use of the Co(III) ammine cations as precipitants, various compounds have been obtained from aqueous sulfate [8,9] and carbonate [10,11] media as crystalline hydrates. Since these compounds may be regarded as double complexes composed of Co(III) ammine cations and the sulfato or carbonato complex anions of those metal cations, the temperature of deamination is expected to vary within a certain range. Therefore, we might be able to see how the deamination temperature is associated with the oxidation of the evolved  $\text{NH}_3$ . Moreover, the amount of gas evolved by thermal decomposition of solids is generally proportional to the amount of sample at a constant temperature, and increases with increasing temperature. Therefore, the reaction rate can be controlled to some degree by varying the heating rate and the amount of sample in the DTA–TG measurements. In the present study, we prepared a variety of Co(III) ammine complexes for which deamination would be expected to occur without further decomposition due to the counter anions. Thermal analytical measurements were conducted on these under various conditions to find a more rigorous description of the phenomena.

## EXPERIMENTAL

### *Preparation of the Co(III) ammine complexes*

Co(III) ammine complexes  $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  [12],  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$  [13] and *cis*- $[\text{Co}(\text{H}_2\text{O})_2(\text{NH}_3)_4]_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$  [14]

were prepared by the methods described in the references. These salts were used to prepare various complexes. A series of compounds of the composition  $[\text{Co}(\text{NH}_3)_6][\text{Ln}(\text{SO}_4)_3] \cdot n\text{H}_2\text{O}$ , where Ln is Sc(III), Y(III) or a lanthanide(III) were crystallized from aqueous sulfate solutions. A detailed description of the composition of the aqueous solutions was given in the previous reports [1,9]. With the Co(III) aquaammine complex cations, Nd(III) compounds with the formulae  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5][\text{Nd}(\text{SO}_4)_3] \cdot 3\text{H}_2\text{O}$  and  $[\text{Co}(\text{H}_2\text{O})_2(\text{NH}_3)_4][\text{Nd}(\text{SO}_4)_3] \cdot 3\text{H}_2\text{O}$  were obtained as crystalline precipitates by a similar procedure to that with hexaamminecobalt(III) cation.

*Preparation of  $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$  and  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5][\text{Co}(\text{CN})_6]$*

$\text{K}_3[\text{Co}(\text{CN})_6]$  (Aldrich) was used as received. Two beakers filled with solutions each containing Co(III) amines and  $\text{K}_3[\text{Co}(\text{CN})_6]$  were placed in a large beaker into which distilled water was poured until the two solutions were covered. Orange–yellow or brick-red crystals were grown gradually, separated from the solutions and washed with water. In the preparation of these complexes, care was taken to allow precipitation to proceed very slowly to give well-formed crystals, since we found that the crystallinity of Nd(III) complexes affects the thermal decomposition behavior significantly, as described previously [1].

Composition of the compounds was determined by analysis for Co and the rare earth elements by standard complexometric titration or inductively coupled plasma atomic emission spectrometry (ICP-AES).

*Thermal analysis*

DTA–TG measurements were made by use of an instrument which records differential temperature and weight change simultaneously. A detailed description of the instrument was given in a previous report [1]. Crystals of the complexes, which were dried in a silica gel desiccator, were crushed to 50–100 mesh particles just before use. Sample holders, 5 mm in diameter and 5 mm in height, made of Pt, Pd, Rh, Al, quartz glass and alumina porcelain were used. Only Pt sample holders were used repeatedly. After each measurement they were soaked in concentrated  $\text{HNO}_3$  overnight, then washed with water and dried in an oven at  $100^\circ\text{C}$ . This practice seems to ensure the uniformity of surface conditions necessary to give reproducibility in DTA–TG measurements. An apparatus composed of a furnace, a programmable temperature regulator and a vacuum line was used to determine the fraction of  $\text{NH}_3$  evolved as a gas when the complexes were heated under the conditions with which the DTA–TG measurements were performed. Samples of 200–300 mg of the compounds were packed in rectangular crucibles made of various materials, of dimensions  $10\text{ mm} \times 15$

mm  $\times$  5 mm, and placed in a quartz glass reaction tube which is immersed in the furnace. At a gas flow rate of 100 ml min<sup>-1</sup>, the sample was heated at 10°C min<sup>-1</sup> up to the temperature at which NH<sub>3</sub> liberation is expected to be completed and held constant for an hour or two. Evolved NH<sub>3</sub> in the gas stream was collected in a trap containing standardized hydrochloric acid solution, and determined by titrating the remaining acid with a standard NaOH solution.

## RESULTS

### *DTA-TG measurements of various complexes*

DTA-TG curves were obtained for complexes of the same composition as [Co(NH<sub>3</sub>)<sub>6</sub>][Ln(SO<sub>4</sub>)<sub>3</sub>] · nH<sub>2</sub>O, with *n* varying from one to five, depending on the Ln(III) cation, with an air flow rate of 100 ml min<sup>-1</sup>, using Pt sample holders. All the DTA curves for the lanthanide(III) complexes in the temperature range from 200 to 450°C are reproduced in Fig. 1. The curves show characteristic exothermic peaks in this temperature range following the endotherms due to dehydration of water of crystallization. These exotherms obviously coincide with the weight losses due to NH<sub>3</sub> liberation in TG curves. For most of the lanthanides, deflection of the temperature differen-

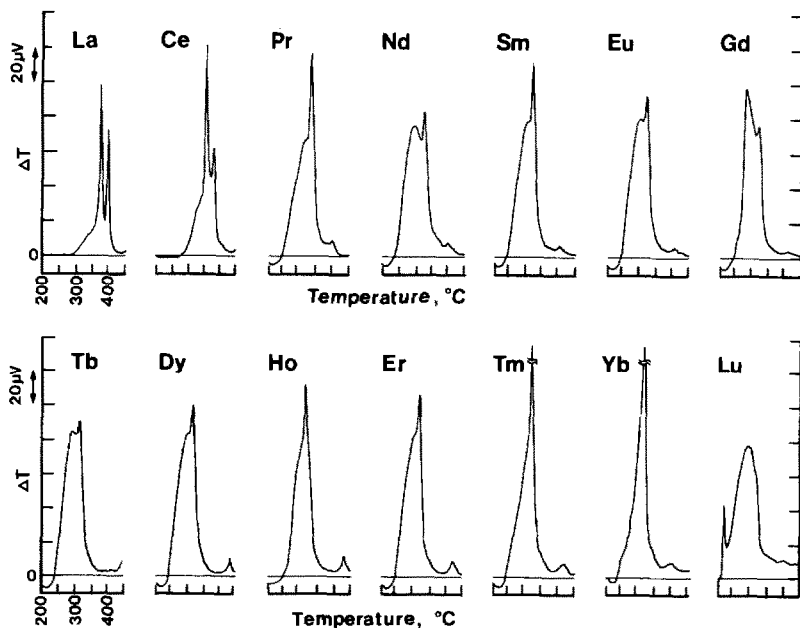


Fig. 1. Exothermic peaks in DTA curves for the complexes [Co(NH<sub>3</sub>)<sub>6</sub>][Ln(SO<sub>4</sub>)<sub>3</sub>] · nH<sub>2</sub>O; 25 mg sample, Pt sample holder, heating rate: 10°C min<sup>-1</sup>, air flow rate: 100 ml min<sup>-1</sup>.

tial in the exothermic direction begins at around 235°C and reaches the maximum at about 310°C. As seen in the figure, the shapes of the exotherms are rather complicated, which may reveal that they have resulted not from a simple process but by quite complicated steps. Exceptionally, for La(III) and Ce(III) complexes, the exotherms began at 278 and 272°C respectively and had two well-resolved, sharp peaks at 370 and 390°C for La(III), and at 350 and 374°C for Ce(III). In spite of their complicated shapes, the areas of the exotherms are nearly the same. This may mean that the amount of heat evolved is of the same order of magnitude, and furthermore, that the overall reaction which evolves heat is the same. The complexes of Sc(III) and Y(III) gave similar curves to those of the heavy lanthanides, though they are not included in the figure. In the previous study of the Nd(III) complexes [1], we described their deamination and the effect it caused on DTA curves, and their dependence on crystallinity and crystal structure. Comparison of X-ray diffraction patterns shows that there may be at least three different structures in the series of compounds with the composition  $[\text{Co}(\text{NH}_3)_6][\text{Ln}(\text{SO}_4)_3] \cdot n\text{H}_2\text{O}$ . Perhaps there is a correlation between deamination mechanism and the crystallographic nature of the complexes.

*DTA–TG for aquapentaamminecobalt(III) and cis-diaquatetraamminecobalt(III) complexes*

The DTA–TG curves for the sulfates and the Nd(III) sulfato complexes of  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]^{3+}$  and  $[\text{Co}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{3+}$  were measured under the same conditions as those used for the series of  $[\text{Co}(\text{NH}_3)_6]^{3+}$  complexes. The results are shown in Fig. 2. The DTA curves for both the salts, A and B in Fig. 2, suggest that the dehydration of the coordinated water takes place first, and then deamination occurs, producing endotherms in the DTA plot between 250 and 300°C—slightly higher than for the  $[\text{Co}(\text{NH}_3)_6]^{3+}$  salt. There are very sharp exothermic peaks after these endotherms at 300 and 290°C. This feature of the curves is common to all the Co(III) ammine sulfates (see Fig. 4). However, as shown in C and D of Fig. 2, the decomposition of the Nd(III) double complexes gave DTA–TG curves very similar to those observed for the hexaammine complexes of the corresponding compositions, as reported in the previous reports [1,2]. Thus, as far as deamination is concerned, no significant difference was found among three Co(III) ammine complexes.

*Thermal decomposition of  $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$  and  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5][\text{Co}(\text{CN})_6]$*

DTA–TG curves for the double complexes containing  $[\text{Co}(\text{CN})_6]^{3-}$  were obtained in the air flow by use of the Pt sample holder, and are shown in

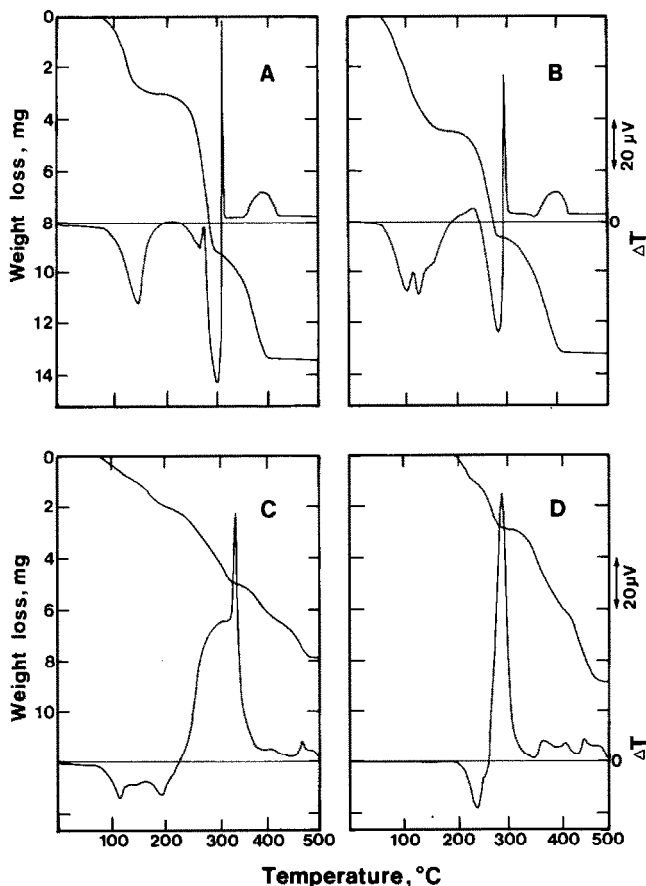


Fig. 2. DTA-TG curves of the compounds containing  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]^{3+}$  and  $[\text{Co}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{3+}$  complex cations; conditions are as given in Fig. 1. A:  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$ ; B:  $[\text{Co}(\text{H}_2\text{O})_2(\text{NH}_3)_4]_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$ ; C:  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5][\text{Nd}(\text{SO}_4)_3] \cdot 3\text{H}_2\text{O}$ ; D:  $[\text{Co}(\text{H}_2\text{O})_2(\text{NH}_3)_4](\text{NH}_4)_3[\text{Nd}(\text{SO}_4)_3]_2 \cdot 3\text{H}_2\text{O}$ .

Fig. 3. The hexaammine complex liberated  $\text{NH}_3$  at about  $300^\circ\text{C}$ , while the aquapentaammine complex first released the water molecule, then  $\text{NH}_3$  at  $250^\circ\text{C}$ . As reported in ref. 7, no decomposition associated with the complex anion  $[\text{Co}(\text{CN})_6]^{3-}$  occurred before deamination was completed at  $350$  and  $306^\circ\text{C}$ . In both complexes, only endotherms were observed in the DTA curves due to the deamination, even in the presence of atmospheric oxygen. Extreme exothermic effects at higher temperatures are considered to be caused by a reaction involving cyano ligands.

#### *DTA-TG with various sample holder materials*

Figs. 4 and 5 show the DTA-TG curves of  $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  and  $[\text{Co}(\text{NH}_3)_6][\text{Nd}(\text{SO}_4)_3] \cdot 4\text{H}_2\text{O}$ , obtained by use of sample holders made

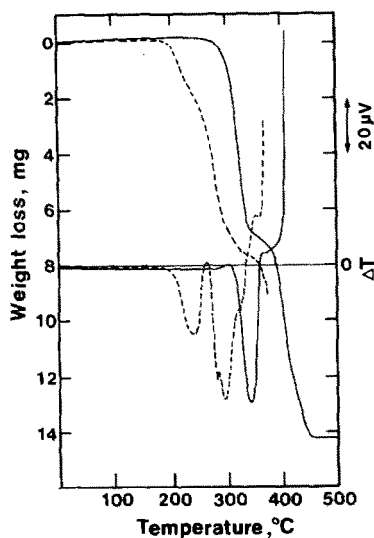


Fig. 3 DTA-TG curves of  $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$  (solid line) and  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5][\text{Co}(\text{CN})_6]$  (broken line); conditions are as given in Fig. 1.

of Pt, Pd and Rh in the air flow. For the sulfate, there seems to be no difference at all in either DTA or TG curves obtained by use of these metal sample holders, except that a very sharp exothermic peak at  $306^\circ\text{C}$  was recorded on the DTA curve only for the Pt holder. For the Nd(III) complex, in contrast, the characteristic exotherm was observed when a Pd holder was used as well as a Pt holder. In this case, positive deflection of  $\Delta T$  started at  $277^\circ\text{C}$ , which is higher than that for Pt by  $40^\circ\text{C}$ , and consequently recorded as a narrower peak. Although the peak temperatures of the sharp

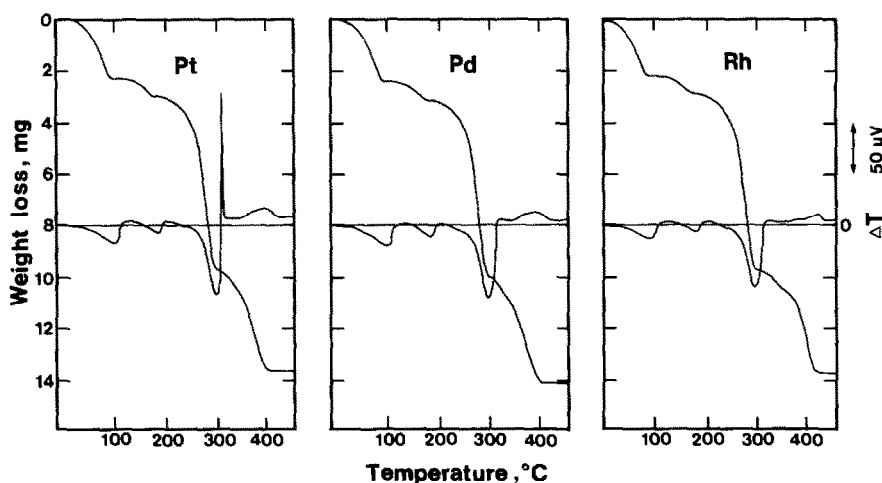


Fig. 4. DTA-TG curves of  $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  obtained by use of Pt, Pd and Rh sample holders; other conditions are as for Fig. 1.

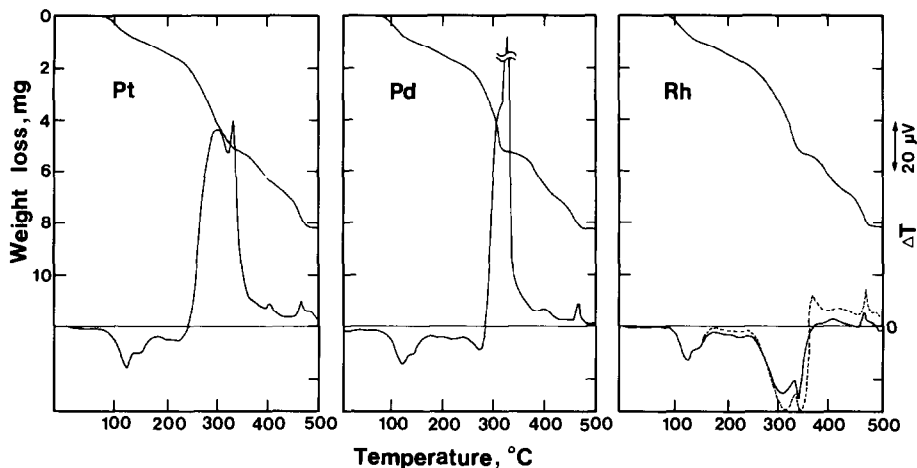


Fig. 5. DTA-TG curves of  $[\text{Co}(\text{NH}_3)_6][\text{Nd}(\text{SO}_4)_3] \cdot 4\text{H}_2\text{O}$  obtained by use of Pt, Pd and Rh sample holders; other conditions are as for Fig. 1. A DTA curve under Ar flow is included for Rh (shown with a broken line).

exotherms are very similar, i.e.  $326^\circ\text{C}$  for Pd and  $321^\circ\text{C}$  for the Pt holder, their heights are very different:  $80 \mu\text{V}$  for Pt,  $300 \mu\text{V}$  for Pd under the conditions given in the caption in Fig. 4. Since the DTA curves show a strong resemblance to each other, there is no doubt that the exotherm was caused by the catalytic oxidation of the evolved  $\text{NH}_3$  on the surface of the Pd sample holder. It seems that this reaction does not occur on the Rh surface because the DTA curve shows an endotherm in the corresponding temperature region. In addition to Rh, when sample holders made of such materials as Al,  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$  were used the DTA curves were almost the same as when obtained in an inert atmosphere.

#### Determination of evolved $\text{NH}_3$

In order to see what fraction of the  $\text{NH}_3$  coordinated to Co(III) would be oxidized after release, experiments were carried out to determine the unoxidized  $\text{NH}_3$  for a complex in crucibles of various materials and for complexes of various compositions using the Pt crucible. Table 1 shows the results of the determination of the evolved  $\text{NH}_3$  when the complex  $[\text{Co}(\text{NH}_3)_6][\text{Nd}(\text{SO}_4)_3] \cdot 4\text{H}_2\text{O}$  was thermally decomposed when packed in crucibles made of Pt, Pd, Rh and  $\text{SiO}_2$ . In Table 2 the results are given for various complexes by use of the Pt crucible.

In each run, the sample was weighed after the measurement. The observed weight losses confirmed that the samples were transformed to the intermediate products such as  $\text{CoSO}_4$ ,  $\text{Co}[\text{Co}(\text{CN})_6]$  or a new phase or phases formally composed of  $\text{CoSO}_4$  and  $\text{Ln}_2(\text{SO}_4)_3$ . In the case of two complexes which contain  $\text{NH}_4^+$  ions, the temperature was kept so low as to exclude further decomposition involving this ion.



TABLE 1

The fraction of  $\text{NH}_3$  evolved as a gaseous product when  $[\text{Co}(\text{NH}_3)_6][\text{Nd}(\text{SO}_4)_3] \cdot 4\text{H}_2\text{O}$  was decomposed using various crucibles

Sample crucible	$\text{NH}_3$ (g) (%) <sup>a</sup>	
	Air	Ar
Pt	1.11 <sup>b</sup>	75.3
Pd	8.70	75.0
Rh	52.8	73.0
$\text{SiO}_2$	79.3	80.0

<sup>a</sup> The fraction of evolved  $\text{NH}_3$  is expressed in terms of a percentage of the total amount of  $\text{NH}_3$  coordinated to Co(III).

<sup>b</sup> The previous value (ref. 1) seemed too large. Repeated measurements gave this value.

TABLE 2

The fraction of  $\text{NH}_3$  evolved as a gaseous product when various complexes were decomposed by use of a Pt crucible under an air flow of  $100 \text{ ml min}^{-1}$

Complex	$T_i$ ( $^\circ\text{C}$ )	$\text{NH}_3$ (g) (%)
$[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$	205	68.0 <sup>a</sup>
$[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$	220	63.6
$[\text{Co}(\text{H}_2\text{O})_2(\text{NH}_3)_4]_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$	230	55.0
$[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$	290	77.8
$[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5][\text{Co}(\text{CN})_6]$	230	84.4
$[\text{Co}(\text{NH}_3)_6][\text{La}(\text{SO}_4)_3] \cdot \text{H}_2\text{O}$	280	10.9
$[\text{Co}(\text{NH}_3)_6][\text{Nd}(\text{SO}_4)_3] \cdot 4\text{H}_2\text{O}$	240	1.11
$[\text{Co}(\text{NH}_3)_6][\text{Tm}(\text{SO}_4)_3] \cdot 3\text{H}_2\text{O}$	235	2.79 <sup>b</sup>
$[\text{Co}(\text{NH}_3)_6](\text{NH}_4)_3[\text{La}(\text{SO}_4)_3]_2 \cdot 3\text{H}_2\text{O}$	250	0.79
$[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5][\text{Nd}(\text{SO}_4)_3] \cdot 3\text{H}_2\text{O}$	220	< 0.5
$[\text{Co}(\text{H}_2\text{O})_2(\text{NH}_3)_4](\text{NH}_4)_3[\text{Nd}(\text{SO}_4)_3]_2 \cdot 3\text{H}_2\text{O}$	240	3.84

<sup>a</sup> Previous work (ref. 1).

<sup>b</sup> Previous work (ref. 2).

The fractions of  $\text{NH}_3$  recovered in the trap are expressed as the percentage of the total amount of  $\text{NH}_3$  coordinated to Co(III). The limit of detection is about 0.5% of the  $\text{NH}_3$  contained in the sample. Deviation among repeated determinations is not greater than 2%, since the procedure is quite simple.

## DISCUSSION

### *The fraction of oxidized $\text{NH}_3$*

As expected from the DTA–TG data,  $\text{NH}_3$  is quite efficiently oxidized on the Pd holder as well as on the Pt holder. The difference between Pd and Pt

is due to the fact that the temperature at which the deamination starts is slightly higher for Pd than for Pt, as shown in the previous section. That is, the fraction evolved during the lower temperature stage would have escaped into the air stream without being oxidized. The results obtained by use of the Rh sample holder are interesting. The difference between the values in air and in the Ar flow suggests that at least 20% of the  $\text{NH}_3$  must be oxidized in the former system. Actually, the peak area of the endotherm produced in the air flow is 76% of that observed in the Ar atmosphere, as seen in Fig. 5. Since the peaks in both atmospheric gases resemble each other over their entirety, partial oxidation of  $\text{NH}_3$  would appear to occur on the Rh surface throughout the evolution, but far less effectively than oxidation on Pt or Pd.

It has been found already that the reduction of Co(III) to Co(II) proceeds to completion with deamination for either the sulfates or sulfate complexes [1], whereas it does only partly for the double complexes with  $[\text{Co}(\text{CN})_6]^{3-}$ , regardless of the atmospheric nature [7]. With this reduction,  $\text{NH}_4^+$  must be formed by a certain mechanism, and has in fact been identified by IR spectral study of the intermediates. Therefore, not all of the coordinated  $\text{NH}_3$  will necessarily be liberated directly even at  $300^\circ\text{C}$ . This may explain why it was that just 80% was the largest value of all the determinations for the Nd(III) complexes. As well as this, 82% was recovered when  $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  was decomposed in the Ar atmosphere. In the air flow, although all of the sulfates of Co(III) ammine complexes showed endotherms, the oxidation fractions are lower than the above value, and decrease with decreasing number of amines coordinated to Co(III). The percentages correspond to the liberation of approximately 8, 6, and 4 mol  $\text{NH}_3$  out of 12, 10 and 8 mol of  $\text{NH}_3$  contained per formula weight of  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]^{3+}$  and  $[\text{Co}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{3+}$  complexes, respectively. In other words the number of moles oxidized, which is 4 mol for each complex, was approximately the same for all of these salts. Furthermore, we believe that about 2 mol of the total ammine per complex was oxidized in the air flow, since the other half was not recovered even in the inert atmosphere. The oxidation of this fraction in the air flow must have caused the very sharp exothermic peaks observed for the Co(III) ammine sulfates, as shown in Fig. 2, A and B, and in Fig. 4. Of course, these sharp exotherms are not produced if they are heated in an inert atmosphere [6].

#### *Conditions of ammonia oxidation*

The experimental results given in the former section may be summarized as follows: when Co(III) ammine complexes are gradually heated, liberation of ammonia takes place at temperatures (around  $200\text{--}300^\circ\text{C}$ ) which are more or less dependent on the counter anions; for some of the complexes, almost simultaneous oxidation of the liberated ammonia takes place quite

efficiently when they are heated in Pt or Pd sample holders in the presence of atmospheric oxygen; these complexes necessarily contain other metal cations formally regarded as sulfato complex anions; and for the rest of the complexes studied, the oxidation does not occur as efficiently as above, under the same conditions.

Hereafter we will discuss the factors which bring about the difference in the behavior of the liberated ammonia.

There are three thermodynamically possible reactions between  $\text{NH}_3$  and  $\text{O}_2$ , all of which are highly exothermic:



In the presence of catalysts such as platinum metal, the reactions obviously consist of several elementary steps [3,4]. Moreover, both  $\text{N}_2\text{O}$  and  $\text{NO}$  are more or less unstable and may undergo further decomposition or oxidation in actual reaction systems. Therefore, the product distribution depends on the many variables of the system. In order to elucidate the reaction mechanism and to find optimum conditions for maximal conversion of  $\text{NH}_3$  to one of these nitrogen oxides, extensive studies have been made. Compared to the reaction systems used in basic studies, the system involved in the DTA-TG apparatus under the working conditions is much more complex. As it is, the DTA-TG curves obtained for each of the complexes were satisfactorily reproducible and, moreover, the thermal effects in the DTA curves of the complexes were consistent with the results of the evolved  $\text{NH}_3$  analyses, although a different reaction system was used for them. In addition, the samples were measured by use of another DTA-TG apparatus which has a different configuration. The results showed no significant difference at all. Thus it seems certain that the phenomena summarized above are intrinsic characteristics of the complexes studied here. This is the justification for our interest in understanding what leads to the above differences in the behavior of  $\text{NH}_3$  when being liberated from the complexes.

In the course of the DTA-TG run, air is flowing at a constant rate upwards around the sample holder, and as the temperature is raised the following processes must take place successively: dehydration occurs and is completed by about  $200^\circ\text{C}$ ; the sample starts to liberate  $\text{NH}_3$  at a temperature which is specific to each complex, but is higher than  $200^\circ\text{C}$ ; for one group of complexes, most of the  $\text{NH}_3$  reacts with oxygen on the surface of the holder, while for the rest of the complexes, most of the  $\text{NH}_3$  diffuses or is carried away into the stream of air. Chemisorption of oxygen on platinum group metals occurs extensively and very rapidly [15]. In the temperature range of concern, from  $200$  to  $400^\circ\text{C}$ , the chemisorbed oxygen is known to exist in the atomic state. Therefore, we are able to assume that the surface of

the metal sample holders is covered with adsorbed oxygen atoms throughout the DTA–TG run under the air flow. Except for  $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ , the complexes studied contain water molecules, either water as of crystallization or as a ligand. In every case dehydration precedes deamination, but it is not necessarily completed before the latter starts. Therefore, the evolved water vapor may coexist with  $\text{NH}_3$  at the beginning of the deamination. However, there is no indication that water affected the reaction of  $\text{NH}_3$  on the surface. The same conclusion was reached in the previous report [2]. Consequently, we have to consider other factors which depend on the intrinsic nature of the complexes. Two of them must be the temperature at which the deamination occurs and the rate of  $\text{NH}_3$  evolution, at least when Pt or Pd sample holders are used in the presence of atmospheric oxygen.

### *The effect of temperature,*

The temperature at which a Co(III) ammine complex begins to liberate  $\text{NH}_3$  varies by some degree depending on the conditions under which the DTA measurement is made. Furthermore, it is characteristic of the particular complex, as long as the measurements are performed under invariant conditions. Values of the liberation temperature,  $T_i$ , defined as above, were obtained from the DTA–TG curves and are included in Table 2. These temperatures are naturally identical to those at which the DTA curves start to deflect from the baseline in either endothermic or exothermic directions. All the values of  $T_i$  for the complexes which produced exotherms fall in the range  $220^\circ\text{C}$  (for Lu(III) complex) to  $280^\circ\text{C}$  (for La(III) complex), with most around  $240^\circ\text{C}$ . For the series of complexes shown in Fig. 1,  $T_i$  tends to decrease as the atomic number of the cation increases, but is never less than  $220^\circ\text{C}$ . However, the values of  $T_i$  observed, for the endotherms of chloride, carbonate and sulfate of  $[\text{Co}(\text{NH}_3)_6]^{3+}$  are all about  $210^\circ\text{C}$ , which is slightly lower than the lowest of the other group of complexes. The difference is too small to suggest that the temperature is too low for catalytic oxidation to proceed at sufficient velocity. Some of the compounds given in Table 2 showed a value for  $T_i$  higher than  $220^\circ\text{C}$ , but the oxidation did not occur as effectively as that of the compounds containing the rare earth sulfato complexes. In contrast to these compounds, however, the complex  $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$  begins to release  $\text{NH}_3$  at about  $290^\circ\text{C}$ , which is much higher than for the sulfates, or even for the sulfato double complex for which oxidation always took place. In spite of this, the oxidation did not occur. Therefore, the results for various compounds show that temperature alone is not a determining factor, although there will be a lower limit to the release temperature, possibly at around  $200^\circ\text{C}$ .

It has been found that the oxidation velocity of  $\text{NH}_3$  on a Pt surface increases suddenly within quite a narrow range of temperatures between 200 and  $400^\circ\text{C}$ . One study [4] on the effect of temperature showed that the

differences between the temperatures at which the reaction starts and at which  $\text{NH}_3$  has almost completely disappeared is less than  $50^\circ\text{C}$  on a Pt surface. Another study [5] found that the onset temperatures of  $\text{NH}_3$  oxidation on the platinum metal surfaces seem to be rather uncertain, and vary depending on the conditions. However, the order is invariably  $\text{Pt} < \text{Pd} < \text{Rh}$ , which must be the reversed order of their catalytic activity. The fraction of  $\text{NH}_3$  evolved, given in Table 1, is consistent with this order of catalytic activity of these metal surfaces. Even when a Rh sample holder was used, about half of the  $\text{NH}_3$  was oxidized; nevertheless an endotherm was observed on the DTA curve.

### *Rate of $\text{NH}_3$ evolution*

In the industrial process for the production of nitric acid, the oxidation of  $\text{NH}_3$  is performed on a Pt–Rh gauze catalyst at high temperature. To maximize the conversion to  $\text{NO}$ , a reactant mixture with an  $\text{O}_2/\text{NH}_3$  ratio of about two is passed at a very high flow rate. The excess  $\text{O}_2$  is needed to supply it to the catalyst surface sufficiently. In the DTA–TG instrumental system,  $\text{NH}_3$  comes out from the packed sample into the holder space where air is flowing at a constant rate. Previously, we studied the effect of the oxygen content in the flow gas, and found that 3% (v/v)  $\text{O}_2$  in a flow of  $200\text{ ml Ar min}^{-1}$  produced an exotherm, though its peak height was nearly one third of that found in the air flow [1]. As discussed later, the way oxygen is involved in the  $\text{NH}_3$  oxidation in the DTA–TG system seems to be quite complicated. Instead, it is feasible to examine the effect of the liberation rate of  $\text{NH}_3$  under a constant flow of air, since it might be different depending on the counter anions of the complexes. When comparing the DTA–TG data of two groups of compounds, one giving exotherms and the other giving endotherms, the rates of weight loss for the former are found to be smaller than those for the latter. Evidently, the rate of decomposition also depends on the variables associated with the DTA–TG measurements such as heating rates, sample amounts or gas flow rates. Therefore, we will be able to see the effect of the weight loss rate on the DTA–TG curve by carrying out the measurements for some of the compounds under different conditions. Since the weight loss due to the deamination was approximately linear, the rate of  $\text{NH}_3$  evolution was estimated as the slope of the TG curve. The results are given in Table 3 for the complex  $[\text{Co}(\text{NH}_3)_6][\text{Nd}(\text{SO}_4)_3] \cdot 4\text{H}_2\text{O}$  obtained under various conditions, and in Table 4 for the sulfates and the double complex  $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ . The DTA curves for all of the measurements given in Table 3 showed prominent exotherms, indicating that the oxidation of  $\text{NH}_3$  proceeded effectively. Even at the largest rate of  $7.3 \times 10^{-6}\text{ mol s}^{-1}$ , which was accomplished when 50 mg of the complex was heated at  $20^\circ\text{C min}^{-1}$ , much heat was evolved. In contrast, in all of the cases given in Table 4, no sign that the oxidation

TABLE 3

Estimated average rate of  $\text{NH}_3$  evolution by  $[\text{Co}(\text{NH}_3)_6][\text{Nd}(\text{SO}_4)_3] \cdot 4\text{H}_2\text{O}$  under various conditions

Sample amount (mg)	Heating rate ( $^{\circ}\text{C min}^{-1}$ )	Air flow rate ( $\text{ml min}^{-1}$ )	Rate ( $\text{mol s}^{-1}$ )
13.1	10	100	$2.3 \times 10^{-7}$
25.1	10	100	$3.9 \times 10^{-7}$
51.6	10	100	$1.1 \times 10^{-6}$
25.4	5	100	$1.5 \times 10^{-7}$
50.8	20	100	$7.3 \times 10^{-6}$
27.8	10	10	$4.2 \times 10^{-7}$
25.4	10	200	$4.0 \times 10^{-7}$

occurred as effectively as in the other group of complexes was found in the DTA curves. This situation did not change even when pure oxygen was used as the flow gas instead of air.

Since the oxidation of  $\text{NH}_3$  takes place on the surface of Pt which must be in adsorption equilibrium with the atmospheric oxygen, a lower rate of  $\text{NH}_3$  evolution will favor effective oxidation. However, no exotherm was observed even at the lowest heating rate of  $2.5^{\circ}\text{C min}^{-1}$  in the measurement for the compounds  $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  and  $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ . Therefore, these provide an example of the ammine complexes for which the oxidation of evolved  $\text{NH}_3$  does not occur in spite of the fact that the temperature is high enough and that the rate is as low as those observed for the double complexes.

TABLE 4

Estimated average rate of  $\text{NH}_3$  evolution by various compounds under various conditions

Sample amount (mg)	Heating rate ( $^{\circ}\text{C min}^{-1}$ )	Air flow rate ( $\text{ml min}^{-1}$ )	Rate ( $\text{mol s}^{-1}$ )
$[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$			
21.7	2.5	100	$6.5 \times 10^{-7}$
21.7	5	100	$1.1 \times 10^{-6}$
25.9	10	100	$1.8 \times 10^{-6}$
26.2	10	100 <sup>a</sup>	$1.7 \times 10^{-6}$
$[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$			
25.1	10	100	$9.8 \times 10^{-7}$
$[\text{Co}(\text{H}_2\text{O})_2(\text{NH}_3)_4]_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$			
25.2	10	100	$1.5 \times 10^{-6}$
$[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$			
19.0	2.5	100	$6.9 \times 10^{-7}$
20.3	5	100	$1.2 \times 10^{-6}$
25.4	10	100	$2.0 \times 10^{-6}$

<sup>a</sup> Pure oxygen was used as the flow gas instead of air.

It is reasonable to think that the oxidation of  $\text{NH}_3$  takes place mainly on the inner surface of the sample holders. If the outer surface contributes to it, a larger fraction of  $\text{NH}_3$  must be oxidized when the sulfates are decomposed, because the outer surface of the holder is always surrounded by an adequate supply of oxygen. The surface area available for the reaction is nearly  $1 \text{ cm}^2$ . The number of adsorbed O atoms will never be larger than  $10^{15} \text{ atoms cm}^{-2}$ , that is  $2 \times 10^{-9} \text{ mol cm}^{-2}$ . Since the rate of oxidation was of the order of  $10^{-7}$  to  $10^{-6} \text{ mol s}^{-1}$ , whether or not a sufficient amount of oxygen is continuously supplied to the inner surface is critical. The evolution rate of  $\text{NH}_3$  ranges from  $8 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1}$  to  $8 \times 10^{-2} \text{ cm}^3 \text{ s}^{-1}$ . The volume of the open space over the sample was about  $0.1 \text{ cm}^3$  when 25 mg of the sample was packed in the holder. Therefore, if ammonia is evolved at a greater rate, the space will be filled within a few seconds, and thus the supply of oxygen from the surroundings will be prevented. This was probably true for most of the cases given in Table 4, in which efficient oxidation did not occur. When deamination is completed, the  $\text{NH}_3$  filling the space of the holder will diffuse or be transported into the stream of air. At some point in this process, circumstance which meets the requirements for effective oxidation of  $\text{NH}_3$  will arise. This may explain the very sharp exotherms observed at around  $300^\circ \text{C}$  on the DTA curves of Co(III) ammine sulfates.

Thus far, we have tried to explain the experimental results from the standpoint that the ammonia evolved from Co(III) ammine complexes will be oxidized when the following conditions are fulfilled: either Pt or Pd sample holders are used; an adequate supply of oxygen exists in the atmospheric gases; the temperature is higher than a certain lower limit, probably around  $220^\circ \text{C}$ ; and the rate of  $\text{NH}_3$  evolution is lower than a certain limit. Roughly speaking, these conditions are satisfied, yet it cannot be said that this fully explains why the oxidation does not occur for Co(III) ammine sulfates or their double complexes with  $[\text{Co}(\text{CN})_6]^{3-}$ . Apparently, the phenomenon we are dealing with is intrinsically complicated, and is made more so by the nature of the DTA-TG system. Further study will be needed to ascertain whether there are any other factors involved not considered here. The techniques we have applied so far have limited capability, and therefore other approaches, such as to analyse the evolved gases simultaneously with the DTA-TG measurements, or to gain direct information on what is happening in the complex itself are definitely needed.

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