Gas Chromatographic Studies of the Thermal Decompositions of Hexaammine-, Chloropentaammine-, and *trans*-Dichlorotetraamminecobalt(III) Chloride in the Solid State

Sukeo Onodera*

Department of Chemistry, Faculty of Science, Tokyo University of Science, Kagurasaka, Shinjuku-ku, Tokyo 162

(Received June 2, 1976)

This paper will describe gas chromatographic studies of the thermal decomposition of cobalt(III) ammine complexes in the solid state. The sample is pyrolyzed in a chamber in a helium atmosphere at a heating rate of 1 °C/min. The evolved products are directly led into a chromatographic separation column at periodic intervals of 10 °C. The preliminary gaseous product for these compound is ammonia. The gas evolution(GE) curves for each compound could be made as function of the temperature on the basis of the various gas chromatograms. These GE curves show two maximum peaks; the first is a sharp peak at about 250 °C, while the second is a broad peak in the 280—340 °C temperature range. The combination of these GE curves with the results of TG and DTA studies allows more complete interpretations of the thermal-decomposition reactions of the cobalt(III) ammine complexes.

Thermogravimetric analysis(TG) and differential thermal analysis (DTA) have been widely used by earlier investigators for studying the thermal-decomposition reactions of some transition metal complexes. These techniques gives information concerning the weight loss or the thermal changes in the compounds during the thermal reactions, but they do not give information on the species and the composition of the produced gases.

When the metal complexes are heated under various experimental conditions, volatile ligands or their gaseous decomposition product are usually liberated from the compounds. Thus, gas evolution analysis (GEA) is required for the above reactions in order to obtain exact information on the decomposition processes of the compounds. The combination of GEA with a TG or DTA apparatus allows more complete interpretations of their curves.

The simultaneous measurements of TG and DTA have been reported by Logers, Yamada and Zinn,[1] and, those of DTA and GEA, by Ayres and Bens,[2] Langer and Gohlke,[3] and Wendlandt *et al.*[4]

In earlier studies by Wendlandt *et al.*,[4] GEA curves were obtained by the use of a thermister thermal conductivity cell, and the composition of the pyrolyzed gases was determined by such conventional techniques as mass spectrometry, gas chromatography, and infrared absorption spectroscopy. Further works by Wendlandt *et al.*[3] have reported the method of leading the evolved product gases directly into a mass spectrometer for studying the thermal decomposition reactions of $[Cu(NH_3)_4]SO_4 \cdot H_2O$, some metal-cupferron chelates, and halogenopentaamminecobalt(III) complexes.

This paper will describe a method of leading the evolved product gases directly into a gas chromatograph, the so-called pyrolysis-gas chromatograph, for studying the thermal decomposition reactions of some chloroammine cobalt(III) complexes in the temperature range of 25—400 °C; on the basis of the GEA curves, the stoichiometries of the thermal-decomposition reactions of these compounds will be presented.

Experimental

Materials. The hexaammine-,[6] chloropentaammine-,[7] and *trans*-dichlorotetraamminecobalt(III) chloride[8] were prepared according to the methods given in the literature. They were identified by the measurements of the infrared absorption spectra. Sample ranging in perticle size between 100—200 mesh were used in these studies. These chloroammine cobalt(III) chlorides were selected because they are the ammine complexes most extensively studied by earlier workers.

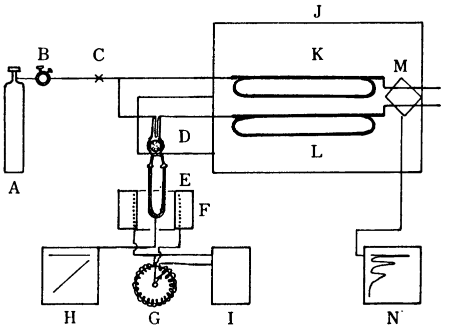

Fig. 1. Schematic diagram of pyrolysis-gas chromatographic apparatus.
A: Helium cylinder. B: Pressure regulator. C: Stop valve. D: Gas sampler. E: Pyrolysis chamber. F: Furnace. G: Slide transformer. H: Temperature recorder. I: AC voltage stabilizer. J: Gas chromatograph. K: Reference column. L: Separation column. M: Thermistor thermal conductivity cell. N: Gas chromatogram recorder.

GEA Apparatus. A schematic diagram of the GEA apparatus is given in Fig. 1, while the pyrolysis part of the apparatus is illustrated in Fig. 2.

The GEA apparatus consisted of a pyrolysis chamber(E), a furnace(F), a furnace temperature controller(G), a sample temperature recorder (H), and a Shimadzu model GC-2C gas chromatograph (J) with a thermal conductivity detector (M). Helium from a cylinder (A) and a pressure regulator (B) was passed through into reference column (K), into the pyrolysis chamber (E), and then into a separation column(L) packed with a 20% Silicon oil SF-96 on Fluoro Pack-80 (60—80 mesh) in a Teflon tube 5 m long by 0.3 cm in diameter.

The pyrolysis chamber consisted of a U-type Pyrex glass tube 15 cm long by 0.4 cm in diameter, which was terminated

---

* Present adress: Faculty of Pharmaceutical Science, Tokyo University of Science, Ichigaya-funagawara, Shinjuku-ku, Tokyo 162.

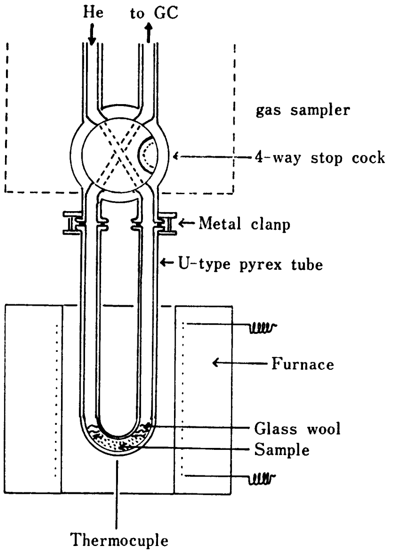

Fig. 2. Pyrolysis part of the apparatus.

on both ends by a 0.4-cm-inner-diameter "O"-ring joint (silicon gem). Two "O" -ring joints were attached to the joint of the gas sampler of the gas chromatograph by means of a metal clamp. The Pyrex tube was electrically heated by Nichrom wire enclosed in the furnace. The furnace was made by an asbestos tube, 15 cm long by 4.0 cm in diameter, which was wound by Nichrom heater wire and then insulated by additional asbestos paper so as to make a layer about 1.0 cm thick. The temperature of the wall of the Pyrex tube was measured by means of a chromel–alumel thermocouple. The pyrolysis temperature rise was controlled by means of the transformer(G).

The glass tubing from the pyrolysis chamber to the gas sampler of the gas chromatograph was maintained at about 60 °C by means of external heating jackets.

Procedure for Pyrolysis of Sample. Twenty mg of a sample was placed in the Pyrex tube and fixed with glass wool. The air in the system was swept out with a helium gas at a flow rate of 40 ml/min for about 30 min. During this time, gas-chromatographic conditions were allowed to be stabilized.

After the flow of helium had been directly passed through into the gas sampler by the changing of the stop cock, the heating of the furnace was begun. Usually, a furnace heating rate of 1 °C/min was employed, but this could be varied at will. The temperature-rising curve was recorded on the strip-chart recorder (H).

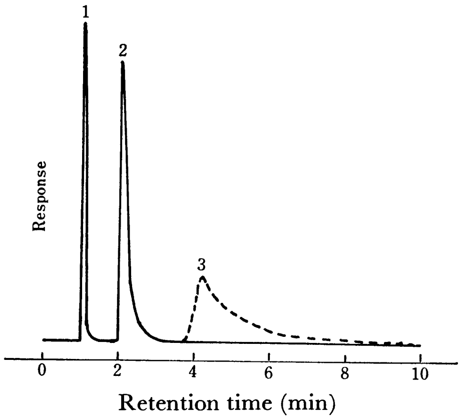

Fig. 3. Gas chromatogram of nitrogen (1), ammonia (2) and water (3) using 20% silicon SF-96 on fluoro Pack-80.

Procedure for the Analysis of the Gaseous Products. The gaseous products evolved during the above pyrolysis procedure were quickly swept into the chromatographic separation column at periodic intervals of 10 °C by changing the stop cock. Thus, the various gas-chromatographic patterns for the evolved gases could be obtained as a function of the temperature.

The peaks appearing on the gas chromatograms were identified by the use of the retention times of various pure substances which may be expected to be formed during the decomposition of the sample. From the peak areas of the various peaks, the amount of the decomposition product could be ascertained as a function of the temperature. The chromatographic patterns for various pure substances are shown in Fig. 3.

Results and Discussion

The GEA curves of the cobalt(III) ammine complexes in the temperature range of 25—400 °C in a helium atmosphere are given in Fig. 4, while the data on gaseous decomposition products are summarized in Table 1. These results were reproducible under the experimental conditions employed in the present work.

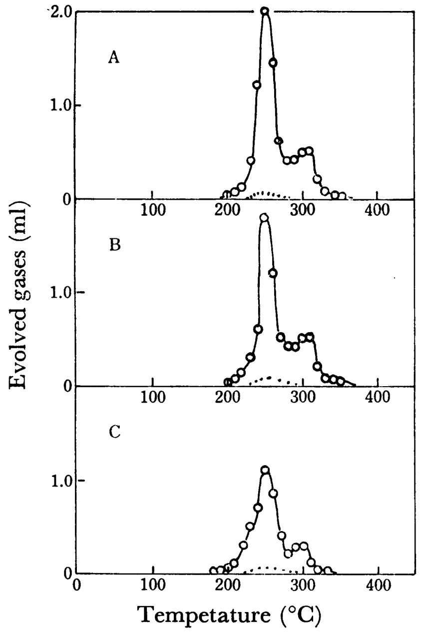

Fig. 4. Gas evolution curves for $[Co(NH_3)_6]Cl_3$ (A), $[CoCl(NH_3)_5]Cl_2$(B) and *trans*-$[CoCl_2(NH_3)_4]Cl$(C) in helium atmosphere.
N_2; ······, NH_3; –○–○–○–.

TABLE 1. DATA ON GASEOUS DECOMPOSITION PRODUCTS

Compound	Moles of NH_3/mol of compound	Moles of N_2/mol of compound
$[Co(NH_3)_6]Cl_3$	4.75	0.18
$[CoCl(NH_3)_5]Cl_2$	3.80	0.15
$[CoCl_2(NH_3)_4]Cl$	2.70	0.15

$[Co(NH_3)_6]Cl_3$. Clark, Quick, and Harkins[9] have reported that the evolution of ammonia from this compound *in vacuo* began at about 173 °C, while a sublimate of ammonium chloride was observed at 181 °C.

They also confirmed, on the basis of an analysis of a solid mixture and the gaseous products (for ammonia only), that the stoichiometry of the thermal dissociation of this compound given as;

$$6[Co(NH_3)_6]Cl_3 \longrightarrow 6CoCl_2 + 6NH_4Cl + N_2 + 28NH_3 \qquad (1)$$

The TG curves of this compound in a nitrogen atmosphere reported by Watt[10] and by Tanaka and Nanjo[11] indicated that the first mass-loss (evolution of ammonia) began at about 250 °C. On the other hand, the DTA curves of this compound in a helium or nitrogen atmosphere reported by Wendlandt[12] and Watt[10] show that the endothermic peak began at about 200 °C, resulting in a peak with a $\Delta T_{\min}$ of 280 °C, and that this was followed by a second broad endothermic peak in the 300—375 °C temperature range.

The GEA curve given in Fig. 4A shows that the evolution of ammonia from this compound began at about 200 °C, the maximum intensity for gas evolution being obtained at 250 °C, and that this was followed by a second broad peak in the 280—340 °C temperature range. These temperature ranges and the number of peaks observed in this curve are in agreement with those appearing on the DTA curves reported by Watt[10] and Wendlandt,[12] but the first and second peak maxima were somewhat lower than those appearing on the DTA curves.[10,12]

The stoichiometry of the thermal decomposition of this compound, based on the data given in Table 1, agrees with that previously proposed by Clark *et al.*,[9] Watt,[10] and Wendlandt,[12] as given in Eq. 1.

$[CoCl(NH_3)_5]Cl_2$. The TG curves of this compound have been reported by a number of investigators. Wendlandt[13] found that the compound began to loss mass at 180 °C. However, the TG curves reported by Kawakubo[14] and Watt[10] indicated that the mass-loss of this compound began at 200 °C.

The DTA curves for this compound have been reported by Lavanov *et al.*,[15] Kawakubo,[14] Watt[10] and Wendlandt and Smith.[16] The DTA curves in a nitrogen atmosphere reported by the above investigators contained two endothermic peaks; the first began at about 200 °C, with a $\Delta T_{\min}$ value of about 280 °C, while second began with a $\Delta T_{\min}$ value of about 320 °C.

Watt[10] confirmed, from his TG and DTA curves and an analysis of the gaseous decomposition products, that the over-all reaction leading to the formation of $CoCl_2$ is:

$$6[CoCl(NH_3)_5]Cl_2 \longrightarrow 6CoCl_2 + 6NH_4Cl + N_2 + 22NH_3 \qquad (2)$$

The GEA curve given in Fig. 4B shows that the evolution of ammonia from this compound began at about 200 °C, the corresponding maximum intensity for gas evolution being found at about 250 °C, and that this was followed by a second broad peak in the 280—320 °C temperature range. These temperature ranges and the number of peaks observed in this curve are in agreement with those appearing on the DTA curves reported by Watt[10] and Wendlandt and Smith.[16]

The stoichiometry of the thermal decompositions of this compound, based on the data given in Table 1, agrees with that previously proposed by Watt[10] and Wendlandt and Smith[16] as given in Eq. 2.

trans-$[CoCl_2(NH_3)_4]Cl$. Ocone *et al.*[17] have reported the TG curves for *cis*- and *trans*-types of this compound in a nitrogen atmosphere. The curve for the *trans*-type indicated that the mass-loss began at 181 °C, corresponding to the loss of three moles of ammonia in the over all reaction. Also, the curve for the *trans*-type of this compound was essentially in agreement with that obtained by Watt.[10]

The DTA curve for the *trans*-type of this compound in nitrogen reported by Watt[10] was very similar to that for $[CoCl(NH_3)_5]Cl_2$, exhibiting well-defined endothermal minima at 283 and 347 °C. Watt[10] also confirmed, from his TG and DTA curves, and based on an analysis of the gaseous decomposition products, that the stoichiometry of the thermal dissociation reaction of this compound given as:

$$6[CoCl_2(NH_3)_4]Cl \longrightarrow 6CoCl_2 + 6NH_4Cl + N_2 + 16NH_3 \qquad (3)$$

The GEA curve given in Fig. 4C shows that the thermal decomposition of this compound begins with the evolution of ammonia at about 180 °C, the maximum intensity of the gas evolution appearing at 250 °C, and that this followed by a second broad peak in the 280—340 °C temperature range. These temperature ranges and the number of the peaks observed in this curve are in agreement with those appearing on the DTA curves reported by earlier researchers.[10,11]

The stoichiometry of the thermal dissociation of this compound, based on the data given in Table 1, agrees with that previously proposed by Watt[10] given in Eq. 3.

From the GEA curves in Fig. 4 and the results obtained by earlier investigators,[10,11,18–20] it may be seen that the starting of the thermal decomposition reactions of chloroammine cobalt(III) chlorides in a helium atmosphere at a slow heating rate takes place by means of the following competition reactions:

$$\begin{tikzcd} & {[Co^{III}Cl(NH_3)_5]Cl_2 + NH_3} \\ {[Co^{III}(NH_3)_6]Cl_3} \arrow[ur] \arrow[dr] & \\ & \text{low ammine cobalt(II) complexes} \end{tikzcd}$$

$$\begin{tikzcd} & {[Co^{III}Cl_2(NH_3)_4]Cl + NH_3} \\ {[Co^{III}Cl(NH_3)_5]Cl_2} \arrow[ur] \arrow[dr] & \\ & \text{low ammine cobalt(II) complexes} \end{tikzcd}$$

$$\begin{tikzcd} & {[Co^{III}Cl_3(NH_3)_3] + NH_3} \\ {[Co^{III}Cl_2(NH_3)_4]Cl} \arrow[ur] \arrow[dr] & \\ & \text{low ammine cobalt(II) complexes} \end{tikzcd}$$

Although the peak maximum temperature is dependent upon the furnace heating rate, the sample size, the carrier gas flow rate, the furnace atmosphere, and so on, the use of simultaneous GEA-gas chromatographic analysis gives exact data concerning the thermal decomposition reactions of metal complexes.

The author wishes to thank Professor Masaakira Iguchi, Tokyo University of Science, for his valuable advice.

References

1) R. N. Rogers, S. K. Yamada, and J. Zinn, *Anal. Chem.*, **32**, 672 (1960).

2) W. M. Ayres and E. M. Bens, *Anal. Chem.*, **33**, 568 (1961).

3) H. G. Langer and R. S. Gohlke, *Anal. Chem.*, **35**, 1301 (1963).

4) W. W. Wendlandt, *Anal. Chim. Acta*, **27**, 309 (1962); W. W. Wendlandt, S. I. Ali, and C. H. Stembrige, *ibid.*, **30**, 84 (1964); W. W. Wendlandt and E. Sturm, *J. Inorg. Nucl. Chem.*, **25**, 535 (1963).

5) W. W. Wendlandt, S. I. Ali, and C. H. Stembrige, *Anal. Chim. Acta*, **31**, 501 (1964); W. W. Wendlandt and T. M Southern, *ibid.*, **32**, 405 (1965).

6) J. Bierrum and J. P. McReynolds, *Inorg. Synth.*, **2**, 216 (1946).

7) W. A. Hynes, L. K. Yanowsky, and M. Schiller, *J. Am. Chem. Soc.*, **60**, 3253 (1938).

8) S. M. Jorgensen, *Z. Anorg. Chem.*, **14**, 404 (1897).

9) G. L. Clark, A. J. Quick, and W. D. Harkins, *J. Am. Chem. Soc.*, **42**, 2483 (1920).

10) G. W. Watt, *Inorg. Chem.*, **3**, 325 (1964).

11) N. Tanaka and M. Nanjo, *Bull. Chem. Soc. Jpn.*, **37**, 1330 (1964).

12) W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, **25**, 545 (1963).

13) W. W. Wendlandt, *Texas J. Sci.*, **10**, 271 (1958).

14) S. Kawakubo, *Nippon Kagaku Zasshi*, **83**, 274 (1962).

15) N. I. Labanov, I. R. Rassonskaya, and A. V. Ablov, *Zh. Neorg. Khim.*, **3**, 1355 (1958).

16) W. W. Wendlandt and J. P. Smith, *J. Inorg. Nucl. Chem.*, **25**, 843 (1963).

17) L. R. Ocone, J. R. Soulen, and B. P. Block, *J. Inorg. Nucl. Chem.*, **15**, 76 (1960).

18) W. W. Wendlandt and J. P. Smith, *J. Inorg. Nucl. Chem.*, **25**, 1267 (1963).

19) E. L. Simmons and W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, **28**, 2183, 2437 (1966).

20) N. Tanaka and K. Nagase, *Bull. Chem. Soc. Jpn.*, **40**, 546 (1967).