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Gas-chromatographic Studies of the Thermal Decompositions of Carbonatopentaammine-, Carbonatotetraammine-, and Dicarbonatodiamminecobalt(III) Complexes in the Solid State

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Synopsis. This paper will describe gas-chromatographic studies of the thermal decompositions of $[CoOCO_2(NH_3)_5]X\cdot H_2O$ (I), $(CoCO_3(NH_3)_4]X\cdot nH_2O$ (II), and $K[Co(CO_3)_2(NH_3)_2(NH_3)_2]\cdot H_2O$ (III) (where, X=Cl, NO_3, SO_4, and n=0, 0.5, 3). The GEA curves for these compounds show that the complexes lose water between 80 and 160 °C, and that the decomposition of the anhydrous compounds begins with an evolution of ammonia at about 140 °C (for I) and 180 °C (for II and III).

The thermal decompositions of the cobalt(III) carbonatoammine complexes are usually studied by means of thermogravimetric analysis (TG)[1–3] and differential thermal analysis (DTA).[4,5] These techniques give information concerning the weight-loss and thermal changes in the compounds during the thermal reactions, but they do not give information on the species and the composition of the gases produced. Thus, gas-evolution analysis (GEA) is required for the above reactions in order to obtain more exact information on the decomposition processes of the compounds.

Although gas-chromatographic (GC) analysis may be expected to be useful to ascertain the composition of the gaseous decomposition products of the metal ammine complexes, few papers have been published on GC studies of thermal dissociation, even in simple metal complexes.[6–8] The present work illustrates the applicability of pyrolysis-gas chromatography in elucidating the mechanism of the decomposition of the cobalt(III) carbonatoammine complexes.

Experimental

The complexes, $[CoOCO_2(NH_3)_5]X\cdot H_2O$, $[CoCO_3(NH_3)_4]$-$X\cdot nH_2O$, and $K[Co(CO_3)_2(NH_3)_2]\cdot H_2O$ (where, X=Cl,NO_3, SO_4, and n=0, 0.5, 3), were prepared according to the methods given in the Literature.[1,9] They were identified by measurements of the infrared absorption spectra. Samples ranging in particle size between 100 and 200 mesh was used in the present work.

The GEA apparatus employed has been described previously.[8] The procedure used for the pyrolysis of the sample and the analysis of the gaseous products are essentially the same as those reported in our previous paper.[8] The GC patterns for various pure substances are shown in Fig. 1.

Results and Discussion

In a preliminary examination of the thermal decompositions of the cobalt(III) carbonatoammine complexes, the differential scanning calorimetric (DSC) curves for these complexes were measured using a Rigaku Thermoflex 8001 with a standard differential scanning calorimeter in a dynamic nitrogen atmosphere at a heating rate of 5 °C/min. The ΔT_{max} values observed

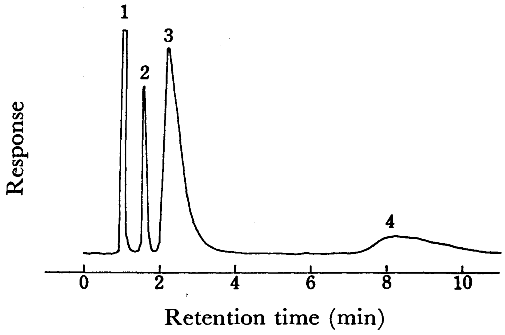

Fig. 1. Gas chromatogram of nitrogen (1), carbon dioxide (2), ammonia (3), and water (4) using 20% Silicon SF-96 on Fluoro Pack-80.

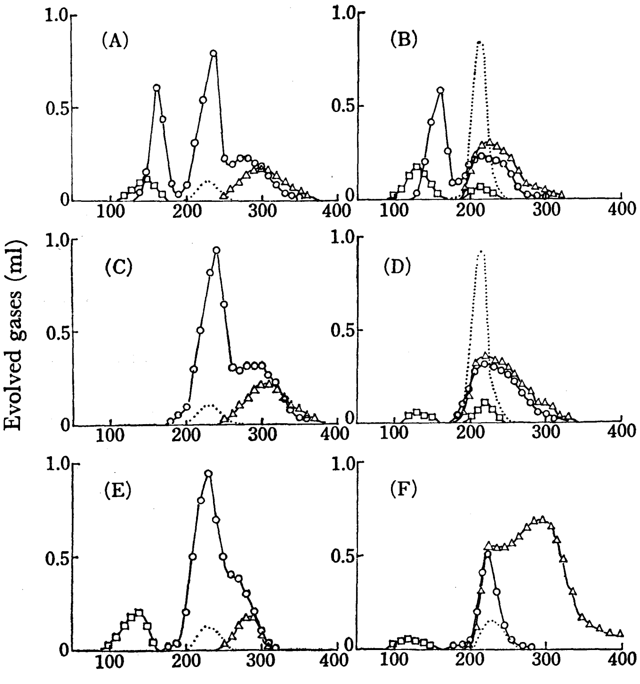

Fig. 2. GEA curves for $[CoOCO_2(NH_3)_5]Cl\cdot H_2O$ (A), $[CoOCO_2(NH_3)_5]NO_3\cdot H_2O$ (B), $[CoCO_3(NH_3)_4]Cl$ (C), $[CoCO_3(NH_3)_4]NO_3\cdot 0.5H_2O$ (D), $[CoCO_3(NH_3)_4]_2SO_4\cdot 3H_2O$ (E), and $K[Co(CO_3)_2(NH_3)_2]\cdot H_2O$ (F) in a helium atmosphere.
H_2O; -□-, NH_3; -○-, CO_2; -△-, N_2; ……

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on the DSC curves for these compounds were (endo= endothermic peak, exo=exothermic peak): $[\mathrm{CoOCO_2(NH_3)_5}]\mathrm{NO_3}\cdot\mathrm{H_2O}$, endo 160, 210, exo 220 °C; $[\mathrm{CoOCO_2(NH_3)_5}]\mathrm{Cl}\cdot\mathrm{H_2O}$, endo 165, 230, 280, and 350 °C; $[\mathrm{CoCO_3(NH_3)_4}]\mathrm{NO_3}\cdot 0.5\mathrm{H_2O}$, endo 140, 210, exo 220 °C; $[\mathrm{CoCO_3(NH_3)_4}]\mathrm{Cl}$, endo 230, 280, and 350 °C; $[\mathrm{CoCO_3(NH_3)_4}]_2\mathrm{SO_4}\cdot 3\mathrm{H_2O}$, endo 140 and 250 °C. The numbers of these endo- and exothermic peaks observed on the DSC curves are in agreement with those appearing on the DTA curves reported by earlier workers,[4,5] but the dissociation temperatures are somewhat different from those appearing on the DTA curves.

The GEA curves for the cobalt(III) carbonatoammine complexes in the 25—400 °C temperature range in a helium atmosphere are given in Fig. 2. The water in the gaseous products could not be exactly determined by means of the gas chromatography employed in the present work, because part of the water remained in the separation column even after a long time. Therefore, the amount of the evolved water given in the GEA curves is smaller than that estimated from the composition of these compounds.

The GEA curves for the cobalt(III) carbonatoammine complexes given in Fig. 2 show that the complexes lose water between 80 and 160 °C, and that the decomposition of the anhydrous compounds begins with an evolution of ammonia. The evolution of ammonia from the pentaammine complexes began at about 140 °C, while from the tetraammine and diammine complexes, it began at about 180 °C. Above 180 °C, both the pentaammine and tetrammine complexes decomposed in the same fashion. These temperature ranges and the number of peaks observed in the GEA curves are in agreement with those appearing on the DSC curves for the compounds obtained in the preliminary examination.

The thermally stable compounds as intermediate species, which may be formed by the evolution of 0.4—0.5 molar ammonia, were detectable in these GEA curves for the pentaammine complexes. However, no intermediate species were detectable in these GEA curves for the tetraammine and diammine complexes. In the GEA curves re-examined for the pentaammine complexes heated up to 170 °C, the first peak, which is due to the evolution of ammonia between 140 and 170 °C, disappeared. In addition, the IR spectra of the compounds heated up to 170 °C were characterized by the disappearance of the band at about 1490 $\mathrm{cm^{-1}}$ which was assigned to the $\mathrm{CO_3}^{2-}$ as an unidentate ligand, and by the appearance of new bands at about 840 and 770 $\mathrm{cm^{-1}}$ which were assigned to the $\mathrm{CO_3}^{2-}$ as bidentates.[10] As Yamada and Tada[5] concluded, this phenomenon indicates that most of the $\mathrm{CO_3}^{2-}$ as an unidentate ligand changed to a bidentate ligand when the pentaammine complexes were heated to 170 °C.

Based on the GEA curves for the cobalt(III) carbonatoammine complexes given in Fig. 2, it is confirmed that the endothermic peaks appearing on the DSC curves for the compounds obtained in the preliminary examination were caused by the evolution of water and ammonia, while, the exothermic peaks were caused by the oxidation of ammonia, with the nitrate anion as outer-ligand.

From the results described above and those obtained by earlier workers,[3,5] it may be seen that the processes of the thermal decomposition reactions of the cobalt(III) carbonatoammine complexes in a helium atmosphere take place by means of the following competition reactions:

$$[\mathrm{CoOCO_2(NH_3)_5}]\mathrm{X}\cdot\mathrm{H_2O} \xrightarrow{140\text{—}170\ ^\circ\mathrm{C}} [\mathrm{CoCO_3(NH_3)_{4.5}}]\mathrm{X} + \mathrm{H_2O} + 0.5\mathrm{NH_3}$$

$$\begin{tikzcd}
 & {[\mathrm{CoXCO_3(NH_3)_3}] + \mathrm{NH_3}} \\
{[\mathrm{CoCO_3(NH_3)_4}]\mathrm{X}} \arrow[ur, "180\text{—}200\ ^\circ\mathrm{C}"] \arrow[r] \arrow[dr, "200\text{—}300\ ^\circ\mathrm{C}"'] & \text{low ammine cobalt(II) complexes} \\
 & \mathrm{Co_2OX_2} + \mathrm{N_2} + \mathrm{NH_3} + \mathrm{CO_2}
\end{tikzcd}$$

Since the evolution of ammonia and nitrogen during the decomposition of these compounds in the 180—250 °C temperature range was observed in these GEA curves, it may be concluded that the Co(III) in the compounds was reduced to Co(II) by ammonia, and that $\mathrm{NH_4X}$ was an intermediate dissociation product.

Although the peak maximum temperature is dependent upon the heating rate of the furnace, the flow rate of the carrier gas, the sample size, the furnace atmosphere, and so on, the combination of the above GEA curves with the results of TG and DTA (and DSC) studies allows a more complete interpretation of the thermal decomposition reactions of the cobalt(III) carbonatoammine complexes.

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