Gas-Chromatographic Studies of the Thermal Decomposition of Nitropentaammine-, Dinitrotetraammine-, Trinitrotriammine-, Tetranitrodiammine-, and Pentanitroamminecobalt(III) Complexes in the Solid State

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The gas-chromatographic study of the thermal decompositions of the complexes, $[Co(NO_2)(NH_3)_5]Cl_2$ (I), *cis*- (II) and *trans*-$[Co(NO_2)_2(NH_3)_4]Cl$ (III), $[Co(NO_2)_3(NH_3)_3]$ (IV), $K[Co(NO_2)_4(NH_3)_2]$ (V), and $K_2[Co(NO_2)_5NH_3]$ (VI) are reported. The EGA curves for these complexes show that the compounds decompose in two or three stages. In the first stage (*ca.* 140—240 °C), all complexes evolve nitrogen with the evolution of ammonia and/or nitrogen monoxide. The second stage (*ca.* 210—300 °C) has been ascribed to the evolution of ammonia from the intermediate dissociation products of compound I, II, and III. The third stage (*ca.* 275—350 °C) has been ascribed to the evolution of nitrogen monoxide from the solid residue with the exception of IV.

The thermal decomposition of the cobalt(III) nitroammine complexes in the solid state are usually studied by thermogravimetry (TG)[1-3] and differential thermal analysis (DTA).[2-5] The various steps in the decomposition often overlap and a mixture of gases is evolved, the composition of the mixture and the residual product depending upon temperature. In TG and DTA, these aspects are often not revealed and consequently the complexity of the decomposition is overlooked. Thus evolved gas analysis (EGA) is required 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 in determining the composition of the gaseous decomposition products of the metal ammine complexes, few papers have been published on the GC study of the 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 cobalt(III) nitroammine complexes.

Experimental

Materials. The complexes, $[Co(NO_2)(NH_3)_5]Cl_2$, *cis*- and *trans*-$[Co(NO_2)_2(NH_3)_4]Cl$, $[Co(NO_2)_3(NH_3)_3]$, $K[Co(NO_2)_4(NH_3)_2]$, and $K_2[Co(NO_2)_5NH_3]$ were prepared according to the methods given in the literature[9] and identified by infrared analysis. Samples ranging in particle size from 100 to 200 mesh were used.

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

Results and Discussion

The EGA curves for the cobalt(III) nitroammine complexes in the 25 to 400 °C temperature range under helium are given in Figs. 2 and 3. The curves of water evolved have not been drawn since it was impossible to exactly determine the water in the gaseous products by means of the GC techniques employed in the present work. Although the chemical analysis of the gaseous products evolved from nitropentaammine- and trinitrotriamminecobalt(III) complexes *in vacuo* have been conducted by Clark *et al.*[10] and the EGA curves of some halogenopentaamminecobalt(III) complexes reported by Wendlandt and Smith[2] and Smith,[5] the EGA curves for *cis*- and *trans*-$[Co(NO_2)_2(NH_3)_4]Cl$, $[Co(NO_2)_3(NH_3)_3]$, $K[Co(NO_2)_4(NH_3)_2]$, and $K_2[Co(NO_2)_5NH_3]$ seem to be the first to appear. The EGA curves of the cobalt (III) nitroammine complexes were reproducible under the experimental conditions employed in the present work.

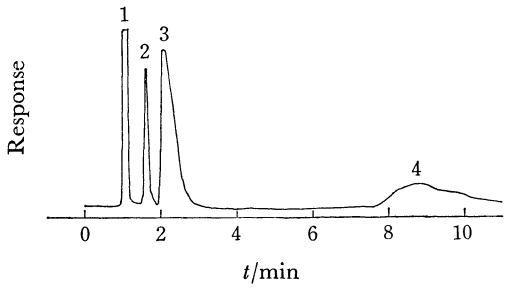

Fig. 1a. Gas chromatogram of nitrogen (1), nitrogen-(II) oxide (2), ammonia (3), and water (4) using 20% Silicon SF-96 on Fluoro Pack-80.

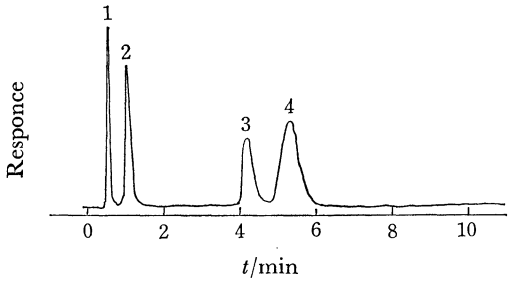

Fig. 1b. Gas chromatogram of nitrogen (1), nitrogen-(II) oxide (2), nitrous oxide (3), and nitrogen dioxide (4) using chromatographic silica gel.

The EGA curves for the cobalt(III) nitroammine complexes given in Figs. 2 and 3 show that the compounds decomposed in two or three stages. In the first stage (*ca.* 140—240 °C), all complexes evolved

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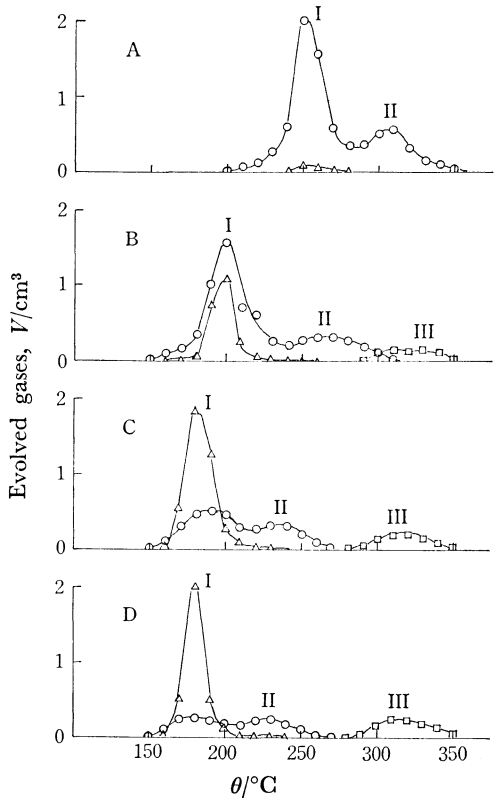

Fig. 2. EGA curves for $[Co(NH_3)_6]Cl_3$ (A), $[Co(NO_2)(NH_3)_5]Cl_2$ (B), *trans*-$[Co(NO_2)_2(NH_3)_4]Cl$ (C), and *cis*-$[Co(NO_2)_2(NH_3)_4]Cl$ (D) in a helium atmosphere.
NH_3; —○—, N_2; —△—, NO; —□—.

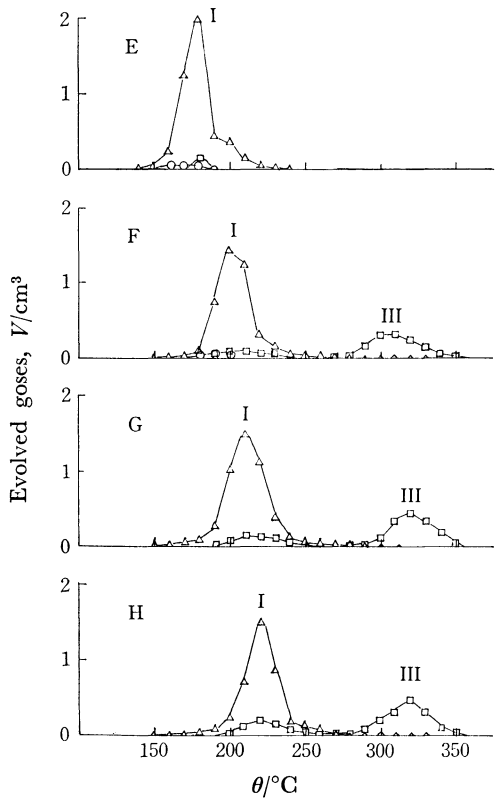

Fig. 3. EGA curves for $[Co(NO_2)_3(NH_3)_3]$ (E), $K[Co(NO_2)_4(NH_3)_2]$ (F), $K_2[Co(NO_2)_5NH_3]$ (G), and $K_3[Co(NO_2)_6]$ (H) in a helium atmosphere.
NH_3; —○—, N_2; —△—, NO; —□—.

nitrogen with the evolution of ammonia and/or nitrogen monoxide. The second stage (*ca.* 210—300 °C) has been ascribed to the evolution of ammonia from the intermediate dissociation products for $[Co(NO_2)(NH_3)_5]Cl_2$ and $[Co(NO_2)_2(NH_3)_4]Cl$. The third stage (*ca.* 275—350 °C) has been ascribed to the evolution of nitrogen monoxide from the solid residue with the exception of $[Co(NO_2)_3(NH_3)_3]$. The temperature ranges and the number of peaks are in agreement with those from the DTA curves reported by earlier workers,[3-5] except that the third peak can not be found in the case of DTA.

Decomposition of the Complexes (Stage I). Upon heating the cobalt(III) nitroammine complexes under helium, the yellow-brown compounds, especially $K[Co(NO_2)_4(NH_3)_2]$ and $K_2[Co(NO_2)_5NH_3]$, changed to orange-red in the 130 to 150 °C temperature range prior to the evolution of gas. Beattie and Sathell[11] and Doron[12] concluded that this phenomenon indicates that most of the nitro-form in the complexes is thermally converted to the nitrito-form.

Upon heating the complexes to temperatures higher than 150 °C, the yellow-brown compounds, $[Co(NO_2)(NH_3)_5]Cl_2$ and $[Co(NO_2)_2(NH_3)_4]Cl$, changed to greenish yellow ones, while the orange-red compounds, $[Co(NO_2)_3(NH_3)_3]$, $K[Co(NO_2)_4(NH_3)_2]$, and $K_2[Co(NO_2)_5NH_3]$, changed to black-brown ones, with the evolution of gas. In addition, thin layer chromatograms for the greenish yellow compounds, developed by a mixed solution, $HClO_4$–DMSO–CH_3OH (0.3 : 60 : 40), on Merck's silica gel G, were characterized by the appearance of new spots, which have been attributed to the tetraamminedianiono- and triammine-trianiono-complexes.[13]

The polarograms for the greenish yellow compounds, recorded in a 0.5 mol dm^{-3} K_2SO_4 containing 0.005% gelatin by use of a Yanagimoto KM-85-3 pen recording polarograph, showed that the limiting diffusion currents of the first wave, attributed to the reduction of cobalt(III) to cobalt(II) for the nitroammine-complexes,[14] decreased in comparison with the original compound. The polarograms for the black-brown compounds were characterized by a decreasing of the limiting diffusion currents of the first wave and a slight decreasing of the second wave, which has been attributed to the reduction of cobalt(II) to cobalt(0) for the nitroammine-complexes,[14] in comparison with those of both for the original complexes.

These results described together with earlier data,[2,16,17] suggest that the thermal decomposition of cobalt(III) nitroammine complexes under helium as:

$[Co(NO_2)(NH_3)_5]Cl_2$

$\xrightarrow{150\text{—}240\,^\circ C}$ $[CoCl(NO_2)(NH_3)_4]Cl + NH_3$

$[CoCl_2(NO_2)(NH_3)_3] + NH_3$

low ammine cobalt(II) complexes

$[Co(NO_2)_2(NH_3)_4]Cl$

$\xrightarrow{150\text{—}220\,^\circ C}$ $[CoCl(NO_2)_2(NH_3)_3] + NH_3$

low ammine cobalt(II) complexes

for other complexes,

$$[Co(NO_2)_3(NH_3)_3] \xrightarrow{140-210\,^\circ C} Co_2O_3 + N_2 + H_2O$$

$$K[Co(NO_2)_4(NH_3)_2] \xrightarrow{150-225\,^\circ C} \begin{cases} Co_3O_4 + KNO_3 + \text{gaseous products} \\ \text{low nitro cobalt(II) complexes} \end{cases}$$

$$K_2[Co(NO_2)_5NH_3] \xrightarrow{150-230\,^\circ C} \begin{cases} Co_3O_4 + KNO_3 + \text{gaseous products} \\ \text{low nitro cobalt(II) complexes} \end{cases}$$

Since large quantities of water and nitrogen were evolved in this stage, it has been concluded that ammonium nitrite was an intermediate dissociation product.

The decomposition temperatures at which the first maximum peaks observed on the EGA curves for the cobalt(III) nitroammine complexes in Figs. 2 and 3 are in the same order as the minimum temperatures where the color changes as observed by Matsui and Nakanishi.[15] This order for the cobalt(III) nitroammine complexes in Figs. 2 and 3 is related to the polarographic reduction potentials of cobalt(III) to cobalt(II) for the complex ions reported by Willis, Friend, and Mellor.[14] Plots of the above temperatures *versus* the potentials did not however give a strick linear relationship. Since the polarographic reduction potentials of the complex ions are considered to measure the relative electron affinities of the central metal ions, it has been concluded that the thermal stability of the cobalt(III) nitroammine complexes is dependent upon the electron affinity of the central cobalt(III) ion.

Subsequent Decomposition (Stage II). Upon heating $[Co(NO_2)(NH_3)_5]Cl_2$ and $[Co(NO_2)_2(NH_3)_4]Cl$ to temperatures higher than 230 °C, it was observed that the greenish yellow compounds, formed at the first stage, subsequently changed to grayish blue ones with the evolution of gas. In addition, the polarograms for the grayish blue compounds showed that the limiting diffusion currents of the first wave disappeared and those of the second wave decreased slightly in comparison with those of the both waves for the original complexes. These results appear to indicate that the greenish yellow compounds, probably $[CoCl(NO_2)(NH_3)_4]Cl$, $[CoCl_2(NO_2)(NH_3)_3]$, and $[CoCl(NO_2)_2(NH_3)_3]$, decomposed to form Co_2O_3, which has poor solubility in water.

The second EGA peaks of $[Co(NH_3)_6]Cl_3$, $[CoCl(NH_3)_5]Cl_2$, and *trans*-$[CoCl_2(NH_3)_4]Cl$ in a previous paper[8a] were obtained in the same temperature range (280—350 °C), although the numbers of coordinated-chloride ions are different, while, the second EGA peaks of $[Co(NO_2)(NH_3)_5]Cl_2$ and $[Co(NO_2)_2(NH_3)_4]Cl$ shifted to lower temperatures with the increase in the numbers of coordinated-nitrite ions. These results indicate that $[CoCl_3(NH_3)_3]$ is an intermediate dissociation product for the above three compounds, while $[CoCl_2(NO_2)(NH_3)_3]$, is for the nitropentaammine-complex, and $[CoCl(NO_2)_2(NH_3)_3]$, is for the dinitrotetraamine-complex.

Subsequent Decomposition (Stage III). When the complexes were heated to temperatures higher than 275 °C, it was observed that the grayish blue compounds, formed by heating $[Co(NO_2)(NH_3)_5]Cl_2$ and $[Co(NO_2)_2(NH_3)_4]Cl$ in stage II, changed to blue-black ones while the black-brown compounds, formed by heating $K[Co(NO_2)_4(NH_3)_2]$ and $K_2[Co(NO_2)_5NH_3]$ in stage I, changed to black ones with the evolution of nitrogen(II) oxide. In addition, the polarograms for the above solid residues were characterized by a decrease or the complete disappearance of the limiting diffusion currents of the second wave in comparison with that in the original compounds. These results suggest that the grayish blue and black-brown compounds, may be Co(ONO)Cl, $KCo(ONO)_3$, and KNO_3, decomposed with the evolution of nitrogen(II) oxide from the compounds to form cobalt oxides, which have poor solubility in water.

Although the exact nature of the solid residues, Co(ONO)Cl and $KCo(ONO)_3$, is not known, Devrainne and Belsot[3] demonstrated that the decomposition products up to 250 °C of $K[Co(NO_2)_4(NH_3)_2]$ consisted of Co_3O_4 and KNO_3.

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