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THE THERMAL DISSOCIATION OF THE $[Co(NH_3)_5Cl]Cl_2$ AND $[Co(NH_3)_5Br]Br_2$ COMPLEXES *IN VACUO*

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ABSTRACT

The thermal dissociation of the $[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_5Br]Br_2$ complexes was studied *in vacuo* by the TG–EGA–MSA technique. Dissociation of the $[Co(NH_3)_5Cl]Cl_2$ complex takes place through the intermediate compounds, *trans*-$[Co(NH_3)_4Cl_2]Cl$, $CoCl_2$ and $(NH_4)_2CoCl_4$. The $[Co(NH_3)_5Br]Br_2$ dissociates in a similar manner but probably does not involve *trans*-$[Co(NH_3)_4Br_2]Br$.

INTRODUCTION

The most widely investigated series of cobalt(III) ammine complexes, after the $[Co(NH_3)_6]X_3$ series, are the $[Co(NH_3)_5X]X_2$ type complexes[1]. The mass loss curves for the chloride complex (X = Cl) have been recorded by numerous investigators[2–4], while the DTA curves have also been reported[3–6]. In general, the thermal stability of the compounds is anion dependent. The chloride complex, $[Co(NH_3)_5Cl]Cl_2$, is the most stable, while the iodo-bromide, $[Co(NH_3)_5I]Br_2$, appears to be the least stable (*in vacuo*)[1,4]. The dissociation sequence for the $[Co(NH_3)_5X]X_2$ (X = Cl, Br) complexes, in helium, was found to be the same as that reported for the $[Co(NH_3)_6]X_3$ compounds[4].

We wish to report here new data on the thermal dissociation of the $[Co(NH_3)_5X]X_2$ (X = Cl, Br) complexes *in vacuo*, using the TG–EGA–MSA technique.

EXPERIMENTAL PART

Compounds

The $[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_5Br]Br_2$ complexes were the same as previously described[7].

Thermal analysis apparatus

The apparatus used and the experimental conditions employed were the same as previously described[8].

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RESULTS AND DISCUSSION

Thermogravimetry

The thermogravimetric curves for the $[Co(NH_3)_5X]X_2$ ($X = Cl$, Br) complexes *in vacuo*, as presented in Fig. 1, appear to have the same general shape as the curves for the $[Co(NH_3)_6]X_3$ ($X = Cl$, Br) complexes previously reported[8]. Analysis of these curves, together with mass spectrometric data, indicates that the anionopentamminecobalt(III) complexes dissociate in a manner analogous to the hexamminecobalt(III) complexes *in vacuo*.

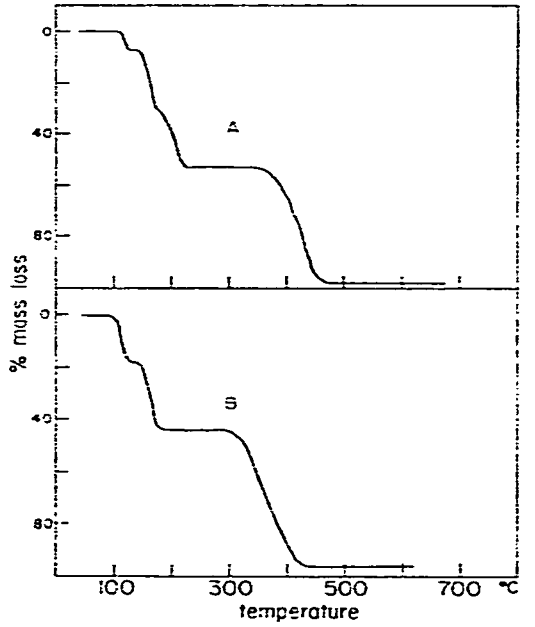

Fig. 1. TG curves of $[Co(NH_3)_5X]X_2$ complexes; A, $[Co(NH_3)_5Cl]Cl_2$; B, $[Co(NH_3)_5Br]Br_2$; pressure of 2×10^{-6} Torr.

The $[Co(NH_3)_5Cl]Cl_2$ complex began decomposing at 110°C to *trans*-$[Co(NH_3)_4Cl_2]Cl$ with the loss of one mole of ammonia per mole of complex. This intermediate compound produced the small plateau in the TG curve at about 8 percent mass loss and was visually observed to have a green color. Decomposition of the *trans*-$[Co(NH_3)_4Cl_2]Cl$ to a 1:1 molar mixture of $CoCl_2$:$(NH_4)_2CoCl_4$ produced an inflection point in the TG curve at about 30 percent mass loss. No horizontal mass level was observed since the $(NH_4)_2CoCl_4$ decomposed to $CoCl_2$ and NH_4Cl at a rate which was only slightly less than the rate of formation. The $CoCl_2$, which appeared as a stable intermediate compound at about 53 percent mass loss, began to sublime at about 350°C with the sublimation continuing to a black residue, probably cobalt metal, at 98 percent mass loss.

The dissociation reactions of $[Co(NH_3)_5Br]Br_2$ appear to be similar to those for $[Co(NH_3)_5Cl]Cl_2$ except for the first reaction step. The TG curve shows that a mass loss corresponding to approximately four moles of ammonia per mole of complex occurs as the initial dissociation process. This can be interpreted as the direct dissociation of the complex to a 1:1 molar mixture of $CoBr_2$:$(NH_4)_2CoBr_4$. However, the sample was visually observed to have a green color during the course of this process which might indicate the presence of *trans*-$[Co(NH_3)_4Br_2]Br$ or $CoBr_2$. The $(NH_4)_2CoBr_4$ decomposed to $CoBr_2$ which sublimed at about 300°C to leave a residue at 96 percent mass loss.

Mass spectroscopy

Gas evolution curves were plotted for both $[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_5Br]Br_2$ by measuring the peak intensities of the mass spectra as a function of temperature. The curves obtained for the $[Co(NH_3)_5Cl]Cl_2$ complex are presented in Fig. 2.

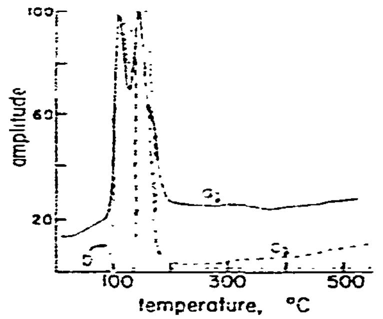

Fig. 2. Mass spectrometric measurement of: (a) total gas evolution; (b) ammonia gas evolution; (c) hydrogen chloride gas evolution.

The total gas evolution curve for the $[Co(NH_3)_5Cl]Cl_2$ complex consists of two sharp peaks between 100 and 200°C followed by a constant rate of gas evolution for the remainder of the curve. The first peak in this curve consists primarily of ammonia released by the dissociation of $[Co(NH_3)_5Cl]Cl_2$ and *trans*-$[Co(NH_3)_4Cl_2]Cl$. The first peak in the ammonia evolution curve will exactly superimpose on the first gas peak which demonstrates that ammonia evolution constitutes a significant portion of the gas evolved in this temperature interval. Also, mass spectra obtained during the interval of the first decomposition contain only ammonia, hydrogen and nitrogen peaks with no peaks above $m/e = 28$.

The second peak in the gas evolution curve consists of both ammonia and HCl which result from the dissociation of *trans*-$[Co(NH_3)_4Cl_2]Cl$ and $(NH_4)_2CoCl_4$. The HCl evolution curve, Fig. 2, shows that essentially all of the HCl is evolved in this reaction step. Since only traces of HCl are evolved above 200°C, sublimation rather than dissociation seems to be responsible for the loss of $CoCl_2$ from the sample container.

The gas evolution curves for $[Co(NH_3)_5Br]Br_2$, as presented in Fig. 3, appear to be similar to those of the corresponding chloride complex. This was expected since

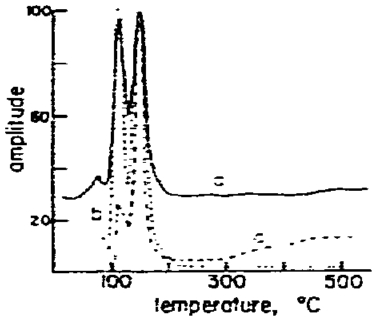

Fig. 3. Mass spectrometric measurement of: (a) total gas evolution; (b) ammonia gas evolution; (c) hydrogen bromide gas evolution.

the TG curves indicated that, with the possible exception of the first decomposition step, the mode of dissociation was the same for both complexes. However, the HBr evolution curve contains a small peak occurring simultaneously with the initiation of the decomposition process which is contradictory to the proposed dissociation reaction. The thermogravimetric data suggests that the first dissociation process involves the decomposition of $[Co(NH_3)_5Br]Br_2$ to a 1:1 molar mixture of $CoBr_2:(NH_4)_2CoBr_4$ through the loss of ammonia and nitrogen. Since this process does not involve the release of bromine, the appearance of the initial small HBr peak indicates either that decomposition occurs through a process which is different from that which has been suggested or that the sample contained traces of impurities which were responsible for the peak. The small size of the peak, when evaluated in comparison to the other data, which show strong similarities with data obtained for the $[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_6]X_3$ ($X = Cl$, Br) complexes, suggests that trace impurities are the most probable explanation. The HBr evolution curve also indicates that the $CoBr_2$ sublimes rather then dissociates at temperatures above 300°C.

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