Thermochimica Acta. 8 (1974) 315–323

THE THERMAL DISSOCIATION OF THE $[Co(NH_3)_6]Cl_3$ AND $[Co(NH_3)_6]Br_3$ COMPLEXES *IN VACUO*

L. W. COLLINS AND W. W. WENDLANDT*
Department of Chemistry, University of Houston, Houston, Texas 77004 (U. S. A.)
E. K. GIBSON
Code TN7, Geochemistry Branch, Johnson Space Center, Houston, Texas 77058 (U. S. A.)
(Received 2 July 1973)

ABSTRACT

The thermal dissociation of the complexes, $[Co(NH_3)_6]X_3$ ($X^- = Cl$, Br), was studied *in vacuo* using the techniques of thermogravimetry, evolved gas analysis and mass spectrometric analysis. It was found that the reaction stoichiometry was identical to that previously determined in air but that the type of intermediate compounds formed were different. The dissociation occurred by the reactions:

$$6[Co(NH_3)_6]X_3 \longrightarrow 6\mathit{trans}\text{-}[Co(NH_3)_4X_2]X + 12NH_3$$

$$6\mathit{trans}\text{-}[Co(NH_3)_4X_2]X \longrightarrow 3CoX_2 + 3(NH_4)_2CoX_4 + N_2 + 16NH_3$$

$$3(NH_4)_2CoX_4 \longrightarrow 3CoX_2 + 6NH_4X$$

$$3CoX_2 \longrightarrow \text{sublimation}$$

INTRODUCTION

The thermal dissociation of the $[Co(NH_3)_6]X_3$ ($X^- = Cl$, Br) type complexes has been of interest since the first investigations of Biltz[1] in 1913. Clark et al.[2] confirmed these basic observations in 1920 and reported the stoichiometry for the thermal dissociation of $[Co(NH_3)_6]Cl_3$ as:

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

Numerous mass-loss studies on these compounds were published in the late 1950's and early 1960's, many of them of a conflicting nature[3–8]. It was reported, for example, that the first dissociation step involved the formation of the pentammine-complexes, $[Co(NH_3)_5X]X_2$[4,6]; however, this was never confirmed by Simmons and Wendlandt[9,10].

The mechanism of the thermal dissociation reaction of $[Co(NH_3)_6]Cl_3$ was first elucidated by Tanaka and Nanjo[8]. They concluded that the reaction was initiated by electron transfer from either a ligand molecule or an outer sphere ion to the

---

*To whom correspondence should be addressed.

central metal cobalt(III) ion. However, it was not until the work of Simmons and Wendlandt[9] in 1966 that the nature of the intermediate compounds was described. Using magnetic susceptibility and reflectance spectroscopy, as well as thermogravimetry, the thermal dissociation reaction was found to take place in three steps:

(a) Electron transfer from a coordinated ammonia to the cobalt(III) ion.
(b) Formation of a $CoCl_2$–$(NH_4)_2CoCl_4$ mixture.
(c) Dissociation of $(NH_4)_2CoCl_4$ to NH_4Cl and $CoCl_2$.

These steps can be described by the equations:

$$6[Co(NH_3)_6]Cl_3 \xrightarrow{190\,^{\circ}C} 3CoCl_2 + 3(NH_4)_2CoCl_4 + N_2 + 28NH_3$$

$$3(NH_4)_2CoCl_4 \xrightarrow{280\,^{\circ}C} 6NH_4Cl + 3CoCl_2$$

and the overall reaction is the same as described by Clark et al.[2], or:

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

A similar series of reactions[10] was used to describe the thermal dissociation of $[Co(NH_3)_6]Br_3$.

Since most of the above investigations[11] were carried out in air or inert gases (N_2, Ar) at ambient atmospheric pressures, it was of interest to study the thermal dissociation reactions of the $[Co(NH_3)_6]X_3$ complexes *in vacuo* (2×10^{-6} Torr), using the simultaneous TG–EGA–MSA technique. It was found that the intermediate compounds obtained were different from those observed at atmospheric pressures in air.

EXPERIMENTAL

Compounds

The $[Co(NH_3)_6]Cl_3$ and $[Co(NH_3)_6]Br_3$ compounds were the same as previously described[12].

Thermal analysis apparatus

The thermobalance–mass spectrometer–computer system consisted of a Mettler vacuum recording thermobalance interfaced with a Finnigan Model 1015 S/L quadrupole mass spectrometer. A Model PDP 8/L computer controlled the mass spectral readout using a System Industries System/150 interface. The operation of the entire system has been described by Gibson[13]. A heating rate of 6 °C/min was used with a mass spectrometer scan rate of $1.2\ min^{-1}$; sample sizes ranged in mass from 2–3 mg.

RESULTS AND DISCUSSION

Thermogravimetry

Thermogravimetric curves for the $[Co(NH_3)_6]X_3$ ($X^- = Cl$, Br) complexes *in vacuo* are presented in Fig. 1.

The decomposition of the $[Co(NH_3)_6]Cl_3$ complex is initiated at about 150 °C *in vacuo* with the first stable intermediate mass plateau occurring at approximately 14 percent mass-loss. This corresponds to the loss of two moles of ammonia per mole of complex, with the formation of $[Co(NH_3)_4Cl_2]Cl$. Visual observation of the sample at 175 °C revealed that it had changed from the initial orange color to a dark green. This green colored compound indicates that the intermediate species has the *trans* isomeric configuration rather than the *cis* form, the latter of which is a light purple color.

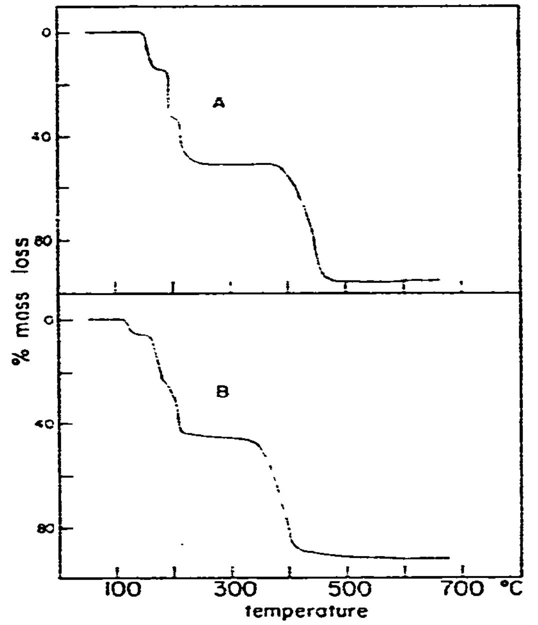

Fig. 1. Thermogravimetric curves for: (A) $[Co(NH_3)_6]Cl_3$; and (B) $[Co(NH_3)_6]Br_3$, at a pressure of 2×10^{-6} Torr.

The *trans*-$[Co(NH_3)_4Cl_2]Cl$ intermediate compound begins to lose mass at approximately 190 °C with the loss continuing at a rapid rate until at about 34 percent mass-loss where a curve inflection point is produced by a change in the decomposition rate. This inflection point occurs at the mass level predicted for the 1:1 molar ratio mixture of $CoCl_2$ to $(NH_4)_2CoCl_4$, which has been observed in the decomposition of $[Co(NH_3)_6]Cl_3$ in air[9]. The residue in the thermobalance was visually observed to have a purple tint at this point in the decomposition process which also indicates the presence of $(NH_4)_2CoCl_4$.

The formation of $(NH_4)_2CoCl_4$ is immediately followed by its dissociation to $CoCl_2$, with the evolution of NH_4Cl. The $CoCl_2$ appears in the TG curve as a horizontal mass level at about 50 percent mass-loss and is stable to slightly over 375 °C. Due to the high temperature and low pressures employed, sublimation of the $CoCl_2$ seems to account for the major portion of the mass-loss between 375° and 475 °C. There is probably some dissociation (or reduction) of the $CoCl_2$ to give a residue of cobalt metal at 96 percent mass-loss but this process is not as important as in the dissociation of the amine complexes, where it is the primary process[14]. This difference is probably due to a lack of suitable reducing agents remaining in the system from the dissociation of the $[Co(NH_3)_6]Cl_3$ while considerable organic matter, which might reduce the cobalt(II) ion, was shown to be trapped during the dissociation of $[Co(en)_3]Cl_3$.

The TG curve for the $[Co(NH_3)_6]Br_3$ complex *in vacuo*, as shown in Fig. 1, is similar to the curve for the $[Co(NH_3)_6]Cl_3$ complex. The first mass-loss begins at 110 °C and is the result of the loss of two moles of ammonia per mole of complex with the formation of *trans*-$[Co(NH_3)_4Br_2]Br$. This intermediate compound produces a horizontal mass level at slightly over 6 percent mass-loss with the *trans* configuration again being indicated by the green color.

The *trans*-$[Co(NH_3)_4Br_2]Br$ intermediate begins decomposing at 150 °C with a change in the decomposition rate appearing at about 24 percent mass loss. Analogous to the chloride complex, this inflection point in the TG curve is thought to be due to the formation and subsequent decomposition of the compound, $CoBr_2{:}(NH_4)_2CoBr_4$, since the inflection point occurs at the mass level calculated for this mixture.

Cobalt(II) bromide appears as a stable intermediate in the decomposition process at about 45 percent mass-loss and begins to sublime at about 340 °C with only traces of residue remaining at 500 °C. The small amount of residue which remains is probably cobalt metal produced by the dissociation of $CoBr_2$ although this was not confirmed by analysis.

MASS SPECTROSCOPY

[Co(NH₃)₆]Cl₃

The gaseous products evolved during the thermal decomposition of the $[Co(NH_3)_6]X_3$ ($X^- = Cl, Br$) complexes were analyzed mass spectrometrically to obtain product gas evolution curves. The gas evolution curves for the $[Co(NH_3)_6]Cl_3$ complex are presented in Fig. 2.

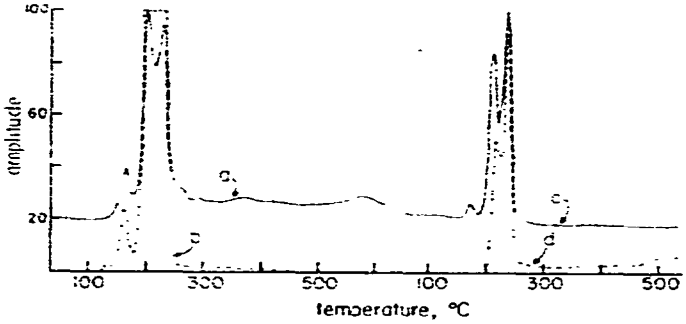

Fig. 2. Mass spectrometric measurement of: (a) gas evolution; (b) ammonia evolution; (c) HCl evolution; and (d) nitrogen evolution resulting from the thermal decomposition of $[Co(NH_3)_6]Cl_3$ *in vacuo*.

The total gas evolution curve consists of three narrow peaks followed by a broad peak. The individual products group at peaks around m/e 17 (Fig. 3). Since this spectrum falls into the temperature region corresponding to the decomposition of the $[Co(NH_3)_6]Cl_3$ complex to *trans*-$[Co(NH_3)_4Cl_2]Cl$, ammonia was expected to be the primary product. However, this spectrum also confirms that no chlorine products were evolved at this stage of the dissociation process. The only significant peaks outside of the ammonia group are at m/e 28, due to nitrogen, and at m/e 1 and 2, due to H^+ and H_2^+, respectively.

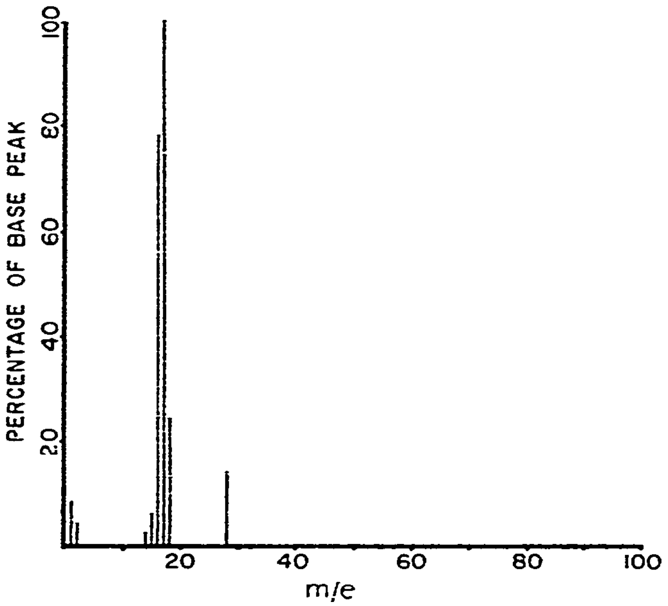

Fig. 3. Mass spectrum of gases evolved from $[Co(NH_3)_6]Cl_3$ at 160 °C *in vacuo*.

The mass spectrum of gases evolved at 195 °C is presented in Fig. 4. This spectrum was obtained as the *trans*-$[Co(NH_3)_4Cl_2]Cl$ decomposed to $CoCl_2$:$(NH_4)_2CoCl_4$ with some decomposition of the $(NH_4)_2CoCl_4$. It shows that the primary product evolved is still ammonia but a small peak at m/e 36 indicates that some HCl is also evolved at this temperature. The TG curve obtained simultaneously with the mass spectrum shows that the $(NH_4)_2CoCl_4$ was just beginning to decompose at this temperature so the HCl peak would be expected to be relatively small.

The mass spectrum obtained at 415 °C, as presented in Fig. 5, shows that the HCl peak is larger than in the previous spectrum but still comparatively small in relation to the other peaks. Ammonia is still the primary product with considerable nitrogen also being evolved. Since this spectrum falls into the region in which $CoCl_2$ is disappearing, the small HCl peak confirms that dissociation is a minor process compared to sublimation. The gaseous $CoCl_2$ does not appear in the mass spectra since the mass is beyond the range of the mass spectrometer. An additional peak appears in the spectrum at 415 °C at m/e 44 for which no explanation can be offered.

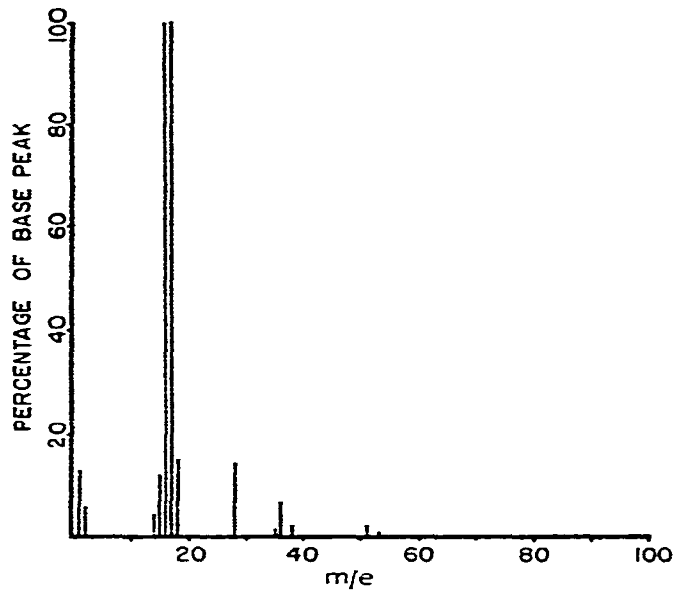

Fig. 4. Mass spectrum of gases evolved from $[Co(NH_3)_6]Cl_3$ at 195°C *in vacuo*.

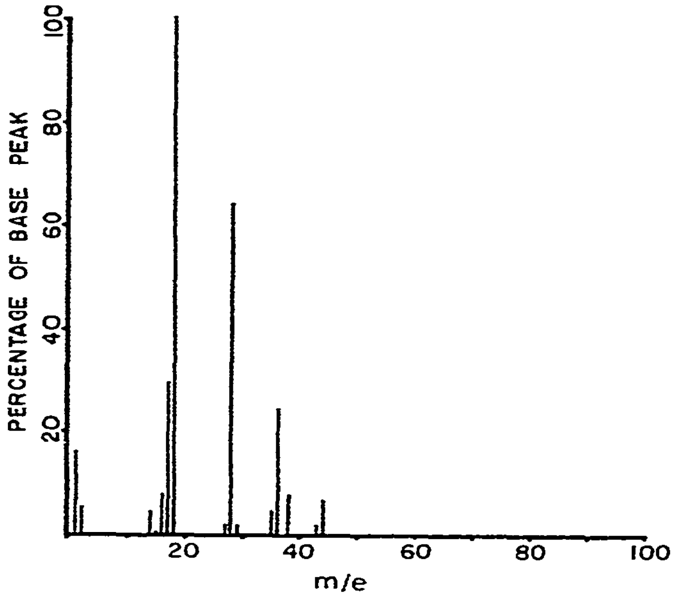

Fig. 5. Mass spectrum of gases evolved from $[Co(NH_3)_6]Cl_3$ at 415°C *in vacuo*.

$[Co(NH_3)_6]Br_3$

The gas evolution curves for $[Co(NH_3)_6]Br_3$ are presented in Fig. 6. These curves are similar to those presented in Fig. 2 for the chloride complex since the modes of decomposition are almost identical for both complexes. The ammonia gas evolution curve consists of two peaks, the first of which originates at 110°C and corresponds to the decomposition of $[Co(NH_3)_6]Br_3$ to *trans*-$[Co(NH_3)_4Br_2]Br$. The second peak is due to the decomposition of this intermediate to $CoBr_2$ and includes the formation and dissociation of $(NH_4)_2CoBr_4$.

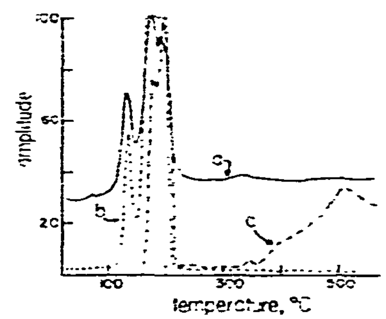

Fig. 6. Mass spectrometric measurement of: (a) gas evolution; (b) ammonia evolution; and (c) HBr evolution resulting from the thermal decomposition of $[Co(NH_3)_6]Br_3$ *in vacuo*.

The HBr gas evolution curve consists of a sharp peak originating at about 180°C which is followed by a broad peak between 300° and 500°C. The first peak is due to NH_4Br formed from the dissociation of the $(NH_4)_2CoBr_4$ intermediate. The second peak results from the dissociation of $CoBr_2$, with the evolution of HBr. Although the major portion of the $CoBr_2$ sublimes, the quantity which dissociates is greater for the bromide complex than for the chloride complex, as can be seen from the final mass levels in the TG curves and a comparison of the HX gas evolution curves.

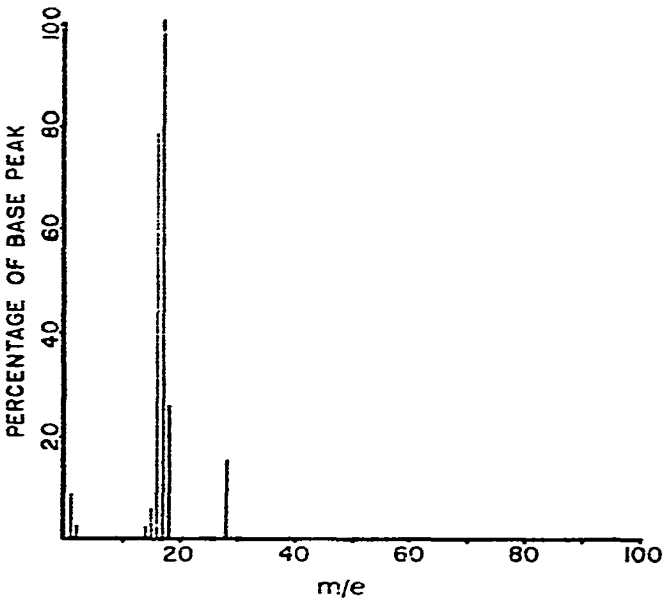

Fig. 7. Mass spectrum of gases evolved from $[Co(NH_3)_6]Br_3$ at 125°C *in vacuo*.

The mass spectrum of gases evolved from the $[Co(NH_3)_6]Br_3$ complex at 125 °C is presented in Fig. 7. It contains only ammonia, nitrogen, and hydrogen peaks. This is in agreement with the TG data indicating that $[Co(NH_3)_6]Br_3$ decomposes to *trans*-$[Co(NH_3)_4Br_2]Br$ with the release of ammonia. The mass spectrum at 200 °C, as shown in Fig. 8, contains the same peaks but the HBr peak is beginning to appear at *m/e* 80 as $(NH_4)_2CoBr_4$ dissociates to $CoBr_2$ and NH_4Br.

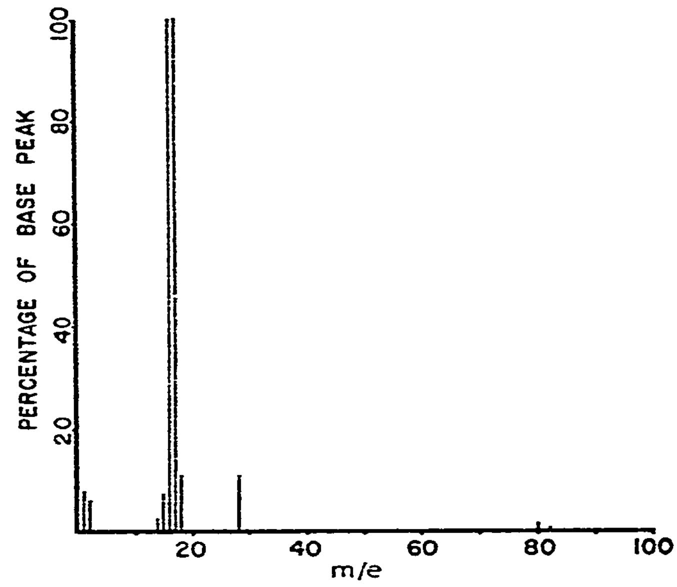

Fig. 8. Mass spectrum of gases evolved from $[Co(NH_3)_6]Br_3$ at 200°C *in vacuo*.

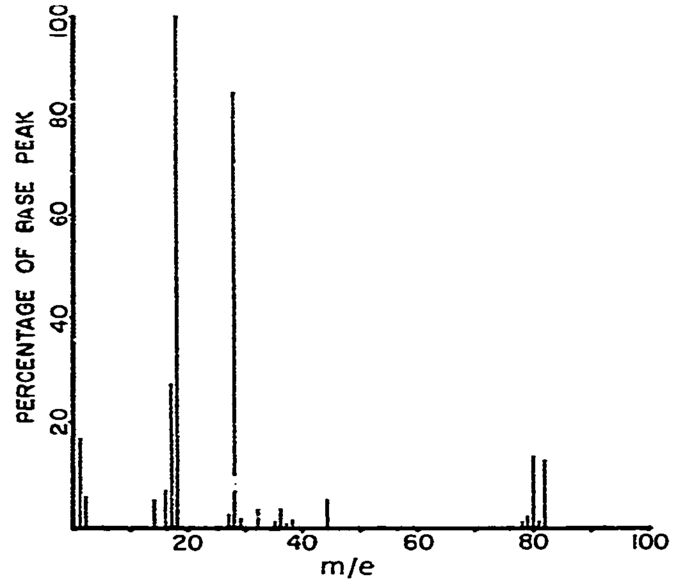

Fig. 9. Mass spectrum of gases evolved from $[Co(NH_3)_6]Br_3$ at 500°C *in vacuo*.

The mass spectrum of gases evolved at 500°C, as given in Fig. 9, contains several new peaks. The small peaks at *m/e* 32 and 36 are thought to be due to traces of oxygen and chloride contained in the sample, which are present in concentrations too small to be detected. The peaks at *m/e* 80 and 82 show that there is probably some dissociation of $CoBr_2$ to cobalt metal and HBr. Again, as in the mass spectra of the chloride complex, there is an unexplained peak at *m/e* 44.

CONCLUSIONS

Although the reaction stoichiometry of the dissociation of $[Co(NH_3)_6]X_3$ ($X^- = Cl$, Br) complexes appears to be the same *in vacuo* as in air, the mode of decomposition seems to be somewhat different. The TG–EGA–MSA data which has been presented indicates that dissociation *in vacuo* is accomplished according to the following reactions:

$$6[Co(NH_3)_6]X_3 \longrightarrow 6\textit{trans}\text{-}[Co(NH_3)_4X_2]X + 12NH_3$$

$$6\textit{trans}\text{-}[Co(NH_3)_4X_2]X \longrightarrow 3CoX_2 + 3(NH_4)_2CoX_4 + N_2 + 16NH_3$$

$$3(NH_4)_2CoX_4 \longrightarrow 3CoX_2 + 6NH_4X$$

$$3CoX_2 \longrightarrow \text{sublimation}$$

ACKNOWLEDGEMENTS

The partial financial support of this work by the Robert A. Welch Foundation of Houston, Texas, is gratefully acknowledged. It is also a pleasure to acknowledge Mr. Gary W. Moore for his assistance in taking the experimental measurements.

REFERENCES

1 W. Biltz, *Z. Anorg. Chem.*, 83 (1913) 177.
2 G. L. Clark, A. J. Quick and W. D. Harkins, *J. Amer. Chem. Soc.*, 42 (1920) 2483.
3 W. W. Wendlandt, *Tex. J. Sci.*, 10 (1958) 271.
4 L. Kekedy, A. Szurkos, P. Kröbl and E. Kekedy, *Stud. Cercet. Chim.*, 9 (1958) 79.
5 L. R. Ocone, J. R. Soulen and B. P. Block, *J. Inorg. Nucl. Chem.*, 15 (1960) 76.
6 G. W. Watt, *Inorg. Chem.*, 3 (1964) 325.
7 M. Viltange, *Microchim. Ichnoanal. Acta*, (1964) 1330.
8 N. Tanaka and M. Nanjo, *Bull. Chem. Soc. Jap.*, 37 (1964) 1330.
9 E. L. Simmons and W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, 28 (1966) 2187.
10 E. L. Simmons and W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, 28 (1966) 2437.
11 W. W. Wendlandt and J. P. Smith, *Thermal Properties of Transition Metal Ammine Complexes*, Elsevier, Amsterdam, 1967, Chapt. 3.
12 Z. Halmos and W. W. Wendlandt, *Thermochim. Acta*, 5 (1972) 165.
13 E. K. Gibson, *Thermochim. Acta*, 5 (1973) 243.
14 L. W. Collins, W. W. Wendlandt and E. K. Gibson, *Thermochim. Acta*, 8 (1974) 205.