

THE THERMAL DECOMPOSITION REACTIONS OF [Co(en)₃]Cl₃ AND [Co(en)₃]Br₃ COMPLEXES*

L. W. COLLINS AND W. W. WENDLANDT

Department of Chemistry, University of Houston, Houston, Texas 77004 (U.S.A.)

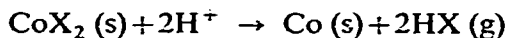
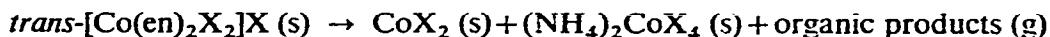
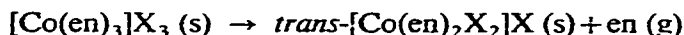
E. K. GIBSON

TN7 Geochemistry Branch, Johnson Space Center, Houston, Texas 77058 (U.S.A.)

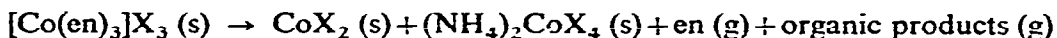
(Received 13 June 1973)

ABSTRACT

The thermal decomposition reactions were determined for [Co(en)₃]Cl₃ and [Co(en)₃]Br₃ in a dynamic nitrogen gas atmosphere and *in vacuo*. Data were obtained using thermogravimetry, differential thermal analysis, thermomagnetic analysis, reflectance spectroscopy, infrared spectroscopy, mass spectroscopy, and pyrolytic techniques. The dissociation reaction in nitrogen was found to be:



In vacuo, the first step is:



The remainder of the reaction is the same as that in nitrogen.

INTRODUCTION

The thermal dissociation of [Co(en)₃]X₃ type complexes has been studied in a preliminary manner by Smith¹. Based on data obtained by thermogravimetry (TG), differential thermal analysis (DTA), thermomagnetic analysis and mass spectroscopy, Smith theorized that there was complete disruption of the molecule as it was thermally decomposed. No mechanisms could be proposed, however, which would satisfactorily explain all of the data which were collected.

Wendlandt et al.^{2,3} reported the thermogravimetry curves for [Co(en)₃]Cl₃ · nH₂O (n = 2, 3) which were similar to those obtained by Smith except for the evolution of hydrated water. All of the complexes began to decompose between 200 and 300 °C

*Presented at the 4th North American Thermal Analysis Society Meeting, Worcester, Mass., June 13-15, 1973.

with the mass loss continuing with no horizontal mass levels, corresponding to stable intermediates, until the oxide was obtained at 600°C.

Horton and Wendlandt⁴ studied the thermal decomposition of some cobalt(III) amine polybromides by DTA and TG. The complex, $[\text{Co}(\text{en})_3]\text{Br}_3 \cdot \text{Br}_2$, was observed to lose a molecule of bromine in two steps. Mass levels which closely corresponded to $[\text{Co}(\text{en})_2\text{Br}_2]\text{Br}$ and CoBr_2 were obtained at elevated temperatures.

The kinetics of the thermal decomposition of $[\text{Co}(\text{en})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ in the solid state were studied by following the change in cobalt(III) ion content with time⁵. The dissociation was found to be a first order reaction. The activation energy and frequency factor were calculated from the first order rate constant using the Arrhenius equation.

Thermogravimetric curves for some bis(ethylenediamine)cobalt(III) complexes have been reported by Wendlandt⁶. Both the *cis*- and *trans*-isomers are reported to begin losing mass at 185°C with the oxide levels being obtained at about 640°C. The DTA curves for these complexes were reported by Lobanov et al.⁷.

Fogel and Christian⁸ studied the thermal dissociation of *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl} \cdot \text{HCl} \cdot 6\text{H}_2\text{O}$. These workers determined the equilibrium dissociation pressures at 9.7, 21.6, and 25.4°C. From these data, the thermodynamic constants were calculated for the loss of HCl and water.

Heating curves for 1,2- and 1,6- $[\text{Co}(\text{en})_2\text{X}_2]\text{Br} \cdot \text{Br}_2$ ($\text{X} = \text{Cl}^-$, NO_3^- , Br^- , or $\text{C}_2\text{O}_4^{2-}$) complexes have been published by Lobanov and Konovalenko⁹. It was established that the strength of the $\text{Br}-\text{Br}_2$ bond depends on the stability of the $[\text{Co}(\text{en})_2\text{X}_2]^+$ cation. The heating curves for the polybromides, unlike those for the bromides, show, in addition to the endothermic effect due to the removal of molecular bromine, an exothermic effect due to the decomposition of the cationic complex as a result of the oxidizing action of bromine.

Although most of the thermal parameters of the $[\text{Co}(\text{en})_3]\text{X}_3$ type complexes have been measured, no mechanisms for the thermal dissociation processes have been reported which will encompass all of the reported data. Therefore, in this study, new data were collected and mechanisms were proposed which unify and explain the thermal data which have been obtained through the various techniques.

EXPERIMENTAL PART

Compounds

The $[\text{Co}(\text{en})_3]\text{Cl}_3$ was prepared according to the method of Work¹⁰. The $[\text{Co}(\text{en})_3]\text{Br}_3$ was prepared by adding HBr to a solution of $[\text{Co}(\text{en})_3]\text{Cl}_3$, filtering, washing with ethanol, and drying at 110°C. The *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ and *trans*- $[\text{Co}(\text{en})_2\text{Br}_2]\text{Br}$ complexes were prepared by methods which have been previously described¹¹. The complexes were analyzed for halide content by gravimetric analysis with silver nitrate. The cobalt content was determined gravimetrically by ignition to the oxide, Co_3O_4 .

Thermobalance

The thermobalance used consisted of a Cahn Model RG Electrobalance converted to a thermobalance by the addition of a small furnace and sample holder. The electrical outputs from the balance and a Chromel–Alumel thermocouple, located in the furnace chamber, were recorded on a Sargent–Welch two-pen strip chart recorder as a function of time. The mass curve was recorded as percent mass change using the variable span control, as described by Wendlandt¹². Sample masses of 5–10 mg were used with heating rates of 5 and 10°C min⁻¹. All thermal decomposition reactions were carried out in a dynamic nitrogen gas atmosphere at a flow rate of 50 ml min⁻¹.

DTA apparatus

DTA studies were performed on the complexes using a Deltatherm instrument. These DTA runs were made in a dynamic nitrogen atmosphere with a flow rate of about 30 ml min⁻¹. Sample sizes were from 5 to 10 mg with heating rates of 5–10°C min⁻¹. Runs were made with the reference pan empty and with an alumina reference. The maximum temperature for any of the runs was 500°C.

Thermomagnetic analysis

Simultaneous magnetic-mass change curves were obtained for the complexes by the method previously described¹³. However, the measurements were qualitative and indicated only whether the complex was diamagnetic or paramagnetic. A heating rate of 10°C min⁻¹ was used with a nitrogen flow rate of 100 ml min⁻¹.

Thermal analyzer/mass spectrometer/computer system

This system, which has previously been described¹⁴, consisted of a Mettler vacuum recording thermoanalyzer interfaced with a Finnigan Model 1015 S/L quadrupole mass spectrometer. The computer system was a specially modified System/150 manufactured by System Industries. A heating rate of 6°C min⁻¹ was used with a mass spectrometer scan rate of 1.2 min⁻¹.

Infrared spectroscopy

All infrared spectra were recorded on a Perkin–Elmer Model 457 Infrared Spectrophotometer. The complexes were pressed into KBr pellets and the infrared spectrum obtained. The pellets were then heated to temperatures of 200, 250, 300, 350, 400, 450 and 500°C for periods of 15 minutes with the infrared spectrum being recorded after each heating. The pellets were repressed after each heating since there was some expansion due to evolution of decomposition products.

Reflectance spectroscopy

The reflectance spectra of the samples were determined by use of a Beckman Model DK-2A Spectroreflectometer. The reference material was magnesium carbonate. The general procedure for reflectance measurements was the same as previously described¹⁵. Spectra were obtained for the complexes at room temperature and at various stages in the decomposition process.

RESULTS AND DISCUSSION

Thermogravimetry

Thermogravimetric curves for the $[\text{Co}(\text{en})_3]\text{X}_3$ and *trans*- $[\text{Co}(\text{en})_2\text{X}_2]\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) complexes are shown in Fig. 1.

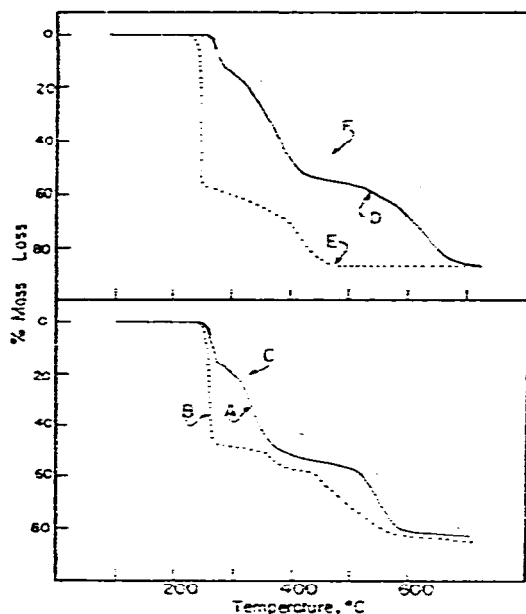


Fig. 1. Thermogravimetric curves for: (A) $[\text{Co}(\text{en})_3]\text{Cl}_3$ in a nitrogen atmosphere; (B) $[\text{Co}(\text{en})_3]\text{Cl}_3$ *in vacuo*; (C) *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ in a nitrogen atmosphere; (D) $[\text{Co}(\text{en})_3]\text{Br}_3$ in nitrogen; (E) $[\text{Co}(\text{en})_3]\text{Br}_3$ *in vacuo*; (F) *trans*- $[\text{Co}(\text{en})_2\text{Br}_2]\text{Br}$ in nitrogen.

The $[\text{Co}(\text{en})_3]\text{Cl}_3$ complex begins to decompose at 245°C in nitrogen and *in vacuo*, while the $[\text{Co}(\text{en})_3]\text{Br}_3$ begins to decompose at 260°C in nitrogen and 250°C *in vacuo*. The first inflection in the TG curves in nitrogen occurs between 15 and 20% mass loss for the chloride complex and between 12 and 15% mass loss for the bromide complex. These inflections correspond to the transition, $[\text{Co}(\text{en})_3]\text{X}_3 \rightarrow \textit{trans}$ - $[\text{Co}(\text{en})_2\text{X}_2]\text{X}$. However, this reaction does not give a plateau in the curve since the *trans*- $[\text{Co}(\text{en})_2\text{X}_2]\text{X}$ intermediate is thermally unstable at the temperature at which it is formed, as is shown in Fig. 1. It should be noted that the shape of the TG curves for the *trans*- $[\text{Co}(\text{en})_2\text{X}_2]\text{X}$ complexes is identical to the portion of the $[\text{Co}(\text{en})_3]\text{X}_3$ TG curves beyond the first inflection point.

The second inflection in the TG curves for the $[\text{Co}(\text{en})_3]\text{X}_3$ complexes in nitrogen occurs at 48% mass loss for the chloride and 35% mass loss for the bromide. This corresponds to the decomposition of the *trans*- $[\text{Co}(\text{en})_2\text{X}_2]\text{X}$ intermediate to an intermediate having a composition which corresponds to a 1/1 molar ratio of CoX_2 to NH_4X . Evidence presented later indicates that the actual composition of this inter-

mediate is $\text{CoX}_2\text{-(NH}_4\text{)}_2\text{CoX}_4$. The TG curves for the *trans*- $[\text{Co(en)}_2\text{X}_2]\text{X}$ complexes have inflection points at 36 and 43% mass loss for the chloride and bromide complexes, respectively, which correspond to the formation of the $\text{CoX}_2\text{-(NH}_4\text{)}_2\text{CoX}_4$ intermediates.

The $\text{CoX}_2\text{-(NH}_4\text{)}_2\text{CoX}_4$ intermediates decompose slowly to give CoX_2 , with the evolution of NH_4X . This reaction gives slight breaks in the TG curves of the $[\text{Co(en)}_3]\text{X}_3$ and *trans*- $[\text{Co(en)}_2\text{X}_2]\text{X}$ complexes. Also, if any of these complexes are heated isothermally at 270°C for one day, a stable mass level is attained which corresponds to the CoX_2 compound for that complex. All of the complexes decompose to the mass level predicted for cobalt metal at temperatures in excess of 600°C.

The decomposition of the $[\text{Co(en)}_3]\text{X}_3$ complexes *in vacuo* is similar to the process in a nitrogen atmosphere except for the first step. *In vacuo*, the complexes decompose directly to the $\text{CoX}_2\text{-(NH}_4\text{)}_2\text{CoX}_4$ intermediate which then undergoes decomposition as in nitrogen. There is no evidence to suggest the formation of the *trans*- $[\text{Co(en)}_2\text{X}_2]\text{X}$ intermediate in the vacuum decomposition of the $[\text{Co(en)}_3]\text{X}_3$ complexes.

Thermomagnetic analysis

The reduction of the cobalt(III) ion to the free cobalt metal in the $[\text{Co(en)}_3]\text{X}_3$ complexes was studied qualitatively by use of simultaneous magnetic-mass change curves. The initial complexes were diamagnetic, as was expected from the electronic structure. As the complexes began to decompose, the magnitude of the diamagnetic moment decreased. In the region from 5 to 15% mass loss for the chloride and 2 to 10% mass loss for the bromide compound the magnitude of the magnetic moment was negligible. During these intervals, the primary reaction which was occurring was the transition of $[\text{Co(en)}_3]\text{X}_3$ to *trans*- $[\text{Co(en)}_2\text{X}_2]\text{X}$, which has a magnetic moment very close to zero. As the decomposition continued, the compounds became paramagnetic as the $\text{CoX}_2\text{-(NH}_4\text{)}_2\text{CoX}_4$ intermediate was formed from the decomposition of the *trans*- $[\text{Co(en)}_2\text{X}_2]\text{X}$ intermediate. At temperatures above 400°C, the remaining residue became increasingly ferromagnetic due to the presence of cobalt metal.

DTA studies

The DTA curves for the $[\text{Co(en)}_3]\text{X}_3$ complexes are presented in Fig. 2.

The DTA curves for the chloride and bromide complexes are almost identical. The decomposition of the tris(ethylene-diamine)cobalt(III) complexes to the $\text{CoX}_2\text{-(NH}_4\text{)}_2\text{CoX}_4$ intermediate gives one large endothermic peak for both the chloride and bromide complexes. The *trans*- $[\text{Co(en)}_2\text{X}_2]\text{X}$ intermediates could not be resolved as separate peaks in the DTA curve. A second, smaller, endothermic peak occurs in both curves immediately following the initial peak. This small peak corresponds to the decomposition of the $\text{CoX}_2\text{-(NH}_4\text{)}_2\text{CoX}_4$ intermediate with the evolution of NH_4X . Further decomposition steps could not be adequately resolved.

The decomposition of the complexes was accompanied by a considerable amount of sample expansion. This created a significant change in the thermal contact

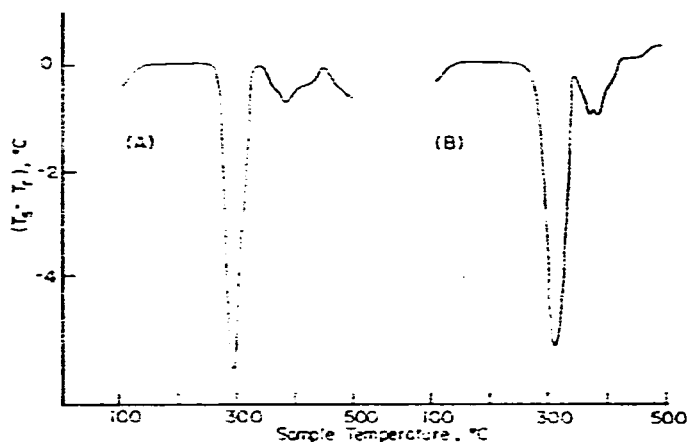


Fig. 2. Differential thermal analysis curves for: (A) $[\text{Co}(\text{en})_3]\text{Cl}_3$; (B) $[\text{Co}(\text{en})_3]\text{Br}_3$ in a dynamic nitrogen atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$.

between the sample and the pan so that no quantitative information could be obtained concerning the energy relationships between the mechanism steps. Diluents could not be used since this has been shown to produce a significant change in the DTA curves of these complexes¹⁶.

Pyrolysis studies

The $[\text{Co}(\text{en})_3]\text{X}_3$ complexes were pyrolyzed at temperatures between 300 and 350°C . Helium gas, which flowed over the sample, carried the evolved gases into an ice-sodium chloride cold trap and then into a standardized acid solution. Analysis of the effluents caught in the cold trap showed that, within experimental error, one mole of ammonium halide was evolved per mole of complex. This was the expected result from the decomposition of $\text{CoX}_2-(\text{NH}_4)_2\text{CoX}_4$ intermediate. Titration with standard acid showed that 1.25 moles of ammonia was evolved per mole of complex as a result of the fragmentation of the ethylenediamine. Halide analysis of the residue indicated that it was cobalt(II)halide.

Reflectance spectroscopy

Reflectance spectra for the $[\text{Co}(\text{en})_3]\text{X}_3$ and *trans*- $[\text{Co}(\text{en})_2\text{X}_2]\text{X}$ complexes at various stages of the decomposition process are shown in Fig. 3.

Both of the $[\text{Co}(\text{en})_3]\text{X}_3$ complexes show a maximum absorption at 460 nm with reflectance bands at 370 nm and a broad band between about 500 and 750 nm. If the complexes are partially decomposed for a few minutes, an absorption band begins to appear which is centered at 630 nm for the chloride and at 655 nm for the bromide complex. These bands are due to the formation of the *trans*- $[\text{Co}(\text{en})_2\text{X}_2]\text{X}$ intermediates as is shown by the spectra for these complexes in Fig. 3. The absorption bands are shifted to slightly longer wavelengths in the spectra of the partially decomposed $[\text{Co}(\text{en})_3]\text{X}_3$ complexes due to the presence of compounds other than the *trans*-

$[\text{Co}(\text{en})_2\text{X}_2]\text{X}$ intermediate. A close match with the spectra of the partially decomposed $[\text{Co}(\text{en})_3]\text{X}_3$ complexes can be obtained by thoroughly mixing a small amount of $[\text{Co}(\text{en})_3]\text{X}_3$ with the corresponding *trans*- $[\text{Co}(\text{en})_2\text{X}_2]\text{X}$ complex. The reflectance band between 500 and 550 nm in the spectra of the partially decomposed $[\text{Co}(\text{en})_3]\text{X}_3$ gives the compound a green appearance and indicates the bis(ethylenediamine)-complex has the *trans*- rather than the *cis*-configuration since the *trans*-form is green and the *cis*-form is a very dark gray.

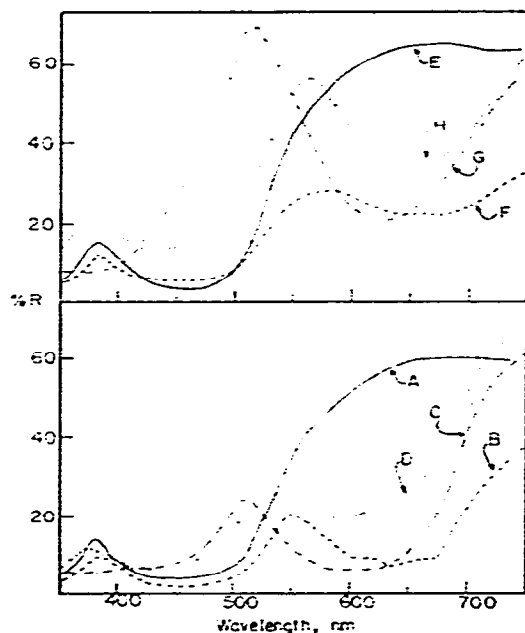


Fig. 3. Reflectance spectra for: (A) $[\text{Co}(\text{en})_3]\text{Cl}_3$ at room temperature; (B) partially decomposed $[\text{Co}(\text{en})_3]\text{Cl}_3$; (C) *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ at room temperature; (D) mixture of $[\text{Co}(\text{en})_3]\text{Cl}_3$ and *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$; (E) $[\text{Co}(\text{en})_3]\text{Br}_3$ at room temperature; (F) partially decomposed $[\text{Co}(\text{en})_3]\text{Br}_3$; (G) *trans*- $[\text{Co}(\text{en})_2\text{Br}_2]\text{Br}$ at room temperature; (H) mixture of $[\text{Co}(\text{en})_3]\text{Br}_3$ and *trans*- $[\text{Co}(\text{en})_2\text{Br}_2]\text{Br}$.

Further decomposition of the complexes gives an absorption band between 600 and 750 nm. This indicates the presence of a tetrahedral cobalt(II) complex and suggests that the 1/1 molar ratio NH_4X to CoX_2 is actually the equimolar mixture of CoX_2 and $(\text{NH}_4)_2\text{CoCl}_4$ as reported by Simmons and Wendlandt¹⁷.

As the complexes decompose, the absorption increases until there is almost total absorption over the entire spectral region between 350 and 750 nm.

Infrared spectroscopy

The infrared spectra for the chloride and bromide complexes appeared identical both before and after decomposition. The infrared spectrum at room temperature and after heating the complex to 350 °C is presented in Fig. 4. The spectra of the complexes after being heated to 350 °C show broad strong absorption bands at slightly over 3

and $7\ \mu$. This indicates that the intermediate is an ammonium compound and not an ammine complex.

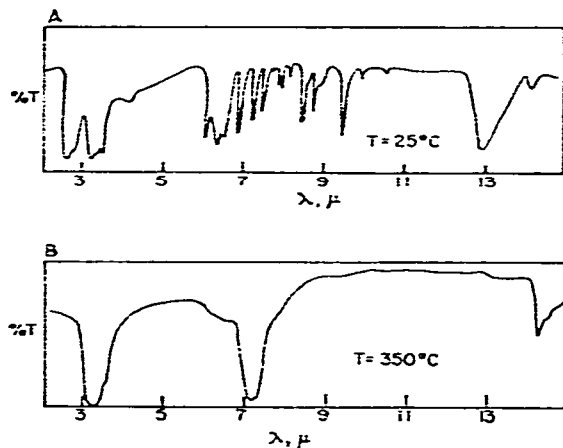


Fig. 4. Infrared spectra of $[\text{Co}(\text{en})_3]\text{X}_3$ ($\text{X} = \text{Cl}, \text{Br}$) (A) at room temperature and (B) after heating to 350°C for 15 minutes.

Mass spectroscopy

The gas evolution curve for the $[\text{Co}(\text{en})_3]\text{Cl}_3$ complex, as measured by mass spectroscopy, is given in Fig. 5, while the curve for the $[\text{Co}(\text{en})_3]\text{Br}_3$ complex is given in Fig. 6. Both curves show that the gas evolution occurs in two distinct steps below 400°C with a broad region of gas evolution at higher temperatures. The mass spectrometric measurement of ethylenediamine evolution, also shown in Figs. 5 and 6, shows that essentially all of the ethylenediamine is evolved in the region under the first peak in the gas evolution curve. Since this decomposition is *in vacuo*, this first decomposition step corresponds to the $[\text{Co}(\text{en})_3]\text{X}_3$ to $\text{CoX}_2-(\text{NH}_4)_2\text{CoX}_4$ transition. Ammonia, which is a fragmentation product of ethylenediamine, is also evolved in this first decomposition step as is shown in the ammonia evolution curves for the

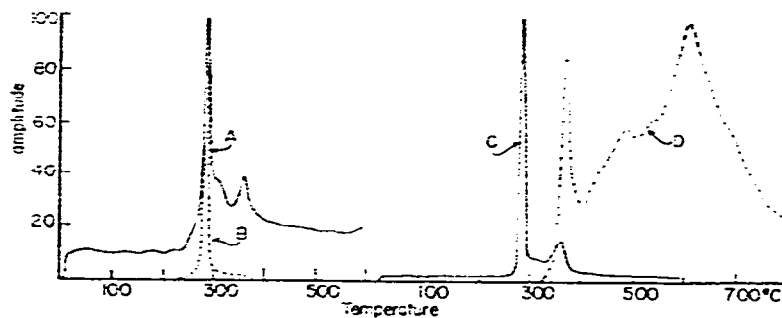


Fig. 5. Mass spectrometric data of: (A) gas evolution; (B) ethylenediamine evolution; (C) ammonia evolution; and (D) HCl evolution resulting from the thermal decomposition of $[\text{Co}(\text{en})_3]\text{Cl}_3$ *in vacuo*.

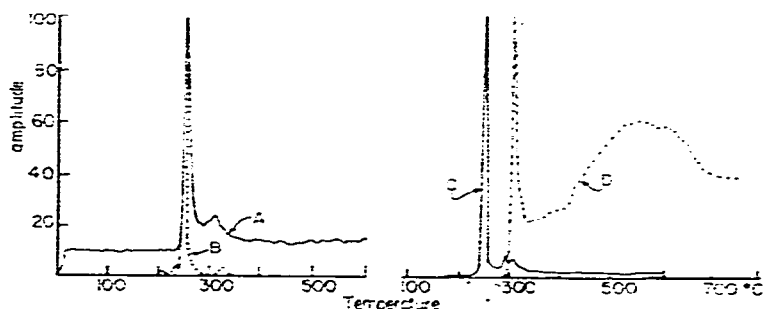


Fig. 6. Mass spectrometric data of: (A) gas evolution; (B) ethylenediamine evolution; (C) ammonia evolution; and (D) HBr evolution from the thermal decomposition of $[\text{Co}(\text{en})_3]\text{Br}_3$ *in vacuo*.

complexes. A second peak in the ammonia evolution curve falls into the region under the second peak of the gas evolution curve. This smaller peak results from the decomposition of $(\text{NH}_4)_2\text{CoX}_4$ with the evolution of NH_4X . The evolved NH_4X gives the second ammonia peak and first peak in the HX evolution curves which exactly superimpose on the ammonia peaks. The relative peak intensities between these product evolution curves are meaningless since each curve is separately normalized to 100% for the most intense peak. The HCl and HBr gas evolution curves, in Figs. 5 and 6, respectively, show that evolution of these products occurs over the entire region above approximately 400°C . This is due to the decomposition of the CoX_2 intermediates to cobalt metal.

Mass spectra from the intervals under each of the three regions of the gas evolution curve of the $[\text{Co}(\text{en})_3]\text{Cl}_3$ complex are presented in Fig. 7. The mass spectrum of the gases evolved at 280°C , in the region of the first decomposition step, is given in Fig. 7a, and is identical to the spectrum obtained for ethylenediamine. There are some small differences in peak intensities due to the thermal fragmentation of the ethylenediamine but the peak groups are the same. This spectrum also verifies that no chlorine or chloride products are evolved in this first step.

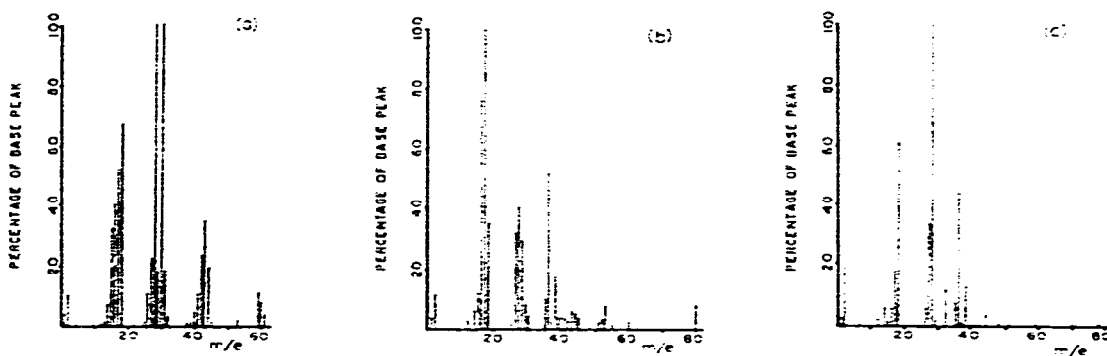


Fig. 7. Mass spectrum of gases evolved from $[\text{Co}(\text{en})_3]\text{Cl}_3$ *in vacuo* (A) at 280°C , (B) at 360°C and (C) at 600°C .

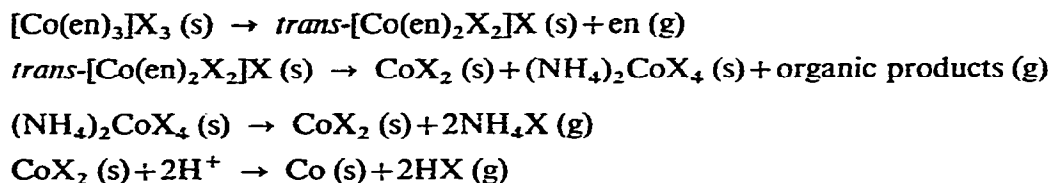
The mass spectrum of the gases evolved at 360°C is given in Fig. 7b. This spectrum was taken during the period of the decomposition of the $(\text{NH}_4)_2\text{CoCl}_4$ intermediate and indicate the evolution of NH_4Cl . The significant feature in this spectrum is the peaks at *m/e* 18, 36, and 53 due to NH_4^+ , HCl^+ , and NH_4Cl^+ , respectively. The peaks at *m/e* 36 and 53 also have a P+2 peak of the correct intensity to indicate a chlorine product. The other peaks are due to organic residues which remain in the system, probably trapped in the solid as it melted and decomposed.

The mass spectrum of the gases evolved at 600°C is given in Fig. 7c. This spectrum was made during the time when the CoCl_2 was decomposing to cobalt metal. The important peaks in this spectrum occur at *m/e* 2, 28, and 36, due to hydrogen, nitrogen, and HCl , respectively. The HCl was expected but the other products were rather unexpected at this elevated temperature. These products, as well as the other peaks, are probably due to organic residues trapped in the system; these trapped products are probably the source of the hydrogen in HCl .

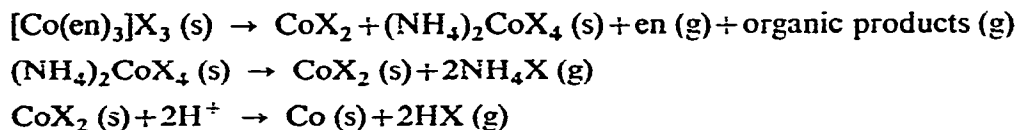
The mass spectra for the $[\text{Co}(\text{en})_3]\text{Br}_3$ complex were similar to those for the chloride except the peaks were at the *m/e* values for bromide rather than chlorine.

CONCLUSION

The evidence obtained in this study indicates that the mechanism for the thermal dissociation of the tris(ethylenediamine)cobalt(III) chloride and bromide in a nitrogen atmosphere is as follows:



In vacuo, the mechanism is:



ACKNOWLEDGEMENTS

The authors would like to express their gratitude to Mr. Gary W. Moore and the Johnson Space Center, Houston, Texas, for their cooperation in obtaining the mass spectral data for this study. The partial support of this work by Robert A. Welch Foundation of Houston, Texas, is gratefully acknowledged.

REFERENCES

- 1 J. P. Smith, *Ph.D. Thesis*. Texas Technological College, Lubbock, Texas, June, 1966.
- 2 W. W. Wendlandt, *Texas J. Sci.*, 10 (1958) 271.
- 3 W. W. Wendlandt, T. D. George and K. V. Krishnamurty, *J. Inorg. Nucl. Chem.*, 21 (1961) 69.
- 4 G. R. Horton and W. W. Wendlandt, *Texas J. Sci.*, 13 (1961) 454.
- 5 N. Tanaka, K. Nagase and S. Nagakura, *Bull. Chem. Soc. Jap.*, 41 (1968) 1143.
- 6 W. W. Wendlandt, *Texas J. Sci.*, 10 (1958) 271.
- 7 N. I. Lobanov, I. S. Rassonskaya and A. V. Ablov, *Zh. Neorg. Khim.*, 3 (1958) 1355.
- 8 N. Fogel and S. D. Christian, *J. Amer. Chem. Soc.*, 80 (1958) 5356.
- 9 N. I. Lobanov and O. S. Konovalenko, *Zh. Neorg. Khim.*, 13 (1968) 409.
- 10 J. B. Work, in W. C. Fernelius, (Ed.), *Inorganic Syntheses*, Vol. II, McGraw-Hill, New York, 1946, p. 221.
- 11 J. C. Bailar, in W. C. Fernelius, (Ed.), *Inorganic Syntheses*, Vol. II, McGraw-Hill, New York, 1946, p. 222.
- 12 W. W. Wendlandt, *Anal. Chim. Acta*, 49 (1970) 185.
- 13 E. L. Simmons and W. W. Wendlandt, *Anal. Chim. Acta.* 35 (1966) 461.
- 14 E. K. Gibson, *Thermochim. Acta*, 5 (1973) 243.
- 15 W. W. Wendlandt and H. G. Hecht, *Reflectance Spectroscopy*, Interscience, New York, 1966.
- 16 M. I. Knudson and J. L. McAtee, *Thermochim. Acta*, 4 (1972) 411.
- 17 E. L. Simmons and W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, 28 (1966) 2187.