

## THE THERMAL DECOMPOSITION REACTIONS OF [Co(en)<sub>3</sub>](NO<sub>3</sub>)<sub>3</sub> AND [Co(en)<sub>3</sub>](HSO<sub>4</sub>)<sub>3</sub>

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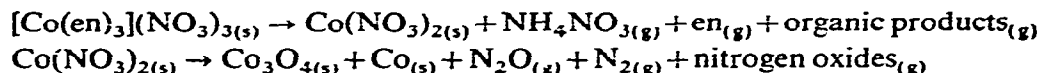
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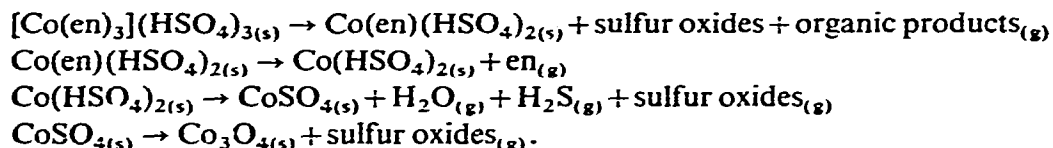
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### ABSTRACT

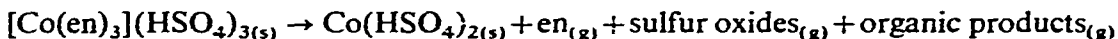
The thermal decomposition reactions were determined for [Co(en)<sub>3</sub>](NO<sub>3</sub>)<sub>3</sub> and [Co(en)<sub>3</sub>](HSO<sub>4</sub>)<sub>3</sub> in a dynamic nitrogen gas atmosphere and *in vacuo*, where en represents ethylenediamine. Data were obtained using thermogravimetry, DTA, thermomagnetic analysis, and mass spectrometry. The dissociation reactions in nitrogen were found to be as follows:



and



*In vacuo*, the dissociation process for [Co(en)<sub>3</sub>](NO<sub>3</sub>)<sub>3</sub> is the same as in nitrogen. Also, the decomposition of [Co(en)<sub>3</sub>](HSO<sub>4</sub>)<sub>3</sub> is the same except for the first step which is:



### INTRODUCTION

Although the physical properties of many cobalt(III) amine complexes and the various substitution and oxidation–reduction reactions involving these complexes have been studied in great detail, the thermal behavior of many of these complexes generally remains unknown or only vaguely understood. One important class of complexes which fall into this latter category is the tris(ethylenediamine) cobalt(III)

complexes. Smith<sup>1</sup> studied the thermal dissociation of these complexes in a preliminary manner but much of the data which was collected was ambiguous or contradictory so that no decomposition mechanisms could be proposed. However, improved thermoanalytical methods have recently led to the determination of the thermal decomposition mechanism for the  $[\text{Co}(\text{en})_3]\text{Cl}_3$  and  $[\text{Co}(\text{en})_3]\text{Br}_3$  complexes<sup>2</sup>. It was shown that these complexes decompose in four reaction steps with *trans*- $[\text{Co}(\text{en})_2\text{X}_2]\text{X}$ ,  $(\text{NH}_4)_2\text{CoX}_4$  and  $\text{CoX}_2$  as intermediates and cobalt metal as the final product.

In this study, the thermal decomposition of  $[\text{Co}(\text{en})_3](\text{NO}_3)_3$  and  $[\text{Co}(\text{en})_3](\text{HSO}_4)_3$  was investigated by thermogravimetry, DTA, thermomagnetic analysis, and mass spectrometry. Analysis of the data produced decomposition mechanisms for these complexes which are substantially different from the mechanisms for the chloride and bromide complexes.

## EXPERIMENTAL PART

### *Compounds*

The starting material for both  $[\text{Co}(\text{en})_3](\text{NO}_3)_3$  and  $[\text{Co}(\text{en})_3](\text{HSO}_4)_3$  was  $[\text{Co}(\text{en})_3]\text{Cl}_3$  which was prepared according to the method of Work<sup>3</sup>. The  $[\text{Co}(\text{en})_3](\text{NO}_3)_3$  complex was prepared by adding concentrated nitric acid to an ice-cold solution of  $[\text{Co}(\text{en})_3]\text{Cl}_3$ , precipitating the crystals with ethanol, filtering, and drying at 110°C. The  $[\text{Co}(\text{en})_3](\text{HSO}_4)_3$  was prepared according to the method of Meyer and Grohler<sup>4</sup>. The cobalt content of the complexes was determined gravimetrically by ignition to the oxide,  $\text{Co}_3\text{O}_4$ .

### *Thermobalance*

The thermobalance used in this study has been previously described<sup>2</sup>. Sample masses of 5 mg or less and heating rates between 1°C min<sup>-1</sup> and 5°C min<sup>-1</sup> were used for the thermal decomposition of  $[\text{Co}(\text{en})_3](\text{NO}_3)_3$  to prevent the complex from decomposing explosively with the loss of sample from the balance pan. Sample masses of 5 to 10 mg were used with heating rates of 5 and 10°C min<sup>-1</sup> for the  $[\text{Co}(\text{en})_3](\text{HSO}_4)_3$  complex. All thermal decomposition reactions were performed in a dynamic nitrogen gas atmosphere at a flow rate of 50 ml min<sup>-1</sup>.

### *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<sup>-1</sup>. Sample sizes were 5 mg or less for the nitrate complex and 5 to 10 mg for the bisulfate complex with heating rates of 5 and 10°C min<sup>-1</sup>. 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 described<sup>5</sup>. However, the measurements were qualitative and indicated only whether the complex was diamagnetic or paramagnetic. A heating rate of  $10^{\circ}\text{C min}^{-1}$  was used with a nitrogen flow rate of  $100\text{ ml min}^{-1}$ .

#### *Thermal analyzer/mass spectrometer/computer system*

This system has been previously described<sup>6</sup>. A heating rate of  $6^{\circ}\text{C min}^{-1}$  was used with a mass spectrometer scan rate of  $1.2\text{ min}^{-1}$ .

## RESULTS AND DISCUSSION

### *Thermogravimetry*

The thermogravimetric curves for the  $[\text{Co}(\text{en})_3](\text{NO}_3)_3$  and  $[\text{Co}(\text{en})_3](\text{HSO}_4)_3$  complexes in a dynamic nitrogen atmosphere and *in vacuo* are presented in Fig. 1.

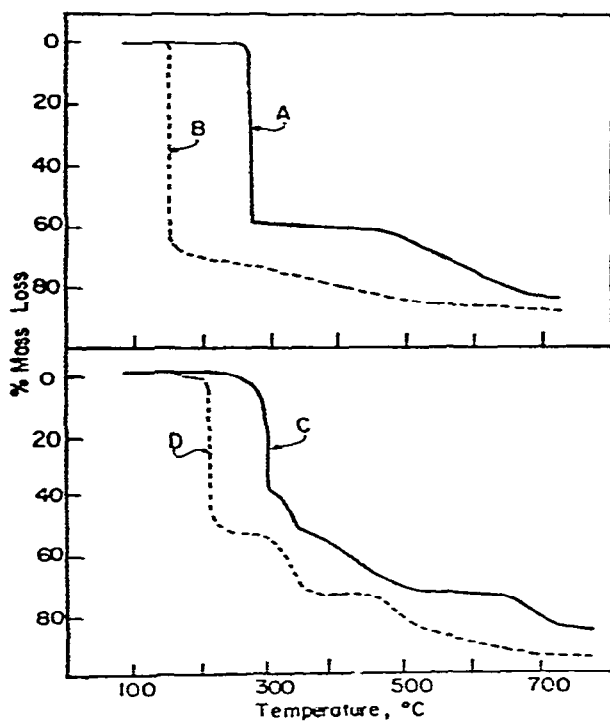


Fig. 1. Thermogravimetric curves for (A)  $[\text{Co}(\text{en})_3](\text{NO}_3)_3$  in a dynamic nitrogen atmosphere, (B)  $[\text{Co}(\text{en})_3](\text{NO}_3)_3$  *in vacuo*, (C)  $[\text{Co}(\text{en})_3](\text{HSO}_4)_3$  in a dynamic nitrogen atmosphere, (D)  $[\text{Co}(\text{en})_3](\text{HSO}_4)_3$  *in vacuo*.

Decomposition of the  $[\text{Co}(\text{en})_3](\text{NO}_3)_3$  complex begins at  $260^{\circ}\text{C}$  in a nitrogen atmosphere and at  $175^{\circ}\text{C}$  *in vacuo*. The TG curves in nitrogen and *in vacuo* bear a close resemblance to each other with respect to their shape which indicates that the decomposition process is probably similar for both sets of conditions. In both cases, the decomposition rate accelerates to an explosion which produces a 60% mass loss. This mass loss corresponds to the decomposition of  $[\text{Co}(\text{en})_3](\text{NO}_3)_3$  to  $\text{Co}(\text{NO}_3)_2$ .

The residue continues to lose mass, totaling 2 to 3%, at a slow rate until about 400°C (in nitrogen) where the rate increases. Mass spectrometric data presented in a later section indicates that the slow mass loss is due to the loss of organic residues and  $\text{NH}_4\text{NO}_3$  which was trapped in the  $\text{Co}(\text{NO}_3)_2$  after the initial decomposition. The increase in the decomposition rate at 400°C is due to the dissociation of  $\text{Co}(\text{NO}_3)_2$  to a mixture which is predominately  $\text{Co}_3\text{O}_4$  but also contains small amounts of cobalt metal. The ratio of these two products varies slightly with each run but the amount of cobalt metal was always significantly higher *in vacuo* than in nitrogen.

The  $[\text{Co}(\text{en})_3](\text{HSO}_4)_3$  complex begins decomposing at 210°C in a nitrogen atmosphere and at 165°C *in vacuo*. In nitrogen, the complex sustains a rapid loss of approximately 40% in the first decomposition step. This corresponds to the formation of an intermediate having the composition,  $\text{Co}(\text{en})(\text{HSO}_4)_2$ , which is analogous to the  $\text{Co}(\text{NH}_3)_2\text{Cl}_2$  complex reported as an intermediate in the thermal decomposition of  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  by Wendlandt and Smith<sup>7</sup>. However, since this intermediate is not thermally stable at the temperature at which it is formed, decomposition continues with the loss of ethylenediamine to slightly over 50% mass loss, corresponding to the formation of  $\text{Co}(\text{HSO}_4)_2$ . *In vacuo*, the  $\text{Co}(\text{HSO}_4)_2$  intermediate is formed directly from the  $[\text{Co}(\text{en})_3](\text{HSO}_4)_3$  complex in one explosive step. Since the  $\text{Co}(\text{HSO}_4)_2$  is formed at a much lower temperature *in vacuo* than in nitrogen, a horizontal mass level, indicating a stable compound, appears at 53% mass loss in the vacuum TG curve of the complex while only an inflection point appears in the TG curve of the complex in nitrogen.

A stable intermediate appears in both the nitrogen and vacuum TG curves of  $[\text{Co}(\text{en})_3](\text{HSO}_4)_3$  at approximately 73% mass loss which is the mass level predicted for  $\text{CoSO}_4$ . This intermediate is also obtained if the complex is heated isothermally at 300°C for a day. At higher temperatures (600°C in nitrogen; 450°C *in vacuo*), the  $\text{CoSO}_4$  decomposes to a stable residue at 85% mass loss in nitrogen and about 93% mass loss *in vacuo*. The mass level in nitrogen corresponds to that predicted for  $\text{Co}_3\text{O}_4$ . *In vacuo*, there could be either some decomposition to cobalt metal or sublimation of  $\text{CoSO}_4$  or both to account for the larger mass loss.

#### DTA studies

The DTA curves for  $[\text{Co}(\text{en})_3](\text{NO}_3)_3$  and  $[\text{Co}(\text{en})_3](\text{HSO}_4)_3$  in a dynamic nitrogen atmosphere are presented in Fig. 2.

The decomposition of the  $[\text{Co}(\text{en})_3](\text{NO}_3)_3$  complex begins with the absorption of thermal energy, as shown by the initial small endothermic peak in the DTA curve. After the decomposition is initiated, the reaction quickly becomes self-sustaining by a large exothermic reaction as the  $[\text{Co}(\text{en})_3](\text{NO}_3)_3$  decomposes to  $\text{Co}(\text{NO}_3)_2$ . This process occurs explosively and appears as a large exothermic peak in the DTA curve. No additional DTA peaks could be resolved since most of the sample was ejected from the pan by the force of the explosion and that which remained was very loosely packed which created poor thermal contact between the sample and the container.

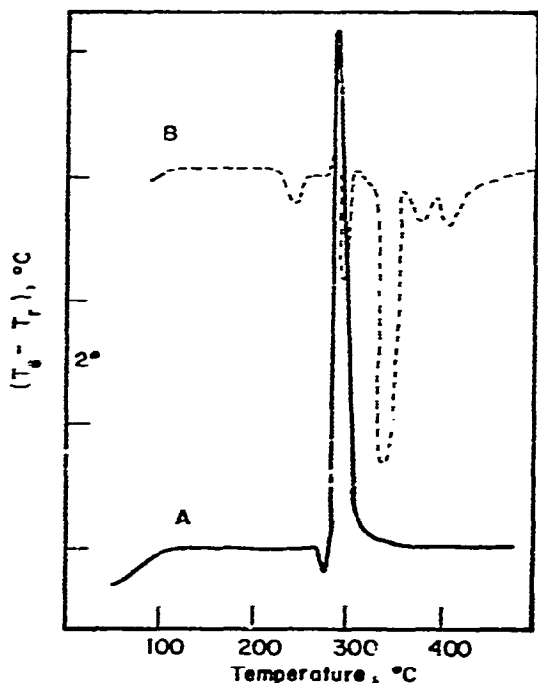


Fig. 2. DTA curves for (A)  $[\text{Co}(\text{en})_3](\text{NO}_3)_3$  and (B)  $[\text{Co}(\text{en})_3](\text{HSO}_4)_3$  in a dynamic nitrogen atmosphere at heating rates of 5 and  $10^\circ\text{C min}^{-1}$ , respectively.

The DTA curve for  $[\text{Co}(\text{en})_3](\text{HSO}_4)_3$  shows a small endothermic peak beginning at  $210^\circ\text{C}$  which coincides with the initiation of the decomposition process. As the reaction progresses, the decomposition rate increases rapidly to an explosion which appears as a small exothermic peak just below  $300^\circ\text{C}$  in the DTA curve. The region covered by these first two peaks corresponds to the decomposition of  $[\text{Co}(\text{en})_3](\text{HSO}_4)_3$  to  $\text{Co}(\text{en})(\text{HSO}_4)_2$ .

The narrow endothermic peak at about  $300^\circ\text{C}$  in the DTA curve of  $[\text{Co}(\text{en})_3](\text{HSO}_4)_3$  was observed to be due to the melting of the  $\text{Co}(\text{en})(\text{HSO}_4)_2$  intermediate. Comparison of the DTA curve with DTG and gas evolution curves verified that this peak resulted from a phase transition rather than a decomposition process. Decomposition of the  $\text{Co}(\text{en})(\text{HSO}_4)_2$  intermediate to  $\text{Co}(\text{HSO}_4)_2$  produces the large endotherm between 300 and  $360^\circ\text{C}$ . This is followed by two small endothermic peaks between 270 and  $450^\circ\text{C}$  which are due to the decomposition of  $\text{Co}(\text{HSO}_4)_2$  to  $\text{CoSO}_4$ . This process appears as a single peak in both the DTG and gas evolution curves. If the  $\text{Co}(\text{HSO}_4)_2 \rightarrow \text{CoSO}_4$  transition is actually a two step process as indicated by the DTA curve, the exact nature of this reaction cannot be determined at this time.

#### Thermomagnetic analysis

Both the nitrate and bisulfate complexes were observed to be diamagnetic at room temperature as was expected from the electronic structure of these compounds.

The  $[\text{Co}(\text{en})_3](\text{NO}_3)_3$  complex became paramagnetic following the initial

explosive mass loss at 260°C with the formation of  $\text{Co}(\text{NO}_3)_2$ . At about 400°C, the residue became ferromagnetic which indicates the presence of some cobalt metal in addition to the  $\text{Co}_3\text{O}_4$  which was the primary product.

The  $[\text{Co}(\text{en})_3](\text{HSO}_4)_3$  complex remained diamagnetic during the initial slow mass loss between 210 and 300°C. However, the residue remaining after the complex exploded,  $\text{Co}(\text{en})(\text{HSO}_4)_2$ , was found to be paramagnetic. The sample remained paramagnetic until the analysis was terminated at 500°C.

#### Mass spectrometric studies

The gas evolution detection (GED) curve for the thermal decomposition of  $[\text{Co}(\text{en})_3](\text{NO}_3)_3$  *in vacuo*, as determined by mass spectroscopy, is presented in Fig. 3.

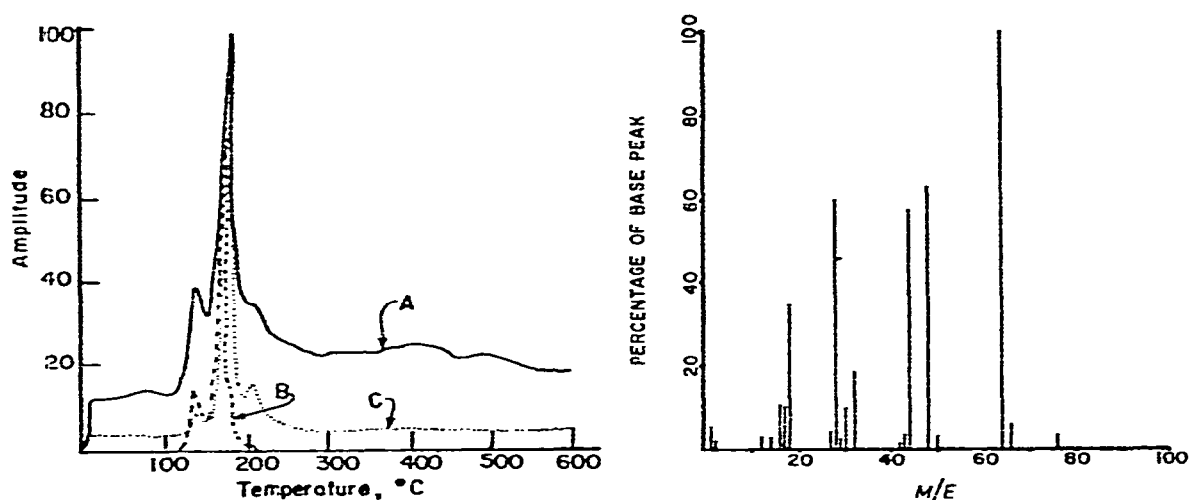


Fig. 3 (left). Mass spectrometric measurement of (A) total gas evolution, (B) ethylenediamine evolution, and (C) ammonia evolution from  $[\text{Co}(\text{en})_3](\text{NO}_3)_3$  during the thermal decomposition *in vacuo*. Fig. 4 (right). Mass spectrum of gases evolved from  $[\text{Co}(\text{en})_3](\text{NO}_3)_3$  at 410°C during thermal decomposition *in vacuo*.

This curve shows two distinct peaks between 100 and 200°C followed by a broad region of gas evolution to over 700°C. The two sharp peaks are due to the initial decomposition step in which  $[\text{Co}(\text{en})_3](\text{NO}_3)_3$  decomposes to  $\text{Co}(\text{NO}_3)_2$ . All of the ethylenediamine and most of the ammonia formed by ethylenediamine fragmentation is evolved in this step as is shown by the gas evolution curves presented in Fig. 3. The broad region of gas evolution between 200 and 600°C is due to the release of trapped residues and to the decomposition of the  $\text{Co}(\text{NO}_3)_2$ . The third small peak in the ammonia evolution curve falls into this region and is due to the release of  $\text{NH}_4\text{NO}_3$  which was trapped in the residue during the initial decomposition step.

The mass spectrum of gases evolved from the  $[\text{Co}(\text{en})_3](\text{NO}_3)_3$  complex at 410°C *in vacuo* is shown in Fig. 4. This spectrum shows that very little of the organic residues remains in the system. The peaks which appear are due primarily to the decomposition of  $\text{Co}(\text{NO}_3)_2$  and are therefore expected to be products formed from the nitrate ion. The base peak occurs at  $m/e = 28$  and is probably due to nitrogen gas.

The second most intense peak is at  $m/e = 18$  which could be either water or the ammonium ion. The peak of medium intensity at  $m/e = 44$  is due to  $N_2O$  and the weaker peaks at  $m/e = 30$  and  $32$  are due to  $NO$  and  $O_2$ , respectively. The mass spectra of gases evolved at higher temperatures are similar to the spectrum in Fig. 4 except that the peaks due to trapped organic impurities are much weaker.

The mass spectrometric measurement of gas evolution from the  $[Co(en)_3](HSO_4)_3$  complex as it undergoes thermal decomposition is given in Fig. 5. This curve shows that the gas evolution occurs in four regions. Examination of the mass spectra of gases evolved in the interval between 175 and 175°C showed that the first small peak at about 150°C in the gas evolution curve is due to the release of water adsorbed by the sample during storage and handling. The large peak between 200 and 300°C results from the decomposition of the  $[Co(en)_3](HSO_4)_3$  complex to the  $Co(HSO_4)_2$  intermediate. The peak at about 350°C is due to the decomposition of  $Co(HSO_4)_2$  to  $CoSO_4$  and the region from 350 to 600°C represents the dissociation and possibly the sublimation of  $CoSO_4$ .

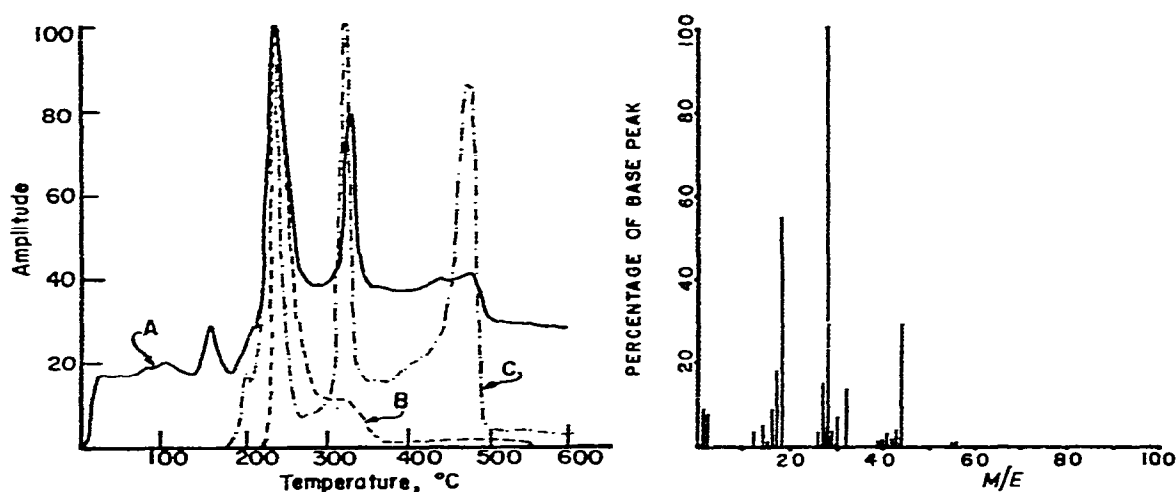


Fig. 5 (left). Mass spectrometric measurement of (A) total gas evolution, (B) ethylenediamine evolution, and (C) sulfur dioxide evolution during the thermal decomposition of  $[Co(en)_3](HSO_4)_3$  *in vacuo*. Fig. 6 (right). Mass spectrum of gases evolved from  $[Co(en)_3](HSO_4)_3$  at 475°C during thermal decomposition *in vacuo*.

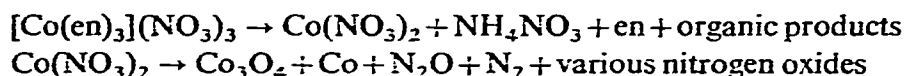
Ethylenediamine and sulfur dioxide evolution curves, also presented in Fig. 5, show that both of these products are evolved in the first decomposition step. The ethylenediamine curve shows that the major portion of this product is released during the first dissociation process but that traces remain in the system to temperatures in excess of 500°C. This trapped ethylenediamine accounts for many of the peaks in the mass spectra of gases evolved at high temperatures. The sulfur dioxide evolution curve shows that this product was evolved in every step of the decomposition process.

The first peak in this curve is due to sulfur dioxide formed in the decomposition of  $[\text{Co}(\text{en})_3](\text{HSO}_4)_3 \rightarrow \text{Co}(\text{HSO}_4)_2$ . The second peak results from the  $\text{Co}(\text{HSO}_4)_2 \rightarrow \text{CoSO}_4$  transition while the final peak corresponds to the dissociation of the  $\text{CoSO}_4$ .

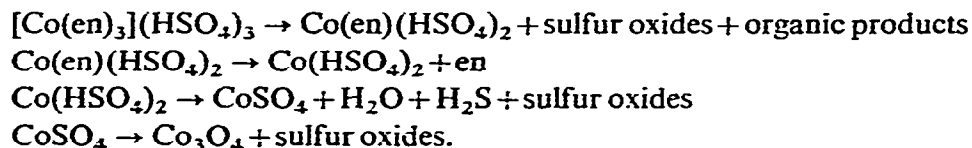
The mass spectrum of gases evolved from  $[\text{Co}(\text{en})_3](\text{HSO}_4)_3$  at  $475^\circ\text{C}$  is presented in Fig. 6. This spectrum contains the expected sulfur-oxygen gases from the decomposition of  $\text{CoSO}_4$  as well as a few peaks from the organic residues remaining in the system. Some of the products which can be identified are  $\text{SO}_2$  at  $m/e = 64$ ,  $\text{SO}$  at  $m/e = 48$ ,  $\text{CS}_2$  at  $m/e = 76$  and  $\text{S}$  at  $m/e = 32$ . These products appear in the spectra at both higher and lower temperatures. A peak at  $m/e = 80$  appeared in some of the spectra at lower temperatures and was due to  $\text{SO}_3$ .

## CONCLUSIONS

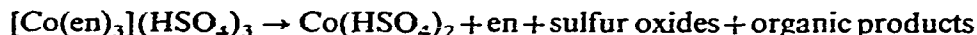
Analysis of the data obtained in this study indicates that the mechanisms for the thermal dissociation of the tris(ethylenediamine) cobalt(III) nitrate and bisulfate complexes in a dynamic nitrogen atmosphere are as follows:



and



*In vacuo*, the mechanisms are the same as in nitrogen except for the first reaction step in the decomposition of the bisulfate complex which is:



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