

## THE THERMAL PROPERTIES OF INORGANIC COMPOUNDS

### II. EVOLVED GAS STUDIES OF SOME MERCURY(I) AND (II) COMPOUNDS

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#### ABSTRACT

The combined thermal analysis techniques of thermogravimetry, evolved gas analysis and mass spectrometry were used to investigate the thermal decomposition of several selected mercury(I), (II) compounds. Although TG curves are presented, the analysis of the evolved gases formed during the thermal decomposition processes was of greater interest. Gaseous products detected included:  $\text{HgSO}_4$ — $\text{SO}$ ,  $\text{SO}_2$  and  $\text{O}_2$ ;  $\text{Hg}(\text{SCN})_2$ — $\text{CS}_2$ ,  $(\text{CN})_2$  and  $\text{N}_2$ ;  $\text{Hg}(\text{NO}_3)_2$ — $\text{NO}$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}_2$  and  $\text{O}_2$ ;  $\text{HgNO}_3 \cdot \text{H}_2\text{O}$ — $\text{NO}$ ,  $\text{NO}_2$  and  $\text{N}_2\text{O}$ ; and  $\text{Hg}(\text{C}_2\text{H}_3\text{O}_2)_2$ —organic fragments. The evolved gas analysis was complicated by sublimation of the compounds at low pressures.

#### INTRODUCTION

The application of sophisticated thermal analysis instrumentation to the study of inorganic decomposition reactions has yielded much valuable insight into the nature of these reactions. However, relatively few compounds have been subjected to an in-depth study and many of the existing studies were performed with inadequate instruments under questionable and often non-reproducible experimental conditions. Some recent studies have focused on the reinvestigation of selected important inorganic compounds with commercial thermoanalytical instrumentation and have applied some of the newer techniques to better characterize significant reactions<sup>1</sup>.

In this study, selected mercury compounds were studied to determine the mode of decomposition under high vacuum conditions. Greater insight into the chemical nature of these compounds was deemed important due to the present industrial and ecological impact of mercury.

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## EXPERIMENTAL

*Chemicals*

The sources of the mercury compounds used were as follows:

Mercury(II) thiocyanate: Reagent, Fisher Scientific Co., Fair Lawn, N.J.

Mercury(II) nitrate: Reagent, Matheson, Coleman and Bell, Norwood, Ohio.

Mercury(II) acetate: Baker Analyzed, J. T. Baker Co., Phillipsburg, N.J.

Mercury(II) sulfate: Reagent, Fisher Scientific Co., Fair Lawn, N.J.

Mercury(I) nitrate: Reagent, Mallinckrodt Chemical Works, St. Louis, Mo.

*Thermal analyzer/ mass spectrometer/ computer system*

This system and the associated operating procedures have been described previously<sup>2</sup>. A heating rate of  $6^{\circ}\text{C min}^{-1}$  was used, with a mass spectrometer scan rate of  $1.2 \text{ min}^{-1}$ . Samples were heated in vacuo with an initial pressure of  $2 \times 10^{-6}$  torr.

## RESULTS AND DISCUSSION

The decomposition reactions for selected mercury compounds were monitored through the simultaneous measurement of thermogravimetric curves and mass spectrometric-evolved gas analysis linked through a computer interface. These techniques provide complementary data from which inferences can be drawn as to the nature of the decomposition process. Data relating to the solid state decomposition products is given in the TG curves in Fig. 1 and will be discussed in conjunction with the gas evolution curves for each compound individually. All curves were obtained for the decomposition process in vacuo.

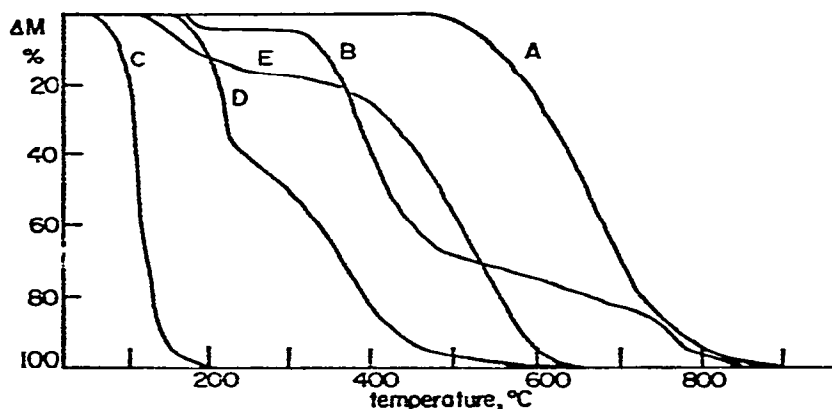


Fig. 1. TG curves for (A)  $\text{HgSO}_4$ ; (B)  $\text{Hg}(\text{SCN})_2$ ; (C)  $\text{Hg}(\text{C}_2\text{H}_3\text{O}_2)_2$ ; (D)  $\text{Hg}(\text{NO}_3)_2$ ; and (E)  $\text{HgNO}_3 \cdot \text{H}_2\text{O}$  in vacuo at a heating rate of  $6^{\circ}\text{C min}^{-1}$ .

*HgSO<sub>4</sub>*

The evolved gas curves for mercury(II) sulfate, presented in Fig. 2, show that decomposition occurs in the temperature interval from 500 to  $750^{\circ}\text{C}$  with the evolu-

tion of SO, SO<sub>2</sub>, and O<sub>2</sub>. No SO<sub>3</sub> could be detected in any of the mass spectra related to the decomposition process. Although this does not preclude the possibility of SO<sub>3</sub> being formed in small quantities which decompose to other sulfur oxides and oxygen, this process seems unlikely as shown in a recent study which indicates that sulfate compounds can decompose through at least two different mechanisms<sup>3</sup>.

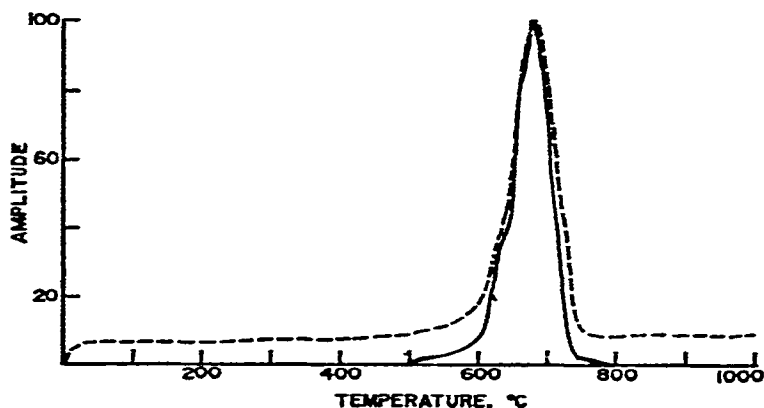


Fig. 2. Mass spectrometric evolved gas curves for HgSO<sub>4</sub>. (—) SO, SO<sub>2</sub>; (---) O<sub>2</sub>.

The TG curve for the HgSO<sub>4</sub> indicates that the mass-loss occurs in one reaction step. However, the magnitude of the total mass-loss, combined with the evolved gas curves, suggests that more than one process is occurring simultaneously since the final mass level stabilizes with less than 1% of the original mass remaining. The anticipated solid state product would be HgO but recent studies<sup>1</sup>, as well as data obtained for other compounds in this study, indicate that HgO is unstable in the temperature range of interest. If HgO is formed at all, it immediately decomposes to elemental mercury and oxygen. Elemental mercury, whether formed directly from HgSO<sub>4</sub> or through an HgO intermediate, would be vaporized and removed from the system since the vapor pressure of mercury is an appreciable value at temperatures in excess of 500°C.

There is some possibility that sublimation of the HgSO<sub>4</sub> occurs since the mass spectra contain a peak at  $m/e = 100$  which corresponds to Hg<sup>2+</sup>; this ion would be expected as a fragmentation product of the sublimed HgSO<sub>4</sub>. The relative importance of the sublimation process as compared to the decomposition process cannot be determined from the available data since the mass loss region probably does not represent a single stoichiometric reaction but rather a combination of processes with an indeterminate quantity of elemental mercury produced.

A typical mass spectrum from the decomposition region, as shown in Fig. 3, shows that the sulfur oxides, SO<sub>2</sub> at  $m/e = 64$  and SO at  $m/e = 48$ , sulfur and oxygen at  $m/e = 32$ , and oxygen at  $m/e = 16$ , constitutes the major evolution products but measurable quantities of nitrogen and water are also present within the system.

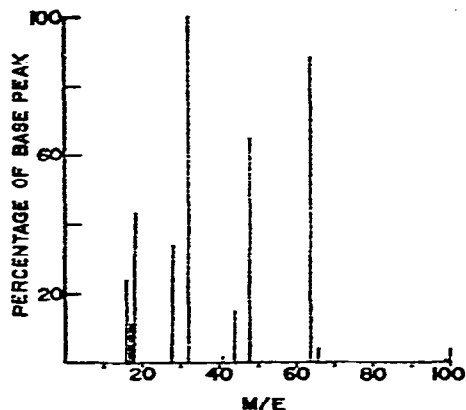


Fig. 3. Mass spectrum of gases evolved from  $\text{HgSO}_4$  at  $675^\circ\text{C}$ .

### $\text{Hg}(\text{SCN})_2$

The TG curve for  $\text{Hg}(\text{SCN})_2$  (Fig. 1) indicates that decomposition occurs as a multistep process over the temperature interval from  $150$  to  $800^\circ\text{C}$ . This observation is also supported by the evolved gas curves in Figs. 4 and 5 which show three distinct regions of gas evolution. The initial evolved gas curve peak occurs between  $150$  and  $200^\circ\text{C}$  and coincides with a mass-loss of about  $4\%$ . The curves in Fig. 4 show that carbon disulfide is a major component of the evolved gases with nitrogen also present in significant quantities, as shown in Fig. 5. The small magnitude of the mass-loss does not correspond to an obvious stoichiometric relationship between the compound and the measured gaseous constituents. However, this loss could be due to  $\text{CS}_2$  and air adsorbed on the material rather than from a true chemical reaction.

The second stage of the reaction produces the major mass-loss and most intense gas evolution. This step involves a mass loss of approximately  $65\%$ , with  $\text{CS}_2$  as the primary evolution product. It is significant that  $\text{CS}_2$  evolution is completed in this

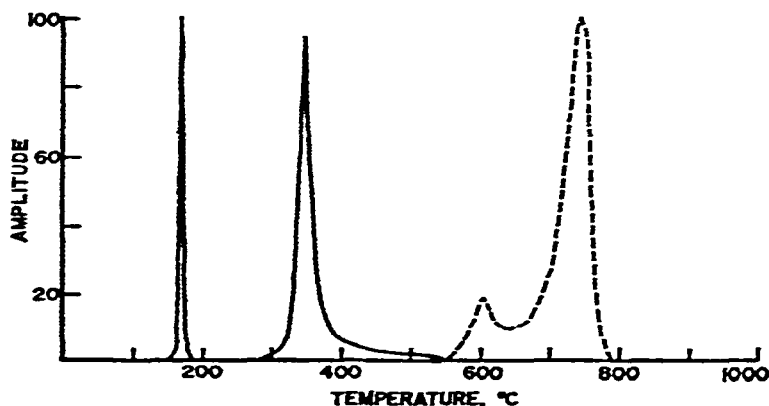


Fig. 4. Mass spectrometric evolved gas curves for  $\text{Hg}(\text{SCN})_2$ . (—)  $\text{CS}_2$ , (---)  $(\text{CN})_2$ .

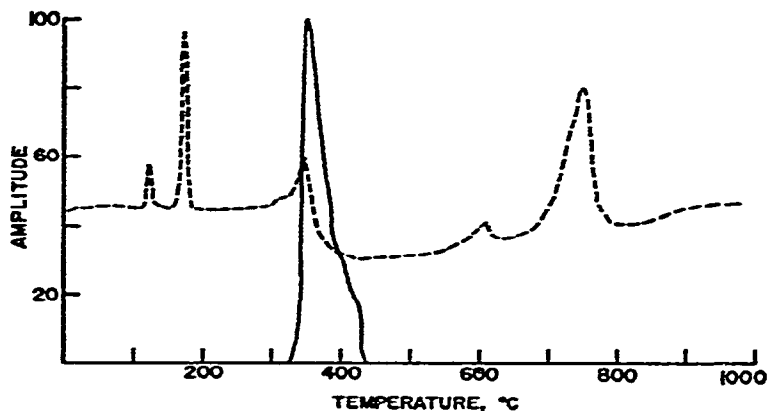


Fig. 5. Mass spectrometric evolved gas curves for  $\text{Hg}(\text{SCN})_2$ . (—)  $\text{Hg}^{2+}$ ; (---)  $\text{N}_2$ .

process but no CN fragment is observed. A plausible explanation might be the reaction:



However, this reaction would produce a mass-loss of only about 21% where an actual mass-loss of about 65% was observed experimentally. Sublimation must be considered as an important alternative process which is also occurring since the magnitude of the mass-loss demands the loss of a substantial quantity of mercury. Also, Fig. 5 shows that the  $\text{Hg}^{2+}$  ion was detected by the mass spectrometer which is a good indication that sublimation of a mercuric compound is occurring under the low pressure conditions. A typical mass spectrum taken during the decomposition interval is given in Fig. 6 and shows  $\text{CS}_2$  to be the major constituent.

The final stage of decomposition occurs with the dissociation of the remaining  $\text{Hg}(\text{CN})_2$ , with the evolution of cyanogen,  $(\text{CN})_2$ , as shown in Fig. 4. A mass spectrum from this interval, given in Fig. 7, shows the presence of the CN fragment at  $m/e = 26$

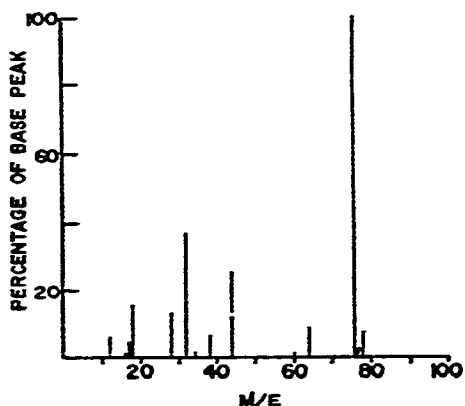


Fig. 6. Mass spectrum of gases evolved from  $\text{Hg}(\text{SCN})_2$  at  $365^\circ\text{C}$ .

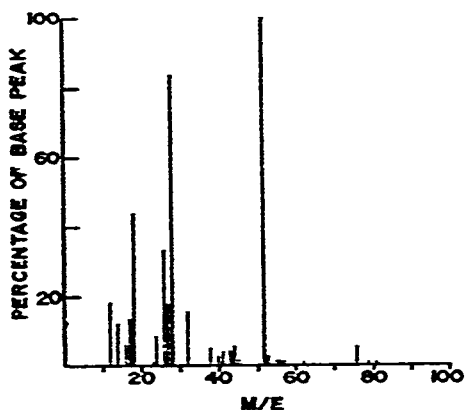


Fig. 7. Mass spectrum of gases evolved from  $\text{Hg}(\text{SCN})_2$  at  $770^\circ\text{C}$ .

but has the dimer,  $(\text{CN})_2$ , at  $m/e = 52$ , as the base peak. This indicates that the dimer is probably the primary gaseous product with the CN formed as a fragmentation product. Since the dissociation of  $\text{Hg}(\text{CN})_2$  results in mercury as a product, evaporation of mercury from the balance pan is also occurring simultaneously with the decomposition.

#### $\text{Hg}(\text{C}_2\text{H}_3\text{O}_2)_2$

The mass-loss from  $\text{Hg}(\text{C}_2\text{H}_3\text{O}_2)_2$  is initiated at about  $75^\circ\text{C}$  in vacuo and continues to about  $175^\circ\text{C}$ , as indicated in Fig. 1. The evolved gas curve for this process, presented in Fig. 8, shows a narrow curve peak at about  $100^\circ\text{C}$  followed by a series of small peaks with a large broad peak between  $400$  and  $600^\circ\text{C}$ . Ordinarily,

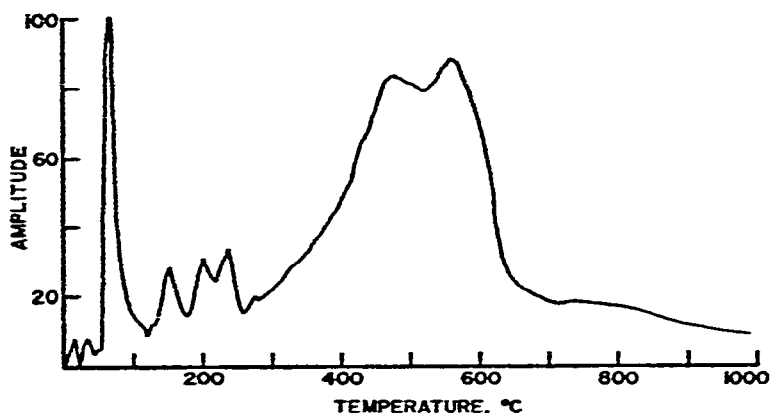


Fig. 8. Mass spectrometric evolved gas curves for  $\text{Hg}(\text{C}_2\text{H}_3\text{O}_2)_2$ .

this would suggest a multistep process for the dissociation of the mercury(II) acetate. However, the TG curve shows that no mass is lost from the sample during the period of greatest gas evolution. In this case, the first curve peak in the gas evolution curve

probably represents the sublimation of the mercury(II) acetate. The subsequent large peak represents the sublimation or decomposition of mercury(II) acetate which condensed on cooler portions of the system and was removed only at the higher temperature. Since all organic fragment evolution curves were superimposable, it was not possible to determine if the compound dissociated or was fragmented by the ionization chamber. A typical mass spectrum of the evolved gases is given in Fig. 9 to illustrate the variety of fragments produced from the acetate radical.

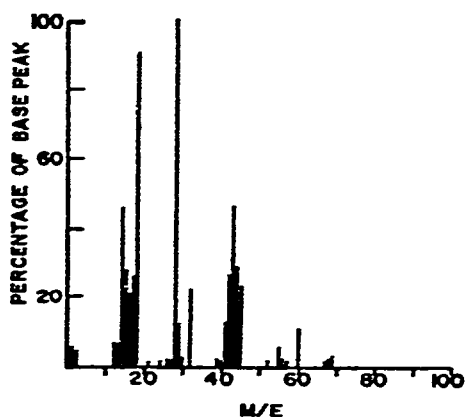


Fig. 9. Mass spectrum of gases evolved from  $\text{Hg}(\text{C}_2\text{H}_3\text{O}_2)_2$  at  $450^\circ\text{C}$ .

### $\text{Hg}(\text{NO}_3)_2$

The decomposition process for  $\text{Hg}(\text{NO}_3)_2$  is initiated at about  $150^\circ\text{C}$  with a mass-loss of about 40% during the first stage. The evolved gas curve in Fig. 10 shows that substantial quantities of  $\text{NO}$ ,  $\text{N}_2\text{O}$ , and  $\text{NO}_2$  are released. The magnitude of the mass-loss and the composition of the gaseous products indicates that decomposition

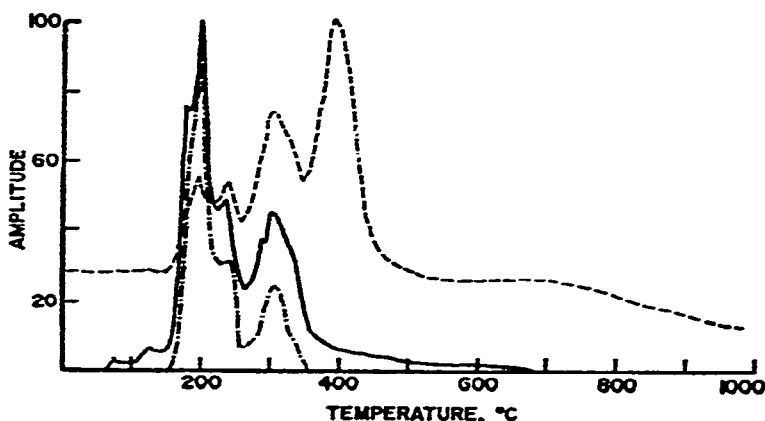


Fig. 10. Mass spectrometric evolved gas curves for  $\text{Hg}(\text{NO}_3)_2$ . (—)  $\text{NO}$ ,  $\text{N}_2\text{O}$ ; (---)  $\text{O}_2$ ; (-·-·-)  $\text{NO}_2$ .

occurs through the following process:



However, neither an exact qualitative nor quantitative distribution of the nitrogen oxides can be determined from these data since the NO could be a fragmentation product of  $\text{NO}_2$  and/or  $\text{N}_2\text{O}$  rather than a thermally generated product. The relative amplitude for each constituent evolved gas curve can be deduced from the mass spectrum obtained at  $200^\circ\text{C}$ , as shown in Fig. 11, which gives the actual relationship between the peak intensities.

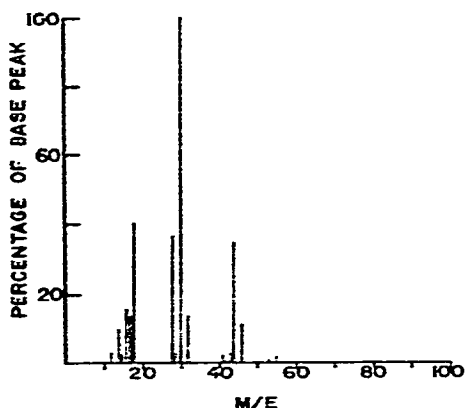


Fig. 11. Mass spectrum of gases evolved from  $\text{Hg}(\text{NO}_3)_2$  at  $200^\circ\text{C}$ .

The second stage of the decomposition process consists of the decomposition of  $\text{HgO}$  coincident with the vaporization of the mercury produced. This process is responsible for the oxygen peak between  $400$  and  $500^\circ\text{C}$  in Fig. 10. Negligible quantities of nitrogen oxides are detectable during this process.

#### *HgNO<sub>3</sub>·H<sub>2</sub>O*

The evolved gas curves for  $\text{HgNO}_3 \cdot \text{H}_2\text{O}$ , as in Figs. 12 and 13, indicate that this material dissociates in three steps. The first step is accompanied by the release of substantial quantities of  $\text{NO}$  and  $\text{NO}_2$  with a small amount of  $\text{N}_2\text{O}$ . This process lies in the temperature interval from  $100$  to  $200^\circ\text{C}$  and represents a mass-loss of about 12%. This is followed by a gradual mass-loss until about  $400^\circ\text{C}$ , at which point the rate of mass-loss becomes more rapid. The second set of evolved gas curve peaks occur between  $350$  and  $475^\circ\text{C}$  and contain large  $\text{N}_2\text{O}$  and  $\text{NO}$  peaks with only traces of  $\text{NO}_2$ . No mechanism can be suggested to account for the two sets of nitrogen oxide peaks occurring below  $400^\circ\text{C}$  when related to the TG curve data. However, the end product is probably  $\text{HgO}$  which dissociates between  $450$  and  $600^\circ\text{C}$ , as indicated by the final oxygen peak in Fig. 13. The presence of the  $\text{Hg}^{2+}$  ion in this interval suggests that sublimation might also occur. No sample remains in the balance pan at temperatures in excess of  $600^\circ\text{C}$ . No water was detected during the initial decomposition



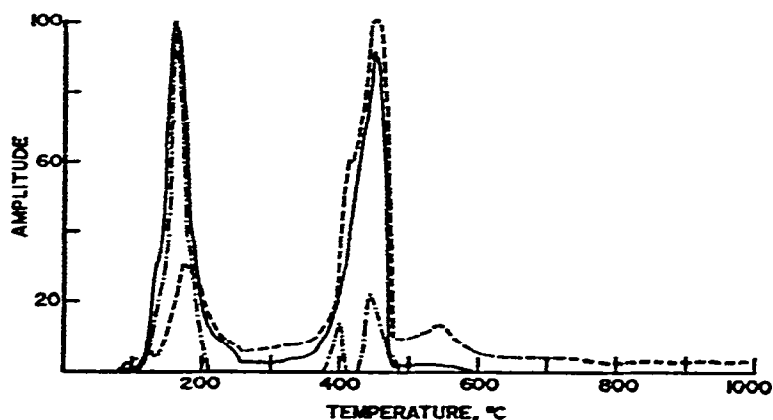


Fig. 12. Mass spectrometric evolved gas curves for  $\text{HgNO}_3 \cdot \text{H}_2\text{O}$ . (—)  $\text{NO}$ ; (---)  $\text{N}_2\text{O}$ ; (-·-·-)  $\text{NO}_2$ .

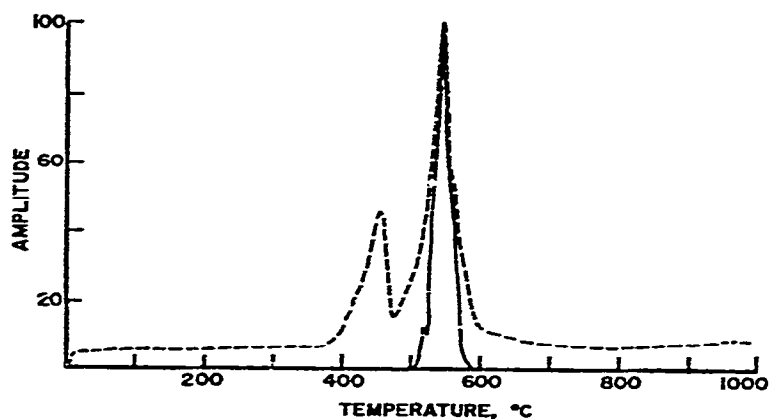


Fig. 13. Mass spectrometric evolved gas curves for  $\text{HgNO}_3 \cdot \text{H}_2\text{O}$ . (—)  $\text{Hg}^{2+}$ ; (---)  $\text{O}_2$ .

process since it was removed by the low pressure conditions below  $50^\circ\text{C}$  and did not appear in the TG curve.

#### ACKNOWLEDGMENTS

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#### REFERENCES

- 1 W. W. Wendlandt, *Thermochim. Acta*, 10 (1974) 101.
- 2 E. K. Gibson, *Thermochim. Acta*, 5 (1973) 243.
- 3 L. W. Collins, E. K. Gibson and W. W. Wendlandt, *Thermochim. Acta*, 9 (1974) 15.