Journal of Thermal Analysis, Vol. 21 (1981) 277–281

THERMAL ANALYSIS OF MERCURY(I) SULFATE AND MERCURY(II) SULFATE

S. A. TARIQ and J. O. HILL

Department of Inorganic and Analytical Chemistry La Trobe University, Bundoora, Victoria 3083, Australia

(Received December 9, 1980)

The thermal decomposition of mercury(I) and (II) sulfates has been investigated by thermogravimetry. The solid-state decomposition products have been characterized by infrared and Raman spectroscopy, mass spectrometry and an X-ray diffraction method. It is concluded that mercury(I) sulfate decomposes in two steps, initially forming a mixture of metallic mercury and mercury(II) sulfate – the latter subsequently decomposes without forming a stable intermediate. The stoichiometry of disproportionation of mercury(I) sulfate and the thermal stability range of mercury(I) and mercury(II) sulfates have been established.

No recent thermal analysis data exist for mercury(I) and mercury(II) sulfates. It has been reported [1] that mercury(I) sulfate decomposes on heating to give mercury, oxygen and sulfur dioxide. Hoschek [2] has reported that mercury(II) sulfate is thermally stable up to 400° but decomposes at 500° to $HgO \cdot HgSO_4$ which subsequently decomposes to $2\,HgO \cdot HgSO_4$. Both these products were characterized by their X-ray powder photographs. Hoschek [2] further reported that if mercury(II) sulfate is heated rapidly to 700°, mercury(I) sulfate is the minor product in the non-volatile residue. No further thermal data on mercury sulfates exist.

This paper reports a TG/DTA study in nitrogen of mercury(I) and mercury(II) sulfates. The intermediate, formed during the thermal decomposition of mercury(I) sulfate, has been characterized by infrared and Raman spectroscopy, mass-spectrometry and by an X-ray diffraction method as mercury(II) sulfate. Thermal decomposition mechanisms are proposed for mercury(I) and mercury(II) sulfates.

Experimental

Materials: Mercury(I) and (II) sulfates (B. D. H. Reagent Grade) were used without further purification.

Instrumentation: Thermogravimetric analysis was performed using a Rigaku-Denki (Thermoflex) modular thermal analysis system capable of simultaneous measurement of thermogravimetry (TG), differential thermal analysis (DTA) and derivative thermogravimetry (DTG). Samples of mass approximately 10 mg were heated at 10° and 20° $\min^{-1}$ in tall open silica crucibles (6 × 5 mm) under a constant nitrogen stream (0.1 litre $\min^{-1}$) using aluminium oxide as the reference material.

Sample masses were determined using a Sartorius Digital Microbalance (Type 2405).

Infrared, Raman and mass spectra were obtained using a Perkin-Elmer 457 grating spectrophotometer (range: 4000–250 cm^{-1}; KBr disc method), a Spex Ramalog 5 Laser-Raman spectrometer and a Jeol JMS D100 mass spectrometer respectively. X-ray diffraction measurements were made on a Siemens counter-tube goniometer using nickel-filtered CuK$_\alpha$ radiation.

The intermediate thermal decomposition products were obtained by heating mercury sulfates in a test tube attached to a vacuum line ($10^{-3}\tau$) at temperatures inferred from the corresponding curves.

Results and discussion

Typical TG/DTA/DTG profiles for mercury(I) and mercury(II) sulfates obtained using a heating rate of 10° min^{-1} and a nitrogen atmosphere are shown in Fig. 1.

The thermal curves for mercury(I) sulfate indicate two distinct stages of decomposition and the corresponding DTA curve indicates that both decomposition processes are endothermic. In the first stage, decomposition occurs between 335° and 500°. The intermediate is stable between 500° and 530°. Decomposition of the

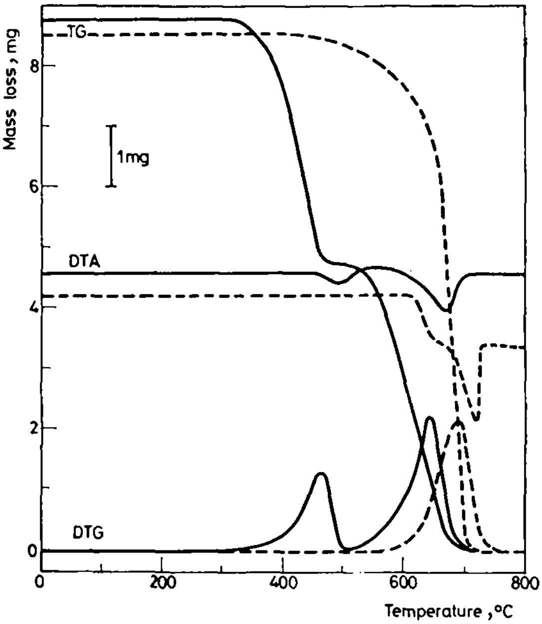

Fig. 1. TG/DTA/DTG profiles for mercury(I) sulfate (——) and mercury(II) sulfate (- - -) in nitrogen

intermediate occurs between 530° and 720°. The average mass loss corresponding to the first stage of decomposition is 40.65 ± 0.34%.

When mercury(I) sulfate is heated in vacuum ($10^{-3}\tau$) to 450°, the mass spectrum of the gaseous product showed the absence of oxides of sulfur. However, metallic mercury was present in the cold traps of the vacuum line. When mercury(I) sulfate was heated to 450° on the internal probe of the mass spectrometer, the mass spectrum obtained showed the presence of metallic mercury only. There was no evidence for the presence of other mercury compounds or the oxides of sulfur.

Mercury(I) sulfate was heated to 500° in a separate experiment and the solid residue was found to be white in colour. The corresponding infrared spectrum indicated a very strong and broad band at 1085 cm^{-1} and strong, narrow band at 620 cm^{-1} which may be attributed to the ν_3 and ν_4 vibrations of the sulfate ion.

The Raman spectrum of mercury(I) sulfate showed a Raman shift due to mercury-mercury stretching at 173 cm^{-1} which compares favourably with 172.2 cm^{-1} reported by Stammreich and Teixeira [3]. However the Raman spectrum of the residue obtained by heating mercury(I) sulfate to 500°, showed no absorption due to mercury-mercury bonding.

The X-ray powder diffraction pattern of this residue gave '*d*' values of 3.87 (m), 3.40 (m), 3.30 (s), 2.36 (m) and 1.64 (m) compared with the ASTM index values of 3.89(65), 3.40(65), 3.29(100), 2.36(35) and 1.64(40) for mercury(II) sulfate.

Thus the products of the initial decomposition of mercury(I) sulfate are mercury(II) sulfate and metallic mercury. The average mass loss of 40.65 ± 0.34%, as derived by thermogravimetry for the first stage of decomposition of mercury(I) sulfate compares with the theoretical value of 40.59% for the loss of one g. atom of mercury per mole of mercury(I) sulfate. Hence the disproportionation of mercury(I) sulfate over the temperature range 335° – 500° may be represented by Eq. (1)

$$Hg_2SO_4 \rightarrow HgSO_4 + Hg \tag{1}$$

The thermal curves for mercury(II) sulfate indicate that decomposition occurs in one step and without the formation of a stable intermediate. Decomposition occurs between 550° and 750° which compares with the decomposition range of 530° – 720° for mercury(II) sulfate formed via disproportionation of mercury(I) sulfate (Fig. 1). The lower temperature range for mercury(II) sulfate produced 'in situ' may reflect the greater decomposition tendency of the nascent intermediate.

When mercury(I) sulfate intermediate or mercury(II) sulfate is heated in vacuum ($10^{-3}\tau$) to 620°, the mass spectrum of the gaseous products obtained in each case showed the presence of O_2, SO_2, and trace quantities of SO_3. There was no evidence for the presence of mercury or mercury compounds. However the temperature was raised to 680°, the mass spectrum of the gaseous products showed that mercury, SO_2 and O_2 were present.

The infrared spectrum of the residue obtained by heating mercury(II) sulfate to 620° indicated the presence of sulfate and the Raman spectrum of this residue confirmed the absence of mercury(I) sulfate. The X-ray powder diffraction pattern of this residue gave '*d*' values of 6.23 (s), 5.53 (s), 3.88 (m), 3.40 (m), 3.30 (s) and 2.93 (s) compared with the ASTM index values of 6.20 (80), 5.50 (80), 2.92 (100) for $HgSO_4 \cdot 2\,HgO$ and 3.89 (65), 3.39 (65) and 3.29 (100) for $HgSO_4$. Hence the decomposition of mercury(II) sulfate may be represented by Eq. (2):

$$3\,HgSO_4 \rightarrow HgSO_4 \cdot 2\,HgO + 2\,SO_2 + O_2 \tag{2}$$

However, the absence of a plateau in the curves over the temperature range 530–720° indicate the instability of the basic sulfate in this region. The presence of mercury, SO_2 and O_2 in the gaseous products obtained at 680° indicates that $HgSO_4 \cdot 2\,HgO$ decomposes without producing a volatile mercury compound. Thus the decomposition of $HgSO_4 \cdot 2\,HgO$ may be represented by Eq. (3):

$$HgSO_4 \cdot 2\,HgO \rightarrow 3\,Hg + SO_2 + 2\,O_2 \tag{3}$$

Hoschek [2] has studied the isothermal decomposition of mercury(II) sulfate at 400° and 500° and has reported a two hour stability period for $HgSO_4$ at 400; at 500°, decomposition to $HgSO_4 \cdot HgO$ occurs which subsequently decomposes to $HgSO_4 \cdot 2\,HgO$. In the present study, $HgSO_4$ was found to be stable to 550 when heated continuously at a rate of 10 or 20° min^{-1} and the production of $HgSO_4 \cdot 2\,HgO$ only is confirmed. The absence of $HgSO_4 \cdot HgO$ in the residue obtained at 620° indicates that this basic sulfate is unstable at this temperature.

When mercury sulfates are heated at the rate of 20° min^{-1}, the contours of the TG/DTA/DTG curves are similar to those obtained at 10° min^{-1} as shown in Fig. 1 but a shift of 10°–40° to higher temperatures occurs in the decomposition temperature ranges. Thus the decomposition ranges for mercury(I) sulfate are 374°–512° and 540°–732°, at 20° min^{-1} heating rate as compared to 335°–500° and 530°–720° respectively at 10° min^{-1} heating rate. Similarly, the decomposition temperature range of mercury(II) sulfate at 20° min^{-1} heating rate is 580°–734° compared to 550°–750° at a heating rate of 10° min^{-1}. This is in concordance with the generally accepted principle [4] that the effect of an increased heating rate is to increase the apparent decomposition temperatures.

References

1. A. F. TROTMANN-DICKENSON, Ed., "Comprehensive Inorganic Chemistry", Pergamon, USA, 3 (1973) 294.
2. G. HOSCHEK, Monatsh. Chem., 93 (1962) 826.
3. H. STAMMREICH and T. TEIXEIRA, J. Mol. Structure, 1 (1967–68) 55.
4. W. W. WENDLANDT, Thermal Methods of Analysis, Interscience, USA, 1964, p. 7.

RÉSUMÉ — La décomposition thermique des sulfates de mercure(I) et de mercure(II) a été suivie par TG. On a caractérisé les produits de la décomposition en phase solide par spectroscopies infrarouge et Raman, spectrométrie de masse et diffraction des rayons X. On en a conclu que le sulfate de mercure(I) se décompose en deux étapes, formant initialement un mélange de mercure métallique et de sulfate de mercure(II), ce dernier se décomposant ensuite sans formation d'un intermédiaire stable. Les proportions stoechiométriques de la dismutation du sulfate de mercure(I) et de l'intervalle de stabilité thermique des sulfates de mercure(I) et de mercure(II) ont été établis.

Zusammenfassung — Die thermische Zersetzung von Quecksilber(I) und (II)-sulfaten wurde durch Thermogravimetrie untersucht. Die Festphasen-Zersetzungsprodukte wurden durch Infrarot- und Ramanspektroskopie, Massenspektrometrie und Röntgendiffraktion charakterisiert. Es wurde gefolgert, dass Quecksilber(I)sulfat in zwei Stufen zersetzt wird, unter anfänglicher Bildung eines Gemisches von metallischem Quecksilber und Quecksilber(II)-sulfat, welches in der Folge ohne Bildung eines stabilen Zwischenproduktes zersetzt wird. Die Stöchiometrie der Disproportionierung des Quecksilber(I)sulfats und der Bereich der Thermostabilität der Quecksilber(I) und Quecksilber(II)sulfate wurden ermittelt.

Резюме — С помощью термогравиметрии исследовано термическое разложение сульфатов одно- и двухвалентной ртути. Продукты твердотельной реакции разложения охарактеризованы ИК спектроскопией, спектроскопией комбинационного рассеяния света, масс-спектрометрией и рентгенографией. Установлено, что сульфат одновалентной ртути разлагается в две стадии, образуя первоначально смесь металлической ртути и сульфата ртути(II), которая затем разлагается без образования какого-либо стабильного промежуточного продукта. Установлена стехиометрия реакции диспропорционирования сульфата ртути(I) и область термической устойчивости сульфатов одно- и двухвалентной ртути.