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THE THERMAL PROPERTIES OF INORGANIC COMPOUNDS

I. SOME MERCURY(I) AND (II) COMPOUNDS

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ABSTRACT

The TG and DTA (DSC) curves of the yellow and red forms of mercury(II) oxide, mercury(II) chloride, bromide and iodide, and mercury(I) iodide are reported. A lower initial procedural dissociation temperature, 400°C, was observed for the yellow form of HgO versus 460°C for the red form. This lower value is consistent with the postulate of a smaller particle size for the yellow form. Although only sublimation behavior was indicated in the DSC curves of the mercury(II) halides, by the use of sealed-tube DTA, fusion transitions were also observed. These data may be of unusual importance in ecological and environmental problems.

INTRODUCTION

There is a need at the present time for new thermal data on many different types of inorganic compounds. Many of the thermal analysis data (TG and DTA) that are available were obtained on relatively low sensitivity instruments under questionable and, in many cases, non-reproducible experimental conditions of furnace atmospheres, heating rate, sample preparation, and so on. With the advent of highly sophisticated commercial thermal analysis instrumentation, new thermal data are relatively easy to obtain and can, hopefully, be reproduced from one laboratory to another.

To begin this series of investigations, the thermal properties of a selected number of mercury(I) and (II) compounds are reported. Due to the ecological and environmental interest in mercury compounds at the present time, the TG and DSC (or DTA) data may be of unusual importance.

EXPERIMENTAL PART

Thermal analysis equipment

Thermobalance. A DuPont Model 950 thermobalance was employed for the TG studies. Sample sizes ranged in mass from 8 to 40 mg and were pyrolyzed at a heating rate of 10°C min^{-1} in a dynamic nitrogen atmosphere (flow-rate of 0.2 SCFH). The sample container was a circular platinum crucible, 6 mm in diameter by 1.5 mm in height.

DSC cell. The DuPont DSC cell was used for the lower temperature (to ~600°C) studies. Samples ranged in mass from 10 to 40 mg and were contained in circular aluminum crucibles, 5 mm in diameter by 2 mm in height. For samples that reacted with aluminum, platinum crucibles of the same dimensions were employed. Pyrolysis conditions were the same as for TG, heating rate of 10°C min^{-1} and in a dynamic nitrogen atmosphere.

DTA cell. The DuPont 1200° cell was used for the higher temperature DTA studies (>600°C). It was only used for those compounds whose thermal dissociation reactions took place above the maximum temperature of the DSC cell. Sample sizes ranged in mass from 20 to 40 mg and were pyrolyzed at a heating rate of 10°C min^{-1} in a dynamic nitrogen atmosphere. Sample containers were circular platinum crucibles of the same dimensions as used for the DSC studies.

Sealed tube DTA apparatus. This apparatus and procedure have previously been described[1,2].

Mercury(I),(II) compounds. The sources of the mercury compounds used were as follows:

Mercury(II) oxide, red form: Bakers' Analyzed, J. T. Baker, Chem. Co., Phillipsburg, N. J.

Mercury(II) oxide, yellow form: U.S.P., Mallinckrodt, Chem. Works, St. Louis, Mo.

Mercury(II) chloride: Reagent, A.C.S., Allied Chemical, Morristown, N.J.

Mercury(II) bromide: Reagent, Fisher Scientific Co., Pittsburgh, Pa.

Mercury(II) iodide: Reagent, Fisher Scientific Co., Pittsburg, Pa.

Mercury(I) iodide, yellow: Eimer and Amend, New York, N.Y.

RESULTS AND DISCUSSION

Mercury(II) oxide

Mercury(II) oxide exists in both a red and a yellow form. According to Remy[3], these forms differ only in their particle size, a fact which was long suspected and was ultimately proven by X-ray diffraction. The yellow form is precipitated on the addition of excess alkali hydroxide to a solution of mercury(II) chloride or nitrate. Red mercury(II) oxide may be prepared by the direct combination of the elements[4] at ~357°C or by the gentle pyrolysis of mercury(I) or (II) nitrates[3], according to the reactions:

$$Hg_2(NO_3)_2 \rightarrow 2HgO + 2NO_2$$

$$Hg(NO_3)_2 \rightarrow HgO + 2NO_2 + \tfrac{1}{2}O_2$$

The red form[5] has a structure of zig-zag chains of –Hg–O–Hg– with Hg–O = 2.03 Å, $\angle$ HgOHg = 109° and $\angle$OHg = 179°. There is only weak bonding between the chains, the shortest Hg–O distance is 2.82 Å.

According to Sidgwick[4], the red form of the oxide begins to dissociate just above the boiling point of mercury or ~357°C; the oxygen pressure[6] is "several" torr at

440 °C and 1240 torr at 610°C. The thermal dissociation of mercury(II) oxide into its elemental constituents is, of course, the famous Lavoisier preparation of oxygen.

Duval[7,8] has recorded the TG curve of red mercury(II) oxide formed during the thermal dissociation of mercury(II) nitrate. A horizontal plateau was observed from 100 to 200°C in the curve which indicated the existence of the oxide. Above 200°C, the compound dissociated into mercury and oxygen, a process which stopped abruptly at 540°C when the crucible was empty. In the thermal dissociation of mercury(II) phosphate, Duval[9] stated that the evolution of oxygen from this compound was rapid at 630°C, "which is the decomposition temperature of mercury(II) oxide".

The TG curves of the yellow and red forms of mercury(II) oxide, under various experimental conditions, are shown in Fig. 1.

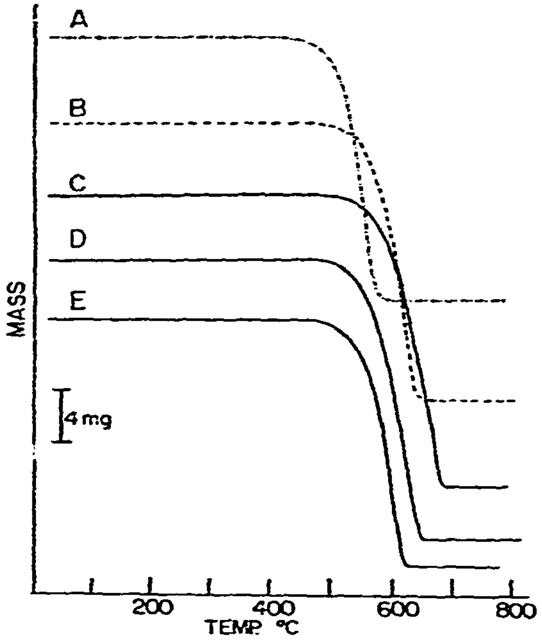

Fig. 1. TG curves of yellow and red forms of mercury(II) oxide. A = Yellow form, 20.4 mg, 10 °C min^{-1} in N_2; B = red form, 21.4 mg, 10 °C min^{-1} in O_2; C = red form, 22.0 mg, 20 °C min^{-1} in N_2; D = red form, 21.5 mg, 10 °C min^{-1} in N_2; E = red form, 19.2 mg, 5 °C min^{-1} in N_2.

The yellow form has a lower initial procedural dissociation temperature (T_i) than the red form. Under the same conditions, $T_i = 400$°C for the yellow form (Curve A) and 460°C for the red form (curve D). Likewise, the final procedural dissociation temperature (T_f) is higher for the latter, 660 compared to 600°C. The reaction interval ($T_f - T_i$), however, is greater for the yellow (200°C) than for the red form (180°C).

Only slight changes were observed for T_i values of the red form with variation in the heating rate. Values of T_i and T_f observed, were: 5°C min^{-1} (460°, 660°C) (Curve D); 10°C min^{-1} (460°, 660°C) (Curve D); and 20°C min^{-1} (470, 680°C)

(Curve C). The T_f values increased with an increase in heating rate as did the reaction interval. On changing the furnace atmosphere from nitrogen to oxygen, the T_i value for the red form increased slightly from 460 to 480°C (Curve B) while the T_f value remained essentially unchanged.

The DTA (or DSC) curves of the yellow and red forms are shown in Fig. 2. Curves A and B of Fig. 2 were obtained on the high temperature DTA cell while Curve C was recorded by use of the DSC cell. The latter cell could not be used to record the curve for the red form due to an upper temperature limitation of 600°C. The initial procedural ΔT deviation temperature (ΔT_i) was about 475°C for the yellow form and, as expected, 550°C for the red form. The minimum procedural ΔT temperatures (ΔT_m) were 575 and 655°C for the yellow and red forms, respectively. Using the DSC data, ΔT_i and ΔT_m values of 450 and 550°C, respectively, were found for the yellow form.

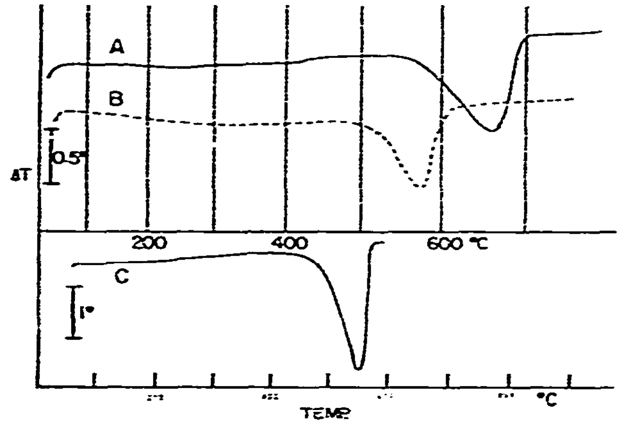

Fig. 2. DTA (or DSC) curves of the yellow and red forms of mercury(II) oxide at 10°C min^{-1} in N_2. A = red form; B = yellow form; C = yellow form (DSC).

In both the TG and DTA (DSC) curves of the yellow and red forms of mercury(II) oxide, the lower procedural dissociation temperatures for the yellow form are consistent with a decrease in particle size. It is well known[9] that a reduction in particle size of a compound such as this lowers the T_i (or ΔT_i) values. The extent of the lowering, however, cannot be predicted.

Mercury halides

Mercury(II) chloride, bromide and iodide, in contrast to the fluoride, show marked covalent character. Mercury(II) chloride crystallizes in an essentially molecular lattice[4], with the two short Hg–Cl distances being about the same length as the Hg–Cl bonds in gaseous $HgCl_2$. In $HgBr_2$, each mercury atom is surrounded by six bromide ions but two are so much closer than the other four that it can be considered that perturbed $HgBr_2$ molecules are present. Mercury(II) iodide has a layer structure with HgI_4 tetrahedra-linked at some of the vertices. At 126–127°C, the red α-form is converted to a β- yellow molecular form. All of the halides have relatively low melting and boiling points[11,12] as is shown in Table 1.

TABLE 1

MELTING AND BOILING POINTS OF MERCURY(II) HALIDES[11,12]

	$HgCl_2$	$HgBr_2$	HgI_2
Melting point (°C)	280 (276)[a]	238 (236)	257 (259)[b]
Boiling point (°C)	302.5 (302)	318 (322)	351 (354)

[a] Ref. 12. [b] For β-HgI_2.

Because of their uses in analytical determinations, Duval[7] recorded the TG curves of Hg_2Cl_2 and HgI_2. The former compound is stable up to 130°C but sublimes at temperatures above this. For HgI_2, it was found to sublime at temperatures above 88°C. The TG curves for these compounds are shown in Fig. 3.

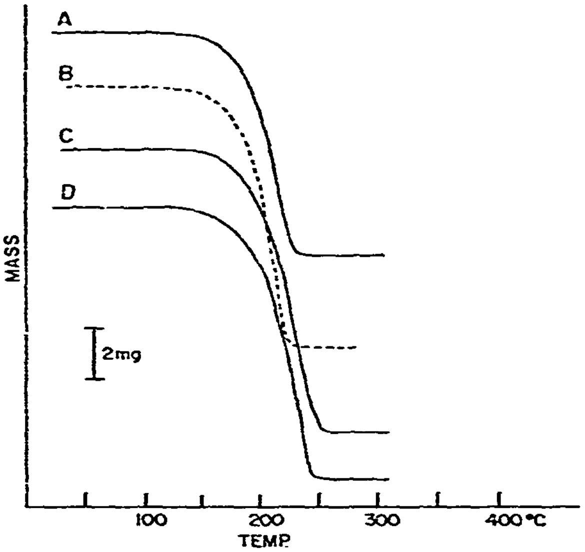

Fig. 3. TG curves of some mercury(I) and (II) halides at 10°C min^{-1} in N_2. A = $HgCl_2$, 8.8 mg; B = $HgBr_2$, 10.3 mg; C = HgI_2, 11.0 mg; D = Hg_2I_2, 10.8 mg.

For all of the mercury(II) halides, the TG curves indicate only a one-step sublimation process. The T_i values found were 100°C for $HgBr_2$, 110°C for $HgCl_2$ and 135°C for HgI_2. Likewise, the T_f values also increased in this order. The T_i value for HgI_2 is somewhat higher than that reported by Duval[7].

The DSC curves for the mercury halides are shown in Fig. 4.

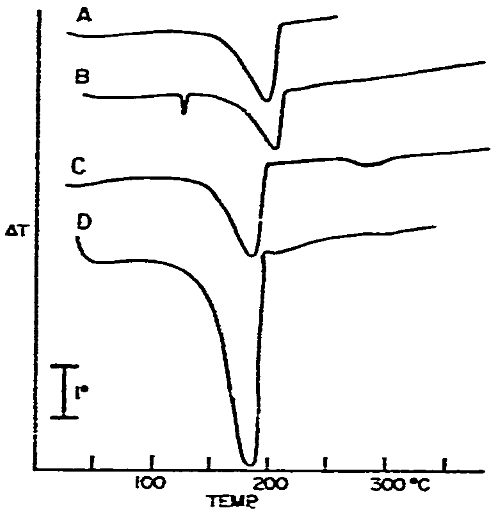

Fig. 4. DSC curves of some mercury halides at 10 °C min^{-1} in N_2. A = Hg_2I_2; B = HgI_2; C = $HgBr_2$; D = $HgCl_2$ (Pt sample container).

Except for α-HgI_2, all of the compounds exhibited a single endothermic peak in the DSC curves indicative of a sublimation process. The ΔT_i and ΔT_m values for the halides are: $HgCl_2$ (100, 185 °C); $HgBr_2$ (125, 185 °C); Hg_2I_2 (125, 200 °C); and HgI_2 (140, 207 °C). A small endothermic peak, due to the α–β crystalline phase transition in HgI_2, is observed at ΔT_i and ΔT_m values of 125 and 127 °C, respectively. All of the curves were obtained using aluminum sample containers except for that of $HgCl_2$ where a platinum container was used due to a displacement reaction between the aluminum and this compound which resulted in an exothermic peak.

Sealed tube DTA results. The sealed tube DTA curves of mercury(II) chloride, bromide and iodide are given in Fig. 5.

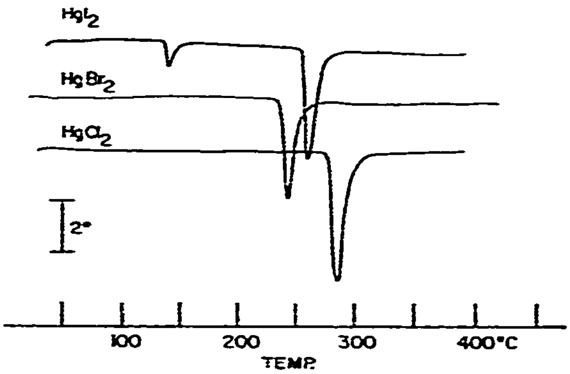

Fig. 5. Sealed tube DTA curves.

As discussed previously[1,2], only first order phase transitions can be observed by this DTA technique. Thus, in the case of the mercury(II) halides, fusion transitions are observed in all three of the compounds. Since it is a sealed system, sublimation (or vaporization) of the compounds does not occur as was found in the case of DSC cell studies. The fusion endothermic peak temperatures agree fairly well with the melting point values reported in Table 1. The ΔT_i and ΔT_m values found are: $HgCl_2$ (252, 257°C); $HgBr_2$ (235, 240°C); and β-HgI_2 (252, 257°C). In the case of the α–β transition in HgI_2, the peak temperatures are somewhat higher, 135 and 140°C, respectively. Boiling points of the compounds, of course, could not be determined by this technique.

ACKNOWLEDGEMENT

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