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ELECTRICAL CONDUCTIVITY–DIFFERENTIAL THERMAL ANALYSIS MEASUREMENTS ON SOME M_nHgI_4 COMPLEXES

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ABSTRACT

The electrical conductivity (EC) and differential thermal analysis (DTA) curves of M_nHgI_4 complexes ($M = Ag^{1+}$, Cu^{1+}, Hg_2^{2+}, Tl^{1+} and Pb^{2+}) and HgI_2 and AgI are reported. The EC–DTA curves were obtained for each of the following heating–cooling modes: (a) initial heating; (b) cooling; and (c) reheating. Each set of curves is discussed. The effect of sample history was also studied.

INTRODUCTION

Thermochromism, the reversible change in color of a compound as a function of temperature, is observed in many inorganic and organic compounds. The mechanism of thermochromic transitions depends upon the molecular or ionic crystalline structure of the compound; for inorganic compounds, in general, the transition is due to a crystalline phase change, a change in ligand geometry, or a change in the number of ligand groups in the coordination sphere. For irreversible thermochromism transitions, the transition is usually due to a thermal decomposition reaction.

The thermochromic M_nHgI_4 complexes ($M = Ag^{1+}$, Cu^{1+}, Hg_2^{2+}, Tl^{1+}, and Pb^{2+}) and simple salts, HgI_2 and AgI, studied here have been the subject of numerous investigations. Ketelaar[1,2] reported that the β-forms of the silver and copper complexes, Ag_2HgI_4 and Cu_2HgI_4, are of pseudocubic tetragonal symmetry and that the α-forms are cubic. Later results by Hahn *et al.*[3] and Hoshino[4] did not confirm this assignment however. Ketelaar[5–7] also measured the electrical conductivity of these compounds and reported that Ag_2HgI_4 is ionic and that its conductivity increases rapidly at just below the transition temperature. At the transition temperature, a rapid, large increase in conductivity occurred. For the Cu_2HgI_4 complex, he explained the observed conductivity change at the thermochromism transition as due to an *order–disorder* mechanism. He did not, however, give the experimental values for the specific conductivity of this compound.

Suchow and Pond[8] reported the activation energies of electrical conductivity for the silver and copper complexes and their eutectoid (for both β- and α-forms).

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The activation energy for the eutectoid was not, as expected, an average value of the two initial complexes. A hysteresis effect was also shown between the heating and cooling curves, at temperatures near the transition temperature. Measurements of the magnetic susceptibility of these two complexes showed no discontinuity at the transition temperature[9]. This was in agreement with an *order–disorder* mechanism involving the movement of metal ions during the transitions with no change in the electron configuration of these ions. These investigators also studied the phase diagrams of Ag_2HgI_4 and Cu_2HgI_4[10].

Neubert and Nichols[11] reported carefully taken electrical conductivity data on Ag_2HgI_4 and Cu_2HgI_4 and showed that the *order–disorder* transitions involved two steps, one of them containing an intermediate β'-form. A certain F factor was calculated which was proportional to the rate of conductivity change. Hysteresis was also observed which was dependent on the rate of heating or cooling at the transition temperature. The heating and cooling rates were very low, 5–10°C day^{-1}, with periodic intervals at which the heating mode was isothermal. Several important variables in the transition temperature determination were the effect of sample history and the schedule of measurements.

TABLE I
SUMMARY OF THERMOCHROMIC TRANSITION TEMPERATURES

Compound	*Transition temp. (°C)*	*Color change*	*Reference*
Ag_2HgI_4	50.7	yellow to orange	2, 9, 10, 18, 26
	50		8
	51.2		15
	25–55		12–14
Cu_2HgI_4	66.6, 67	red to dark purple	8, 10
	25–85	red to black	12
	50–75	red to black	13, 14
	69.5, 70	red to dark brown	2, 24
	71	red to brown-black	15, 26
$HgHgI_3$	160	orange to red	15
	172.6	orange to red	15
	220.1	red to deep red	15
	24–125	orange to red	12–14
Tl_2HgI_4	116.5	orange to red	9
	23–150	orange to red	12–14
$PbHgI_4$	133.8	orange-red to yellow	15
	~100	orange-red to red	12–14
HgI_2	127, 150	red to yellow	9, 18, 26
AgI	147	yellow to brown	12, 18

Dynamic reflectance spectroscopy (DRS) was used by Wendlandt and co-workers[12–14] to determine the thermochromic transition temperatures of most of these complexes. However, fairly high heating rates were employed with no attempt to record the DRS curves at a decreasing rate of temperature change.

The thermochromism of a large number of inorganic and organic compounds has been reviewed by Meyer[15] and Day[16,17]. These compounds have been used as qualitative temperature indicators[18–21] and in electronic display devices[22]. There is some question concerning the thermochromic transition temperatures, as shown by the values listed in Table 1.

The purpose of this investigation is to study the thermochromic transition temperatures of these compounds, both in the heating and cooling modes, by differential thermal analysis (DTA) and scanning direct current electrical conductivity (EC).

EXPERIMENTAL PART

Preparation of compounds

The compounds, Ag_2HgI_4, $PbHgI_4$ and $HgHgI_3$ were prepared by Meyers's procedure[15]. Walton's method[23] was used to prepare Cu_2HgI_4 while the procedure described by Gallis[24] was used to prepare Tl_2HgI_4. The simple salts, AgI and HgI_2, were precipitated from 0.1 M solutions of the respective metal nitrate with 0.1 M potassium iodide. The end-point of the latter precipitation was detected potentiometrically. All of the compounds were washed several times with water, then ethanol, dried at room temperature, and then stored in the dark until used in the thermal measurements.

DTA apparatus

The high resolution DTA apparatus has previously been described[25]. Samples were contained in 1.9 mm ID glass capillary tubes; a furnace heating rate of 5°C min^{-1} was employed in all of the measurements. Measurements were made of the DTA curve in the cooling mode as well as heating. The curves reported here were made in three different modes: (a) the initial heating mode; (b) the cooling mode; and (c) the reheating mode.

Electrical conductivity apparatus

This apparatus has previously been described[27]. Three curves were obtained on each compound as described under the DTA apparatus. A heating rate of 5°C min^{-1} was employed.

RESULTS AND DISCUSSION

Ag_2HgI_4

The DTA and EC curves of this compound are shown in Fig. 1.

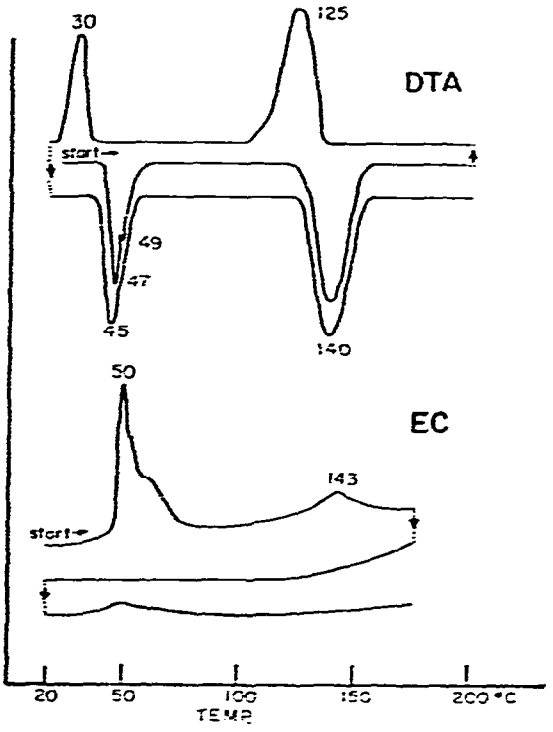


Fig. 1. DTA and EC curves of Ag_2HgI_4. Order of heating and cooling indicated.

During the first heating, two main endothermic peaks were observed at ΔT minimum temperatures of 47 and 140 °C, respectively. A small shoulder peak at 49 °C was observed on the first endothermic peak which was not present in the curve for the second heating. The first peak occurred at a lower temperature than that previously reported as the thermochromic transition temperature (see Table 1). Rather surprisingly, the second transition has not been previously reported. This transition, as can be seen in the cooling mode curve, is also reversible. The color change for the second transition is from a light → darker orange color. For both transitions, the ΔT peak maximum temperature exhibited a hysteresis effect with a peak shift of ~15 °C for both the first and second peaks.

The EC curve obtained during the first heating contained two peaks, at maximum peak temperatures of 50 and 143 °C, respectively. Shoulder peaks were observed on the first peak, which was much larger than the second high temperature peak. No peaks were observed in the cooling curve but a small peak at 50 °C was found during the second heating. The temperature dependence of the EC curves was similar to the *F*-factor curves of Neubert and Nichols[11]. However, the shape of the curves obtained by the latter investigations and others[8,10] can only be obtained at a heating rate of about 0.5 °C min^{-1}.

The differences between these EC data and the earlier work can probably be explained by the difference in the method of measurement and the experimental conditions. In general, increasing disorder of a crystal structure causes an electrical

conductivity increase. For these measurements the compound was far from equilibrium because of the heating rate involved during the transition. However, even at the higher heating rates, two EC curve peaks were observed; only Neubert and Nichols[11] have previously observed the second transition and this was only at very slow heating rates requiring a long period of time.

Decomposition of the Ag_2HgI_4 was not observed up to 200 °C in contrast to earlier reports[8,10,13,15,22]. Apparently, significant thermal decomposition requires a longer reaction period than was used here.

Cu_2HgI_4

The DTA and EC curves of Cu_2HgI_4 during the heating and cooling modes are shown in Fig. 2.

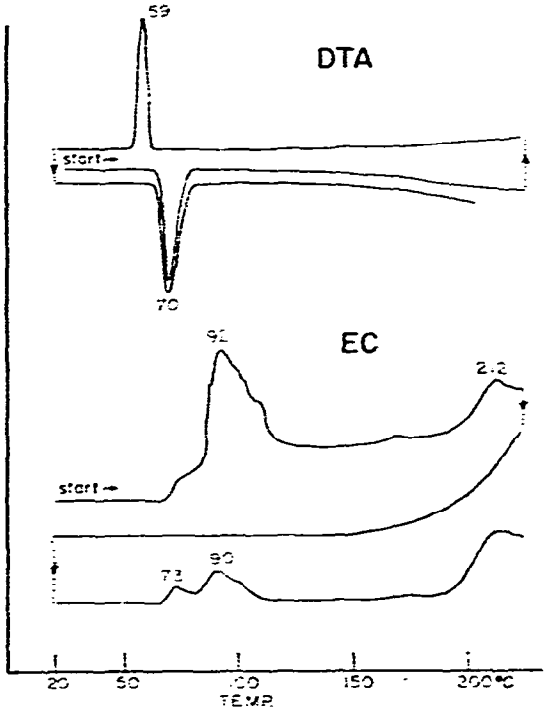


Fig. 2. DTA and EC curves of Cu_2HgI_4; heating and cooling modes indicated.

In the DTA curves, in both the heating and cooling modes, only a single, narrow endothermic peak was observed, which was due to the thermochromic transition. During both heating curves, the peak began at 64 °C with a ΔT minimum temperature of 70 °C. The peak was also observed during the cooling mode, indicating, as expected, that the transition is reversible.

The EC curve peak was not as well pronounced during the thermochromic transition as was the DTA peak. Only a shoulder peak was observed simultaneously with the DTA curve peak but this was followed by a large assymmetric curve peak

with a maximum at approximately 92°C. Apparently, additional disorder occurs above 200°C which results in a curve peak with a maximum at about 212°C. On cooling, none of the initial EC peaks were observed in the curve. Reheating the sample gave the same EC curve peaks but all of them were at a decreased peak height. From the above data, the EC curves appear to indicate multiple disordering processes or transitions involving phases not previously reported. The enthalpy changes must be quite small as they do not appear in the DTA curve as endothermic peaks.

Tl_2HgI_4

The DTA and EC curves of Tl_2HgI_4 are shown in Fig. 3.

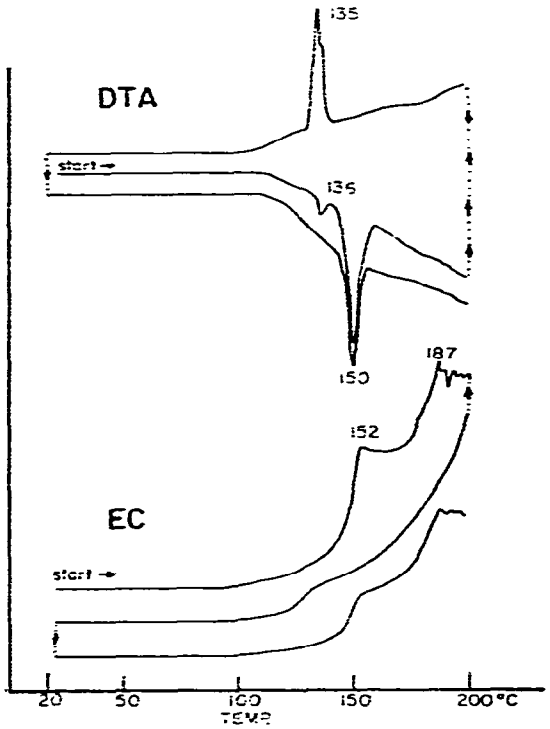


Fig. 3. DTA and EC curves of Tl_2HgI_4; heating and cooling modes indicated.

Asmussen and Anderson[9] reported a thermochromic transition temperature of 116.5°C for this compound while Wendlandt and co-workers[12,13], on the basis of DRS data, described the gradual color change from yellow to red in the temperature range from 23 to 150°C. No changes in the DTA or EC curves were observed here until a temperature of 100°C was attained. In the case of the DTA curves, the baseline began to deviate, starting at about 110°C, and two endothermic peaks were observed during the first heating mode, with ΔT minimum temperatures of 136 and 150°C, respectively. The first peak was present during the second heating of the sample. The second peak was observed during the cooling mode but the ΔT maximum

temperature was shifted to 135 °C. The EC curves indicated a gradual increase on heating with two small peaks superimposed on the sharply rising slope of the curves. Only a small peak was observed on the EC curve during the cooling mode. The behavior of the DTA and EC curves appears to confirm the gradual thermochromic transition observed previously by DRS. There obviously is no definite transition temperature for this compound.

$HgHgI_3$

The DTA and EC curves of $HgHgI_3$ are given in Fig. 4.

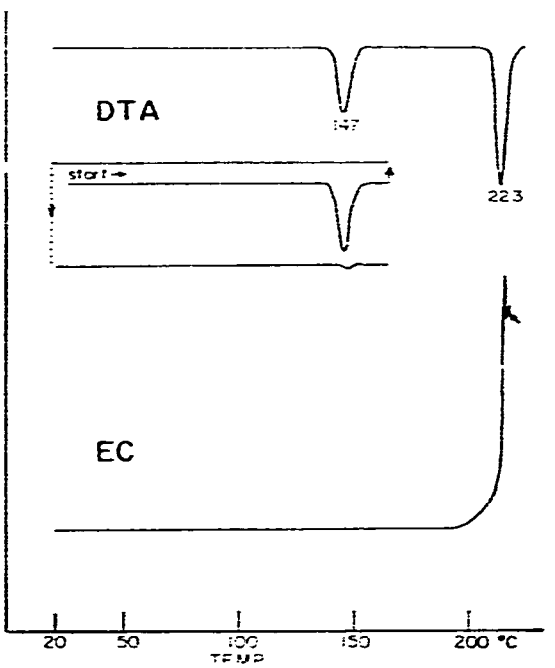


Fig. 4. DTA and EC curves of $HgHgI_3$; heating and cooling modes indicated.

According to Meyer[15], $HgHgI_3$ has several thermal and thermochromic transitions. It begins to change to an orange color above 160 °C and has a definite orange to red color change at 172.6 °C. The red color becomes deeper in color at 220.1 °C with fusion occurring at 224.4 °C. Wendlandt and co-workers[12–14] reported that the color change was gradual and that no transition temperature was observed.

According to the DTA curves, a well defined endothermic peak is observed at ΔT minimum temperature of 147 °C. At higher temperatures, the fusion process takes place as indicated by the endothermic peak at 223 °C. As shown by the cooling curve, the first endothermic peak was not reversible under these experimental conditions. As noted by Meyers[15], the red colored form changes to the yellow colored initial modification on standing at room temperature.

No EC curve peaks were observed on heating the compound to a temperature

of 200 °C. The rapid increase in conductivity above this temperature is due to the fusion of the compound.

$PbHgI_4$

The DTA and EC curves of $PbHgI_4$ are shown in Fig. 5.

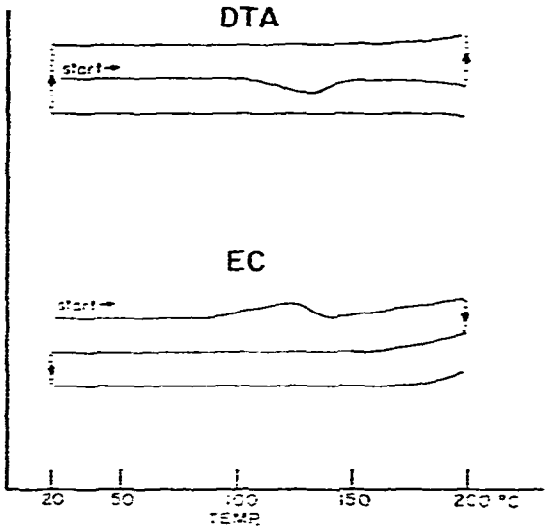


Fig 5. DTA and EC curves of $PbHgI_4$; heating and cooling modes indicated.

Both the DTA and EC peaks were poorly resolved for this compound; both curve peaks were rather broad and of low amplitude. For the DTA curve, this would indicate that a small heat of transition was involved. The endothermic peak minimum was at 129–135 °C which is in agreement with the 133.8 °C transition temperature previously reported[15]. As usual, the transition was reversible but it required more than 24 h to be completed.

HgI_2

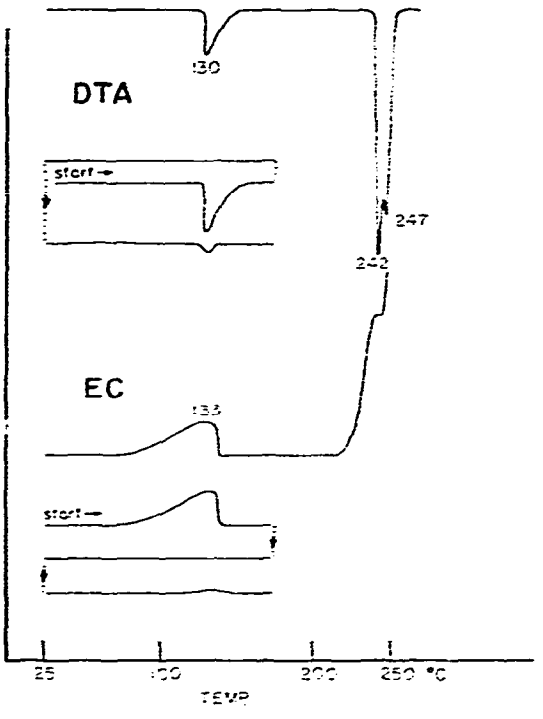
The DTA and EC curves are illustrated in Fig. 6.

According to the literature[9], the red tetragonal form of HgI_2 is transformed into the yellow rhombic form at 127 °C. This transition appeared in the DTA and EC curves at 130 and 133 °C, respectively. At higher temperatures, 242 °C, another crystalline transition occurred which was followed by the fusion of the compounds at 247 °C. The latter is indicated by a shoulder peak on the 242 °C endothermic peak. As in the case of $PbHgI_4$, the transition is irreversible on rapid cooling; the process takes 24 h or longer.

AgI

The DTA and EC curves are shown in Fig. 7.

Although the EC curve indicates only a single curve peak, the DTA curve



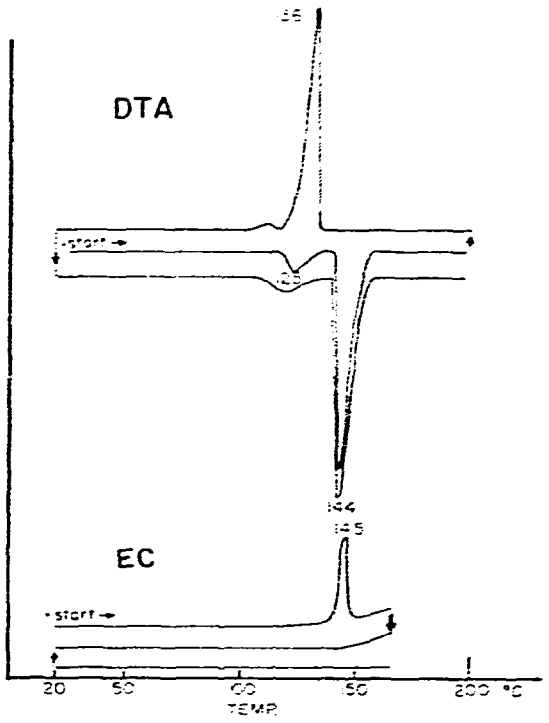


Fig. 6 (left). DTA and EC curves of HgI_2; heating and cooling modes indicated.
Fig. 7 (right). DTA and EC curves of AgI; heating and cooling modes indicated.

indicated two endothermic peaks consisting of a rather small peak followed by a larger one. The peak minimum for the latter occurred at 144°C which is in good agreement with the literature value of 147°C[12,18]. Both peaks were reversible, as shown by the DTA cooling curve. The EC curve peak has a peak maximum temperature of 145°C, also in good agreement with the previously reported value.

SAMPLE HISTORY EFFECTS

The effects of thermal history on the Cu_2HgI_4 and $AgHgI_4$ thermochromic transitions were determined. Both samples were stored in the dark and in lighted containers and at room and liquid nitrogen temperatures for various intervals of time. The Cu_2HgI_4 compound exhibited a color change from red to orange at the lower temperatures. It was also observed that the EC curve peak temperature for Ag_2HgI_4 which had been stored in the light was much higher than for that stored in the dark. No significant change was found for the light storage effect on the Cu_2HgI_4 compound. Thermal history effects were not detectable in the DTA curves; they were indicated only in the EC curves.

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