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Note

SPECIFIC HEAT ANOMALIES IN THERMOCHROMIC COMPOUNDS CONTAINING MERCURY(II) AND IODIDE

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The photochromic phase transitions of salts and complex anions containing mercury(II) and iodide are well known. Their chemistry is related in most major text books [1—3], they are used in undergraduate teaching experiments and have found application [2] as temperature-indicating paints. It is therefore suprising that we found it difficult to find values for the magnitude of the specific heat anomaly associated with the phase transitions in the literature. Further, in this journal [4] it has been suggested that the enthalpy change involved would be too small to be measured by DTA or DSC; this seemed unlikely. We have hence undertaken a study of the phase transitions in HgI_2, $Ag(I)_2HgI_4$ and $Cu(I)_2HgI_4$ by DTA. We wish in this note to report the magnitude of the specific heat anomaly and in the case of the salts of HgI_4^{2-} comment on the magnitude in terms of the theory of order—disorder phase transitions.

EXPERIMENTAL

HgI_2 was used as provided by B.D.H. $Ag(I)_2HgI_4$ and $Cu(I)_2HgI_4$ were prepared by literature methods. DTA measurements were made with a Stanton Redcroft 671 using silica as a reference and water as coolant. Sample weights were between 5 and 10 mg and the heating rate was $10°C\ min^{-1}$. Indium metal was used as a calibrant. Using water as a coolant we were unable to obtain reliable results on cooling the samples; all transitions were, however, reversible, but in many cases sluggishly. Reported results are the average of at least three independent determinations, peak areas being determined by the cut out and weigh method.

RESULTS

Typical DTA traces are shown (Fig. 1). By calibration with indium, the enthalpy associated with the peaks shown was estimated. The results of these experiments are summarized in Table 1, enthalpies and extrapolated onset temperatures are reported and compared with the results of earlier workers.

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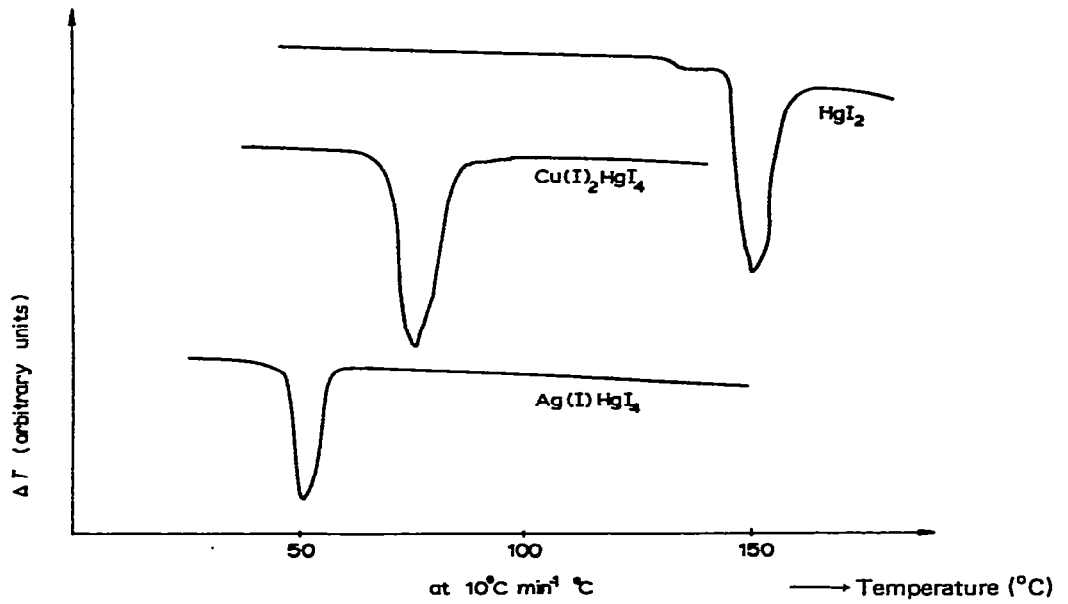

Fig. 1. Typical DTA results.

$Ag(I)_2HgI_4$ and $Cu(I)_2HgI_4$

The silver (I) salt has been the subject of fairly extensive investigations [4,5] and the transitions involved described as

$\beta \rightarrow \beta' \rightarrow \alpha$

We find the overall entropy change to be 15.7 J K^{-1} $mole^{-1}$ (close to $R\ln 6$) suggesting that we are measuring disordering of Ag(I) and Hg(II) over all

TABLE 1

Enthalpies, entropies and extrapolated onset temperatures for compounds used in this study

Compound	Ref.	ΔH (kJ $mole^{-1}$)	T_c (K)	ΔS (J K^{-1} $mole^{-1}$)	x	$R\ln x$ (J K^{-1} $mole^{-1}$)
$Ag(I)_2HgI_4$	This study	+5.09 (∓0.14)	324	+15.7 (∓0.42)	6	14.9
	5	+5.98	321	+18.6		
	6		318—325			
$Cu(I)_2HgI_4$	This study	+4.07 (∓0.06)	342	+11.9 (∓0.17)	4	11.5
	6		344			
HgI_2	This study	+13.13 (∓0.07)	416	+31.6 (∓0.16)		
	8		400			

available sites (viz. $\beta \rightarrow \alpha$). This is in contrast to the $Cu(I)HgI_4$ salt which gives an entropy of 11.9 J K^{-1} $mole^{-1}$ (close to $R\ln 4$), suggesting that less of the available sites are utilized in the phase transition of the copper complex.

HgI_2

The phase transition in HgI_2 is essentially of a different kind and involves the rearrangement of the tetrahedral red form of HgI_4 to a modification involving essentially linear molecular units of HgI_2 in the yellow high temperature phase [7,8]. We find the enthalpy associated with this transition to be 13.1 kJ $mole^{-1}$.

Other compounds

We have sought complexes containing the HgI_3^- anion; reports of solids containing this species are found in the old literature. We made attempts to prepare simple complexes of the type $Cu(I)HgI_3$, all of which were unsuccessful. However, a report by Taurins [9] that the dipositive amino acid complex of copper(II) with L-lysine $[Cu(L\text{-}lysO^+)_2]^{2+}$ was precipitated effectively by HgI_3^- seemed reliable and he further reported photochromism for this complex at ~110°C. We prepared this complex and found it to give three very weak peaks on DTA at 78(∓1), 99(∓1) and 125(∓1)°C, the peak at 125°C being concurrent with the photochromism.

Further studies of such phase transitions are in progress.

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