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THERMAL STUDIES OF URANIUM(V) CHLORIDE–TRICHLOROACRYLYL CHLORIDE AND URANIUM(VI) CHLORIDE–HEXACHLOROPROPENE

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ABSTRACT

The thermal properties of uranium(V) chloride–trichloroacrylyl chloride ($UCl_5 \cdot TCAC$, TCAC = trichloroacrylyl chloride: CCl_2=CClCOCl) and uranium(VI) chloride–hexachloropropene ($UCl_6 \cdot HCP$, HCP = hexachloropropene: CCl_2=$CClCCl_3$) have been studied by DSC techniques. The DSC curve of $UCl_5 \cdot TCAC$ exhibits a strong endothermic reaction in the 86–109 °C and a weak exothermic reaction in the 129–198 °C temperature ranges. The DSC curve of $UCl_6 \cdot HCP$ exhibits a strong endothermic reaction in the 134–146 °C and a strong exothermic reaction in the 148–163 °C temperature ranges.

INTRODUCTION

Uranium(V) chloride–trichloroacrylyl chloride ($UCl_5 \cdot TCAC$ [1]) and uranium(VI) chloride–hexachloropropene ($UCl_6 \cdot HCP$ [2]) have been prepared by the reaction of uranium trioxide and triuranium octoxide with hexachloropropene below 100 °C. They are sensitive to oxygen and moisture, so they must be stored and handled in inert atmospheres. Selbin et al. [1] have determined the melting point of $UCl_5 \cdot TCAC$ in a sealed capillary tube. Hermann and Suttle [3] have reported the preparation of UCl_4 from $UCl_5 \cdot TCAC$.

DSC techniques will be effective for the determination of thermal transformations [4]. The authors determined the thermal properties of $UCl_5 \cdot TCAC$ and $UCl_6 \cdot HCP$ by DSC.

EXPERIMENTAL

The adduct chlorides were synthesized according to methods previously reported [1,2].

Measurements were made using a Perkin-Elmer model 1B DSC. The adduct chlorides were examined at heating and cooling rates of 8 °C min^{-1}.

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The peak areas were determined with a planimeter and were calibrated with the heat of fusion of indium. After weighing the gold pans on a microbalance in an air atmosphere, they were transferred to a dry box. The adduct chlorides were sealed in the gold pans in the dry box to prevent oxidation and hydration. The humidity of the dry box was kept below 2 ppm with a purified nitrogen gas.

RESULTS AND DISCUSSION

DSC curve of $UCl_5 \cdot TCAC$

DSC curves of $UCl_5 \cdot TCAC$ are given in Fig. 1. The DSC curve of $UCl_5 \cdot TCAC$ heated to 250 °C is shown in Fig. 1A. The curve reveals a strong endothermic reaction in the 86–109 °C, and a weak exothermic one in the 129–198 °C temperature ranges.

Uranium(V) chloride–trichloroacrylyl chloride was heated to the final temperature of the endothermic peak as shown in Fig. 1B, and was then cooled to room temperature as shown in Fig. 1C. In this cooling curve an exothermic peak was observed in the 31–26 °C temperature range. From this information, the endothermic peaks of Figs. 1A and B are due to the fusion of $UCl_5 \cdot TCAC$, and the exothermic peak of Fig. 1C is caused by the recrystallization of the melted $UCl_5 \cdot TCAC$. In this thermal hysteresis, the fusion temperature in the heating curve and the recrystallization temperature in the cooling curve were different from each other.

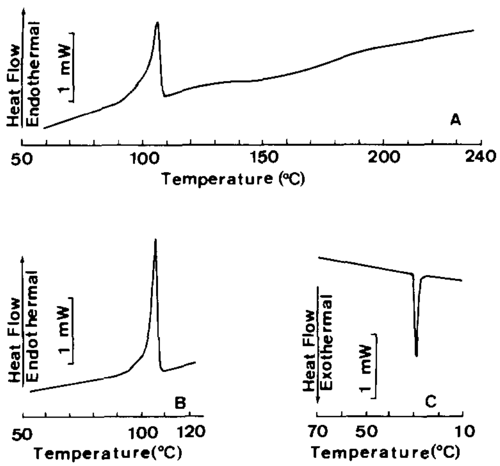

Fig. 1. DSC curves of uranium(V) chloride–trichloroacrylyl chloride. (A) Heating DSC curve up to 250 °C; (B) heating DSC curve up to 109 °C; (C) cooling DSC curve from 109 °C; scan speed, 8 °C min^{-1}; range, 4 mcal s^{-1}; chart speed, 20 mm min^{-1}.

There were no thermal transformations in the DSC curves cooling from 198 ° C for the chloride. The weak exothermic reaction of Fig. 1A is due to the thermal decomposition of fused $UCl_5 \cdot$ TCAC. This information suggests the following reaction [3] above 129 ° C:

$$UCl_5 \cdot CCl_2 = CClCOCl \rightarrow UCl_4 + CCl_2{=}CClCOCl + 1/2Cl_2 \qquad (1)$$

The fusion of UCl_4 was not observed in these measurements, since the melting temperature of UCl_4 is as high as 590 ° C.

The heat of fusion for $UCl_5 \cdot$ TCAC was determined from the peak area of the endothermic reaction in Fig. 1A. The enthalpy of fusion for $UCl_5 \cdot$ TCAC determined using DSC is 19.8 kJ mol^{-1}.

DSC curve of $UCl_6 \cdot$ HCP

DSC curves of $UCl_6 \cdot$ HCP are shown in Fig. 2. The DSC curve of $UCl_6 \cdot$ HCP heated to 200 ° C is shown in Fig. 2A. The DSC curve revealed a strong endothermic reaction in the 134–146 ° C and a strong exothermic reaction in the 148–163° C temperature ranges.

Uranium(VI) chloride–hexachloropropene was heated to the final temperature of the endothermic peak as shown in Fig. 2B, and was then cooled as shown in Fig. 2C. This cooling curve revealed an exothermic peak in the 118–105 ° C temperature range. From this information, the endothermic peaks of Figs. 2A and B are due to the fusion of $UCl_6 \cdot$ HCP, and the exothermic peak of Fig. 2C is caused by recrystallization of the melted $UCl_6 \cdot$ HCP. In this thermal hysteresis, the fusion temperature in the heating

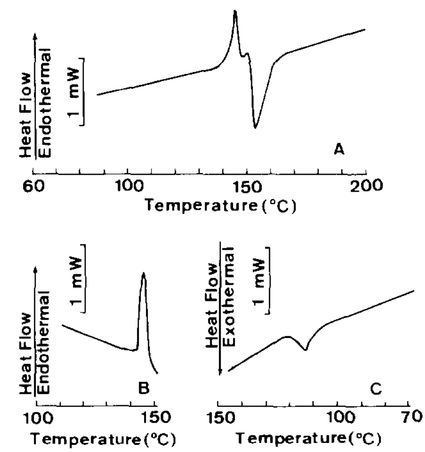

Fig. 2. DSC curves of uranium(VI) chloride–hexachloropropene. (A) Heating DSC curve up to 200 ° C; (B) heating DSC curve up to 146 ° C; (C) cooling DSC curve from 146 ° C; scan speed, 8 ° C min^{-1}; range, 4 mcal s^{-1}; chart speed, 20 mm min^{-1}.

curve and the recrystallization temperature in the cooling curve were different from each other. The endothermic peaks of the heating curves in Figs. 2A and B are due to the fusion of $UCl_6 \cdot HCP$, and the exothermic peak of the cooling curve in Fig. 2C is due to recrystallization of the melted $UCl_6 \cdot HCP$.

There were no thermal transformations in the DSC curve of this adduct chloride cooling from 163°C. From this information, the exothermic peak in Fig. 2A is due to the thermal decomposition of $UCl_6 \cdot HCP$. This exothermic reaction suggests that the following decomposition will occur above 148°C:

$$UCl_6 \cdot HCP \rightarrow UCl_4 + CCl_2{=}CCl \cdot CCl_3 + Cl_2 \qquad (2)$$

The heats of fusion and thermal decomposition for $UCl_6 \cdot HCP$ determined using DSC techniques are 5.9 and 12.9 kJ mol^{-1}, respectively.

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