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Note

THERMAL DECOMPOSITION OF CERIUM(IV), CERIUM(III), CHROMIUM(III) AND TITANIUM(IV) SULPHATES

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The thermal behaviour of transition metal sulphates is of interest due to the formation of different phases, such as sulphides, oxides during the decomposition, through the metal–sulphur complex oxide intermediates [1–5]. The desired products are generally obtained under controlled heating programmes and different atmospheres. Duval and Duval [6] have reported that Ce(III) sulphate is stable up to 845°C, but according to Wendlandt [7] it starts to decompose at 650°C. The aim of the present study is to determine the precise temperatures of dehydration of the sulphates and the thermal stabilities of the anhydrous sulphates. Reported in this paper are thermogravimetric and differential thermal analysis studies both in an oxidative atmosphere, air, and inert atmosphere, argon, of $Ce(SO_4)_2 \cdot 4\ H_2O$, $Ce_2(SO_4)_3 \cdot 14\ H_2O$, $Cr_2(SO_4)_3 \cdot 6\ H_2O$ and $TiOSO_4 \cdot H_2O$. The decomposition products are characterized by wet chemical analysis and X-ray powder diffraction patterns.

EXPERIMENTAL

The sulphates employed are commercially available compounds of acceptable purity. The TG studies in air were made on a Stanton recording thermobalance with 100 mg samples at a linear heating rate of 6°C min^{-1}. Simultaneous TG–DTA studies were carried out on a Mettler thermoanalyzer with 50–70 mg samples in an atmosphere of flowing argon at a heating rate of 4°C min^{-1}. The X-ray powder diffraction patterns were taken using CuK_α radiation.

RESULTS AND DISCUSSION

The thermogravimetric plot of a particular sulphate in air is similar to that in argon, suggesting that air apparently does not influence the course and

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products of decomposition of these sulphates. The TG and DTA plots in an atmosphere of argon are given in Figs. 1 and 2, respectively. As can be seen from the TG curve, $Ce(SO_4)_2 \cdot 4\ H_2O$ decomposes in four stages. It loses 9.0% weight in the temperature range 100–180°C, which corresponds to the calculated value of 8.9% for the removal of two molecules of water of hydration. The second stage begins at 250°C and continues up to 340°C, registering a further weight loss of 9.0% which agrees with the overall loss of 17.8% for the formation of anhydrous cerium(IV) sulphate. $Ce(SO_4)_2$ is stable up to 350°C. In the third stage, between 350 and 520°C, the anhydrous sulphate loses 11.0% weight which corresponds to the total weight loss of 31.0% for the formation of $CeO_2 \cdot 2\ Ce(SO_4)_2$. The pale yellow coloured basic sulphate thus formed loses sulphur dioxide and oxygen in the final stage, between 700 and 940°C, to give CeO_2, as evidenced by the total weight loss of 57.0%. The calculated weight loss for CeO_2 formation is 57.5%. Chemical analysis of the final product confirmed it to be CeO_2. Further, the X-ray powder patterns of the residue could be indexed on the basis of a face-centred cubic lattice of unit cell length 5.41 Å which agrees very well with the reported value of 5.42 Å [8].

The DTA plots (Fig. 2A) showed endothermic peaks at 120 and 320°C which are assigned to the stepwise removal of the water of hydration. The other endothermic effects at 400 and 500°C are attributed to the decomposition of $Ce(SO_4)_2$ to $CeO_2 \cdot 2\ Ce(SO_4)_2$. Though the TG curve indicates a single-step process, the appearance of two endothermic effects suggests the

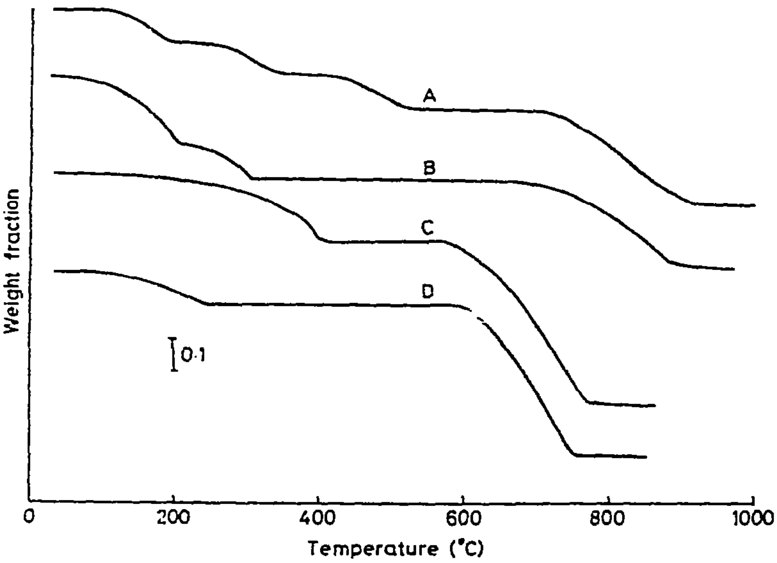

Fig. 1. TG plots of $Ce(SO_4)_2 \cdot 4\ H_2O$ (A), $Ce_2(SO_4)_3 \cdot 14\ H_2O$ (B), $Cr_2(SO_4)_3 \cdot 6\ H_2O$(C), and $TiOSO_4 \cdot H_2O$(D).

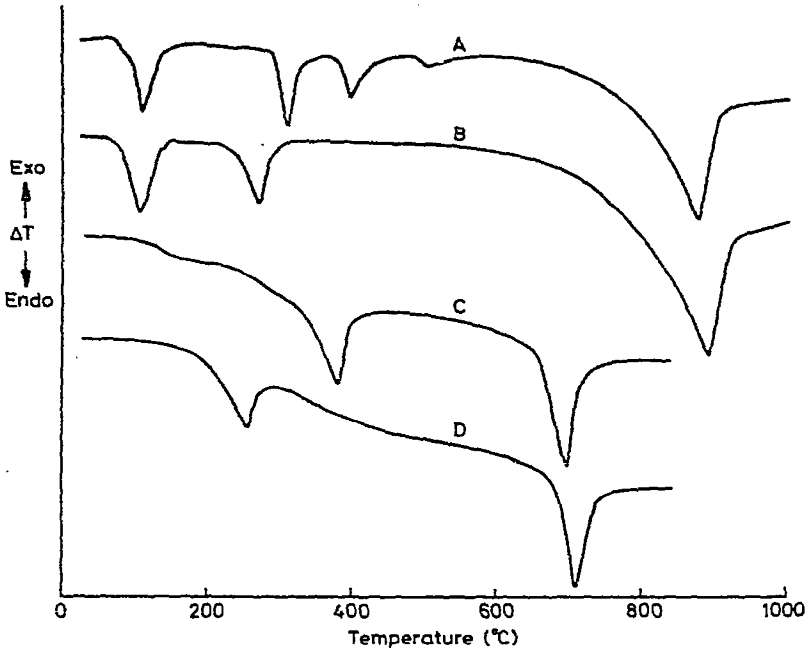

Fig. 2. DTA plots of $Ce(SO_4)_2 \cdot 4\ H_2O$(A), $Ce_2(SO_4)_3 \cdot 14\ H_2O$(B), $Cr_2(SO_4)_3 \cdot 6\ H_2O$(C), and $TiOSO_4 \cdot H_2O$(D).

complex nature of the basic sulphate formation. The final endotherm at 880°C is due to the decomposition of the basic sulphate to CeO_2.

In separate experiments, known amounts of $Ce(SO_4)_2 \cdot 4\ H_2O$ were heated to 340 and 520°C and were cooled. The anhydrous sulphate formed at 340°C rehydrates to give back the parent tetrahydrate. Likewise, the basic sulphate obtained at 520°C absorbs water on cooling to laboratory temperature giving a mixture of CeO_2 and $Ce(SO_4)_2 \cdot 4\ H_2O$.

The TG plot of $Ce_2(SO_4)_3 \cdot 14\ H_2O$ (Fig. 1B) shows that there are three distinct stages of decomposition; the corresponding temperatures are 50–190°C, 210–300°C and 700–920°C. The weight loss associated with the first stage is 20.0% which corresponds to the theoretical value of 19.8% for the loss of nine molecules of water. The second stage over the temperature range 210–300°C is accompanied by a further loss of 11.0% due to the formation of $Ce_2(SO_4)_3$. The calculated weight loss for the complete dehydration process is 31.7%. The DTA peaks observed at 150 and 275°C are attributed to the dehydration steps involving nine and five water molecules, respectively. On cooling, $Ce_2(SO_4)_3$ rehydrates to give the stable pentahydrate which, on exposure to open atmosphere for several days, is slowly converted into $Ce_2(SO_4)_3 \cdot 14\ H_2O$. The anhydrous Ce(III) sulphate is surprisingly very stable and undergoes oxidative decomposition in a single step to CeO_2 between 680 and 920°C. The observed weight loss of 57.0% is in good agreement with the calculated value of 57.5% for the formation of CeO_2 from $Ce_2(SO_4)_3 \cdot 14\ H_2O$. The chemical and X-ray analyses of the final residue confirmed it to be cerium(IV) oxide. The formation of Ce(IV) oxide during the decomposition of Ce(III) sulphate even in the inert atmosphere is attributed to the oxidation of Ce(III) by the evolved oxygen during the sulphate decomposition.

Chromium(III) sulphate hexahydrate decomposes in two stages: the first begins at 100°C with the gradual loss in weight and is complete at 400°C. At higher temperature, the weight loss is comparatively fast. The weight loss observed at 400°C was found to be 21.5%, which is in agreement with the calculated value of 21.6% for the complete dehydration process. The anhydrous $Cr_2(SO_4)_3$ is found to be hygroscopic and absorbs varied amounts of water molecules on exposure to the atmosphere. It decomposes in a single step in the temperature range 550–750°C, losing a total weight of 70.0% which corresponds to the expected value of 69.6% for the formation of Cr_2O_3 from $Cr_2(SO_4)_3 \cdot 6\ H_2O$. The final residue of the decomposition was analyzed by chemical and X-ray powder methods [9] and is confirmed to be Cr_2O_3. The DTA curve exhibited a gradual loss in the base line from the beginning with an endothermic peak maximum at 400°C which has been assigned to the dehydration process. The other endotherm at 700°C is attributed to the decomposition of $Cr_2(SO_4)_3$ to Cr_2O_3.

Titanyl sulphate monohydrate begins to dehydrate at 100°C. The loss in weight at the end of the first stage of decomposition (250°C) is 9.0%, which corresponds to the calculated value of 10.1% for the loss of a molecule of water. $TiOSO_4$ thus obtained is quite stable and apparently does not rehydrate on exposure to the atmosphere. It decomposes in the temperature range 575–750°C in a single step, registering a total loss of 55.0% which agrees with the value of 55.1% calculated for the formation of TiO_2. The final residue is found to be X-ray amorphous; however, chemical analysis confirmed it to be TiO_2. The DTA showed an endothermic effect at 252°C due to the dehydration and another endothermic peak at 720°C which is assigned to the decomposition of $TiOSO_4$ to TiO_2.

The energies of activation for the formation of metal oxides by the decomposition of the sulphates have been evaluated using the equation of Coats and Redfern [10] based on the final stage of the weight loss curves. The values are found to be 45, 47, 40 and 55 kcal $mole^{-1}$, respectively, for the reactions

$CeO_2 \cdot 2\ Ce(SO_4)_2 \rightarrow CeO_2$

$Ce_2(SO_4)_3 \rightarrow CeO_2$

$Cr_2(SO_4)_3 \rightarrow Cr_2O_3$

$TiOSO_4 \rightarrow TiO_2$

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