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Note

Study on the thermal decomposition of tetrahydrated ceric sulphate

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Abstract

The thermal decomposition behaviour of $Ce(SO_4)_2 \cdot 4H_2O$ has been studied by means of simultaneous TG–DTA, TG–DTG and DSC; all the intermediate and end products were characterized by chemical analysis, magnetic moment measurements and X-ray powder diffraction. The activation energy and the order of the decomposition reaction were determined according to the method of Freeman and Carroll: for $Ce(SO_4)_2$ these were 302.2 kJ mol^{-1} and 1.91; for $Ce_2(SO_4)_3$, 298.4 kJ mol^{-1} and 0.383. The dehydration enthalpy and decomposition enthalpy have also been determined.

INTRODUCTION

The literature survey over along period of time, on the thermodecomposition of tetrahydrated ceric sulphate has revealed obvious disagreement among different authors; the reports of intermediate products are also significantly different. An earlier study reported that $Ce(SO_4)_2 \cdot 4H_2O$ decomposed into $3CeO_2 \cdot SO_3$ at 195°C [1], but studies made by Golourya and Trofimov have shown that this high valence cerium compound would be converted first into the anhydrous salt and would then decompose into $CeOSO_4$ and $CeOSO_4$–$Ce(SO_4)_2$; the two end products were CeO_2 and SO_3 [2,3]. The description of the thermal decomposition process of tetrahydrated ceric sulphate is ambiguous even in the authoritative handbook [4]. Hitherto all the work in this field has reported that the oxidation state of cerium does not change, but a recent study of ceric sulphate by X-ray photoelectron spectroscopy (XPS) indicated that the valency of cerium is dependent on the temperature [5]. In the present work an extensive investigation of the thermal decomposition of tetrahydrated ceric sulphate has been carried out by employing simultaneous TG–DTG, DG–DTA and DSC methods, and all the intermediate products and the end products were characterized by means of chemical analysis, X-ray powder diffraction

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and magnetic moment measurements; the mechanism of the decomposition has been established and the evaluation of the kinetic parameters E, n and ΔH has been achieved by non-isothermal methods. Our results also indicate that the oxidation state of cerium is variable during the decomposition procedure, and this constitutes the first report on the phenomenon of the thermal behaviour of ceric sulphates.

EXPERIMENTAL

Tetrahydrated ceric sulphate (A.R.) was pre-dried in a vacuum desiccator containing phosphorus pentoxide. The composition was consistent with the percentages found in the formula $Ce(SO_4)_2 \cdot 4H_2O$.

Cerium(IV) was determined by iodometric titration. A known aliquot was taken in a conical flask, 1 g of solid KI (A.R.) was added and the liberated iodine was titrated with standard thiosulphate solution in 0.2 N acid medium, using starch solution as indicator. Cerium(III) was determined by complexometric titration with standard EDTA solution, using xylenol orange as indicator. The sulphate content was determined by the standard barium sulphate method, and the water contents of the compounds were determined from the TG curves.

Simultaneous TG–DTG curves were recorded on a Dupont 1090 thermogravimeter, and simultaneous TG–DTA curves were recorded on a DCT-2 thermobalance (China); α-Al_2O_3 was used as reference material in both determinations. Samples of about 10 mg were placed in a platinum crucible and heated at a rate of 10°C min^{-1} in an air atmosphere from room temperature up to 1000°C (flow rate 60 ml min^{-1}) at ambient pressure.

DSC was carried out on a Dupont 910 differential scanning calorimeter, which was calibrated using high purity tin as a standard; a weighed amount of the tetrahydrated ceric sulphate (3 mg) was heated from room temperature to 600°C in an air atmosphere (flow rate 30 ml min^{-1}).

X-ray powder diffraction patterns of the decomposition products were obtained with a D/max-III diffractometer (Japan); the Bragg Brentano arrangement was adopted using Cu K_α radiation ($\lambda = 1.541$ Å).

RESULTS AND DISCUSSION

Figure 1 shows the simultaneous DG–DTA and DG–DTG curves, from which it can be seen that the $Ce(SO_4)_2 \cdot 4H_2O$ commences dehydration at 98°C; this continues up to 170°C, and an endothermic peak appears within the temperature range, corresponding to the loss of the first two molecules of coordinated water. The next step of dehydration occurs from 170 to 322°C, and this corresponds to the loss of another two molecules of coordinated water. The third step of weight loss in the TG curve appears in

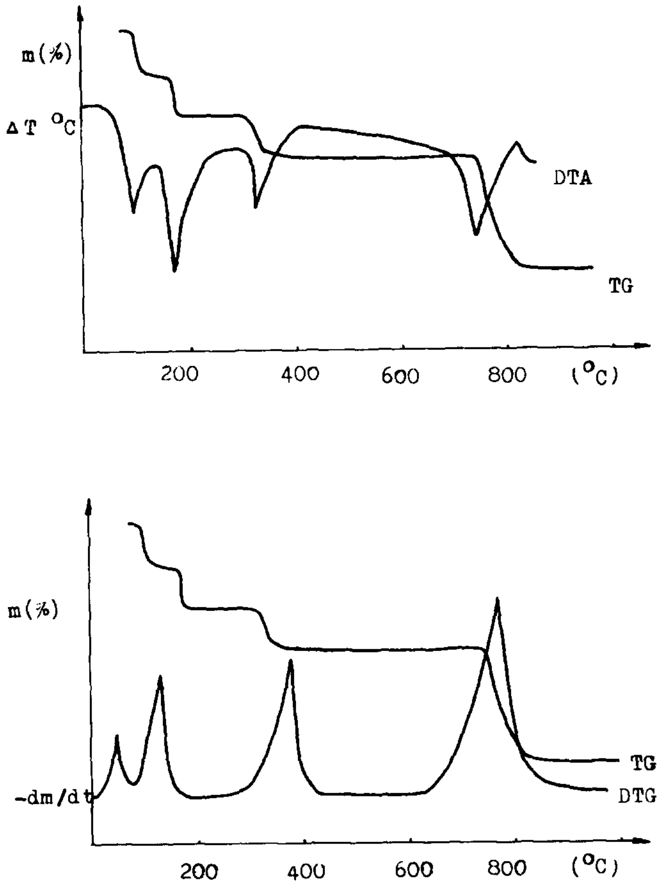

Fig. 1. Simultaneous TG–DTA and TG–DTG curves for $Ce(SO_4)_2 \cdot 4H_2O$ at a heating rate of 10°C min^{-1}.

the temperature range 459–495°C; in addition, an endothermic peak is observed in the DTA curve at 450–495°C, which is due to the reduction of Ce(IV) to Ce(III) sulphate, giving rise to O_2 and SO_3. The last decomposition step is that of anhydrous cerium(III) sulphate, which occurs in the

TABLE 1

Temperature range (°C) and weight loss (%) in the TG curve

Temperature range	Decomposition step	Weight loss obs. (calc.)
98–170	Loss of two molecules of water	9.32 (8.91)
170–322	Loss of two molecules of water	8.90 (8.91)
459–495	Reduction of Ce(IV) sulphate	11.93 (11.88)
749–830	Decomposition of Ce(III) sulphate	27.23 (27.72)

TABLE 2

Results of chemical analysis and magnetic moment of the decomposition products

Firing temperature (°C)	Supposed product	Magnetic moment (B.M.)	Ce(IV) / Σ Ce (%)	Σ Ce (%)		SO_4 (%)		Ratio SO_4:Ce
				Found	Calc	Found	Calc	
250	$Ce(SO_4)_2$	0.03	98.70	41.71	42.17	57.46	57.83	2.01:1
490	$Ce_2(SO_4)_3$	2.51	0.00	49.83	49.50	50.17	50.20	1.49:1
850	CeO_2	0.01	99.62	80.69	80.39	0.13	0.00	0

temperature range 750–830°C with the formation of the end product CeO_2. In the DTA curve, a weak exothermic peak is observed at about 800°C, which is probably due to the oxidation reaction of Ce(III) → Ce(IV) [6]. The temperature ranges of the decomposition associated with the mass loss observed in the TG curve are shown in Table 1.

In order to identify the intermediate and end products, about 1 g of tetrahydrated ceric sulphate was loaded into a crucible and calcined up to a temperature agreeing with each corresponding temperature range of Table 1 for several hours, and the products were then identified by chemical analysis and X-ray diffraction. Table 2 shows the results of chemical analysis and the magnetic moments of the products.

The results of X-ray powder diffraction (Table 3) indicated that Ce(III) sulphate had been formed in the thermal decomposition procedure, which also confirmed that the oxidation state of cerium could change during the thermal decomposition. On the basis of all the results mentioned above, the thermal decomposition of tetrahydrated ceric sulphate appears to proceed by the following stages:

$$Ce(SO_4)_2 \cdot 4H_2O \rightarrow Ce(SO_4)_2 \cdot 2H_2O + 2H_2O \tag{1}$$

$$Ce(SO_4)_2 \cdot 2H_2O \rightarrow Ce(SO_4)_2 + 2H_2O \tag{2}$$

$$2Ce(SO_4)_2 \rightarrow Ce_2(SO_4)_3 + SO_3 + 0.5O_2 \tag{3}$$

$$Ce_2(SO_4)_3 \rightarrow 2CeO_2 + 2SO_3 + SO_2 \tag{4}$$

TABLE 3

X-ray diffraction data of the decomposition products

Compound		X-ray diffraction data							
		Found				Literature [7]			
$Ce(SO_4)_2$	d (Å)	3.31	2.11	6.67	4.62	3.44	2.11	6.69	4.65
	(I/I_0) (%)	90	90	80	100	100	100	90	90
$Ce_2(SO_4)_3$	d (Å)	4.99	2.84	3.47	3.02	5.05	2.85	3.55	3.03
	I/I_0 (%)	100	80	80	80	100	100	80	60
CeO_2	d (Å)	3.13	1.91	1.63	2.75	3.12	1.91	1.63	2.71
	I/I_0 (%)	100	50	40	30	100	51	40	39

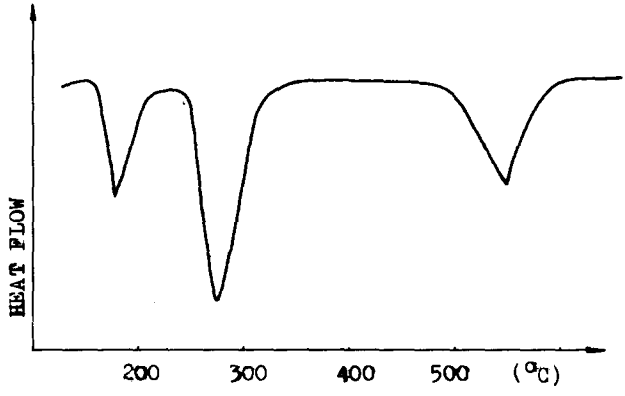

Fig. 2. DSC curve for $Ce(SO_4)_2 \cdot 4H_2O$.

TABLE 4

Enthalpy changes of the thermal decomposition

Step	Reaction	ΔH (kJ mol^{-1})
1	$Ce(SO_4)_2 \cdot 4H_2O \rightarrow Ce(SO_4)_2 \cdot 2H_2O + 2H_2O$	29.73
2	$Ce(SO_4)_2 \cdot 2H_2O \rightarrow Ce(SO_4)_2 + 2H_2O$	134.1
3	$2Ce(SO_4)_2 \rightarrow Ce_2(SO_4)_3 + SO_3 + 0.5O_2$	52.91

The enthalpy change for loss of water and the enthalpy change of reaction (3) were determined on the basis of the DSC curve (Fig. 2), and the results are given in Table 4. The dehydration enthalpy of the second step appears to be reasonably high, which indicates that these two molecules of water are more firmly attached to the Ce(IV) than the other two, i.e. there is a strong coodination bond between two H_2O molecules and Ce(IV). The enthalpy change of reduction of Ce(IV) to Ce(III) sulphate is rather low when compared with the enthalpy change for loss of water; this indicates that the high oxidation state of cerium in the sulphate salt makes it unstable at such a high temperature.

The kinetic parameters for the thermal decomposition of ceric sulphate were evaluated by the method of Freeman and Carroll [8]. For reaction (3), the activation energy E_1 is 302.2 kJ mol^{-1}, and the order of the reaction is 1.91; for reaction (4), the activation energy E_2 is 298.4 kJ mol^{-1}, and the order of the reaction is 0.383.

ACKNOWLEDGEMENT

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CONCLUSIONS

(1) An extensive study of the thermal decomposition behaviour of tetrahydrated ceric sulphate was performed.

(2) The intermediate and end products were identified by means of chemical analysis, X-ray powder diffraction and magnetic moment measurements; all the results indicate that the oxidation state of cerium is changed in the thermal decomposition procedure, and this is the first report of this phenomenon.

(3) The values of the non-isothermal kinetic parameters of the decomposition were evaluated according to Freeman and Carroll's method; the values of enthalpy changes of dehydration and decomposition of cerium(IV) sulphate were also determined.

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