J. Inorg. Nucl. Chem., 1958, Vol. 7, pp. 51 to 54. Pergamon Press Ltd., London

THE THERMAL DECOMPOSITION OF YTTRIUM AND THE RARE EARTH METAL SULPHATE HYDRATES

WESLEY W. WENDLANDT
Department of Chemistry and Chemical Engineering, Texas Technological College,
Lubbock, Texas

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Abstract—The thermal decomposition of lanthanum, cerium (III), praseodymium, neodymium, samarium, gadolinium, dysprosium, holmium, erbium, ytterbium, and yttrium sulphate hydrates was studied on the thermobalance. The formation of intermediate hydrates was more pronounced with the lighter rare earth elements than with the heavier ones. The first weight loss temperatures for the hydrated salts ranged from 40 to 110°C, while the minimum temperatures for the anhydrous metal sulphate levels ranged from 155 to 295°C.

THE rare earth metal sulphates crystallize from aqueous solution at room temperature mainly as the 8-hydrates. On heating the 8-hydrates in air, they evolve the water of hydration readily. The thermal decomposition pattern goes through the following stages: metal sulphate hydrate $\xrightarrow{I}$ anhydrous metal sulphate $\xrightarrow{II}$ basic metal sulphate $\xrightarrow{III}$ metal oxide. Some question exists as to the temperature limits for the various stages of decomposition. The temperature limits for stage I have been set between 250 to 650°C;(1) stage II about 900°C;(2) and stage III at about 1600°C. The values for the last two stages are known with far less certainty than for the first stage.

Since the rare earth metal nitrate and chloride hydrates(3,4) have previously been studied on the thermobalance, it was of interest to extend these studies to include the metal sulphate hydrates as well. Because the maximum temperature limit of the thermobalance was ~900°C, this study was confined only to the determination of the temperature limits for the dehydration process. When a higher temperature furnace becomes available, it is planned to study the thermal decomposition of the anhydrous metal sulphates as well.

EXPERIMENTAL

Thermobalance

An automatic recording thermobalance with a linear heating rate of 5·4°C per minute was used.(5) Sample sizes ranged from 85 to 100 mg and were run in duplicate or triplicate. During the pyrolysis, a slow stream of air was passed through the furnace.

Chemicals

All of the rare earth compounds, except cerium, were obtained as the oxides of 99·9 per cent purity from the Lindsay Chemical Co., West Chicago, Ill.; Research

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(1) J. W. MELLOR, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry* Vol. V, Chap. XXXVIII. Longmans, Green & Co., London (1924).
(2) L. WOHLER and M. GRUNZWEIG, *Ber. dtsch. chem. Ges.* **46,** 1726 (1913).
(3) W. W. WENDLANDT, *Anal. Chim. Acta* **15,** 435 (1956).
(4) W. W. WENDLANDT, *J. inorg. nucl. Chem.* **5,** 118 (1957).
(5) W. W. WENDLANDT, *Analyt. Chem.* **30,** 56 (1958).

Chemicals, Inc., Burbank, Calif.; and Research Laboratories, Inc., Newtown, Ohio. The cerium salt was obtained as $CeCl_3 \cdot 6H_2O$ from the above sources. The purity of the compounds was that listed by the supplier.

Preparation of the rare earth sulphate hydrates

The metal sulphate hydrates, except cerium, were prepared by dissolving about 0·3 g of the metal oxides in 20 ml of hot 3M sulphuric acid. After dissolution, the resulting solutions were filtered and placed in a vacuum desiccator over concentrated sulphuric acid and allowed to crystallize. The crystals were filtered off into sintered porcelain crucibles, washed twice with 10 ml of water and once with 10 ml of 95 per cent ethyl alcohol. After air drying for 4 hr the crystals were ground to a fine powder and decomposed on the thermobalance.

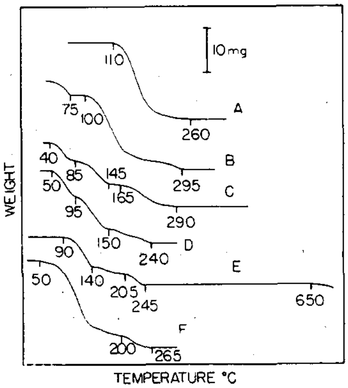

FIG. 1.—Thermal decomposition curves of the metal sulphate hydrates.
A. $Gd_2(SO_4)_3 \cdot 8H_2O$
B. $Sm_2(SO_4)_3 \cdot 8H_2O$
C. $Nd_2(SO_4)_3 \cdot 8H_2O$
D. $Pr_2(SO_4)_3 \cdot 8H_2O$
E. $Ce_2(SO_4)_3 \cdot 5H_2O$
F. $La_2(SO_4)_3 \cdot 9H_2O$

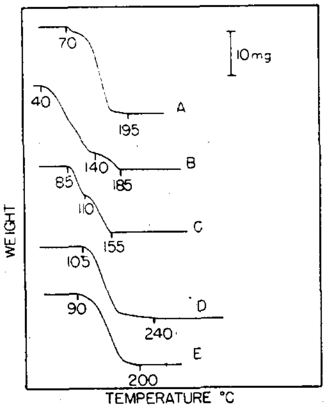

FIG. 2.—Thermal decomposition curves of the metal sulphate hydrates.
A. $Y_2(SO_4)_3 \cdot 8H_2O$
B. $Yb_2(SO_4)_3 \cdot 11H_2O$
C. $Er_2(SO_4)_3 \cdot 8H_2O$
D. $Ho_2(SO_4)_3 \cdot 8H_2O$
E. $Dy_2(SO_4)_3 \cdot 8H_2O$

Cerium sulphate was prepared in a similar manner except that the chloride was first treated with 5 ml of 10 M sulphuric acid, heated to expel the hydrogen chloride gas, 20 ml of water was added, and the resulting solution allowed to crystallize in a desiccator.

DISCUSSION

The thermal decomposition curves of the yttrium and rare earth sulphate hydrates are given in Figs. 1 and 2 with the composition data given in Table 1.

Even with the fairly rapid heating rate employed, intermediate hydrates containing 5 and 2 moles of water per mole of metal sulphate were observed. This tendency towards intermediate hydrate formation was more pronounced with the lighter rare earths; i.e. those from lanthanum to samarium. While those above samarium, with only two exceptions, decomposed directly to the anhydrous metal sulphates.

In only one case was decomposition of the anhydrous metal sulphate noted. This was with cerium (III) sulphate where sulphur trioxide began to come off at 650°C to form the basic sulphate. From the study of the thermal decomposition of cerium

(III) nitrate 6-hydrate,[(3)] such behaviour was expected to occur at a lower temperature with cerium (III) sulphate than with the other rare earth metal sulphates.

TABLE 1.—THE THERMAL DECOMPOSITION OF THE RARE EARTH SULPHATES; COMPOSITION DATA

Rare earth metal	$M_2(SO_4)_3{\cdot}8H_2O$		Composition, % $M_2(SO_4)_3$ $M_2(SO_4)_3{\cdot}5H_2O$		$M_2(SO_4)_3{\cdot}2H_2O$	
	Theor.	Found	Theor.	Found	Theor.	Found
Lanthanum	77·72($9H_2O$)	77·7 77·6			94·01	95·3 95·5
Cerium (III)			86·32	86·5 86·7	94·04	94·4 95·0
Praseodymium	79·81	79·3 79·3	86·35	85·6 85·4		
Neodymium	80·00	80·8 80·6	86·49	86·3 86·9	94·12	93·5 94·0
Samarium	80·34	81·1 80·5				
Gadolinium	80·68	81·1 81·4				
Dysprosium	80·96	80·9 81·6				
Holmium	81·09	81·5 81·4				
Erbium	81·20	81·3 81·0	87·36	88·5 87·8		
Ytterbium	76·19($11H_2O$)	76·3 74·5			92·82	93·5 93·6
Yttrium	76·38	77·0 77·2				

Lanthanum sulphate (Fig. 1/*F*).

According to the composition data in Table 1, lanthanum sulphate crystallized from solution as $La_2(SO_4)_3{\cdot}9H_2O$ and not as the 8-hydrate. Such a hydrate is known.[(6)] The first weight loss began at 50°C with a break in the curve at 200°C which corresponded approximately to the 2-hydrate. The salt was completely dehydrated at 265°C, much lower than the previously reported 600°C.[(1)]

[(6)] R. C. VICKERY, *Chemistry of the Lanthanons* p. 235. Academic Press, New York (1953).

Cerium (III) *sulphate* (Fig. 1/*E*).

The 5-hydrate, instead of the 8-hydrate, was crystallized out of solution. The first weight loss of the 5-hydrate was observed at 90°C with an intermediate break in the curve at 140°C which corresponded approximately to the 2-hydrate. The anhydrous metal sulphate weight level began at 245°C. At 650°C the metal sulphate began to lose SO_3 to form a basic salt. However, the pyrolysis was not completed far enough to obtain the basic metal sulphate weight level.

Praseodymium sulphate (Fig. 1/*D*).

The 8-hydrate began to lose weight at 50°C to give a break in the curve at 95°C which corresponded approximately to the 5-hydrate. Another break in the curve was observed at 150°C but the composition did not correspond to the stoicheiometry for the 2-hydrate. The anhydrous metal sulphate level began at 240°C.

Neodymium sulphate (Fig. 1/*C*).

The 8-hydrate began to lose weight at 40°C. Two intermediate breaks in the curve were observed, one at 85°C and the other at 145°C, corresponding to the 5- and 2-hydrates, respectively. The anhydrous metal sulphate level began at 290°C.

Samarium sulphate (Fig. 1/*B*).

The 8-hydrate, after losing loosely held water, began to decompose at 100°C. The anhydrous metal sulphate level was obtained at 295°C. Unlike the other lighter rare earths, breaks in the curve were not observed which would indicate intermediate hydrates.

Ytterbium sulphates (Fig. 2/*B*).

The composition data for ytterbium sulphate corresponded to that of $Yb_2(SO_4)_3 \cdot 11H_2O$, rather than the 8-hydrate. The thermal decomposition curve shows that the crystallized salt is probably a definite hydrate. If the salt were the 8-hydrate containing occluded water, a curve similar to that of samarium sulphate (Fig. 1/*B*) would have been obtained. The 11-hydrate began to lose water at 40°C, somewhat lower than the initial dehydration temperatures for the other heavier rare earth sulphate hydrates. A break appeared at 140°C which corresponded approximately to the 2-hydrate. The anhydrous metal sulphate level began at 185°C.

Other metal sulphates

The gadolinium (Fig. 1/*C*), dysprosium (Fig. 2/*E*), holmium (Fig. 2/*D*), and yttrium sulphate 8-hydrates (Fig. 2/*A*) decomposed directly to yield the anhydrous metal sulphates without any evidence for the formation of intermediate hydrates. The thermal decomposition curve for erbium sulphate 8-hydrate (Fig. 2/*C*) had a break at 110°C which corresponded to the 5-hydrate. Decomposition of this hydrate resulted in the formation of the anhydrous metal sulphate.