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STUDIES ON LANTHANOID SULPHITES. PART IV. THERMAL DECOMPOSITION OF ERBIUM SULPHITE TRIHYDRATE UNDER VARIOUS EXPERIMENTAL CONDITIONS

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ABSTRACT

Thermal behaviour of $Er_2(SO_3)_3 \cdot 3H_2O$ has been studied by means of TG, DTG, DTA, DSC and EGA techniques. Experimental conditions were also varied, viz. sample size, heating rate and the atmosphere.

The dehydration starts slowly above 150°C but the release of water is rapid around 250°C. SO_2 gas is evolved slowly and simultaneously with H_2O. The anhydrous sulphite is formed below 300°C after which it decomposes through several reactions accompanied by a release of mainly SO_2, but also a small amount of SO_3 near 650°C. In air, there is a clear plateau in the TG curve between 600 and 800°C; the weight loss involved depends strongly on the sample size and heating rate, however. A plausible explanation for the plateau is the formation of a mixture of $Er_2(SO_4)_3$, $Er_2O(SO_4)_2$ and $Er_2O_2SO_4$. The next plateau around 900 - 1000°C corresponds to $Er_2O_2SO_4$. In nitrogen atmosphere, the first plateau after the anhydrous sulphite appears later in the weight scale as compared to air. Although the position of the plateau corresponds to the sesquisulphide, it is according to X-ray diffraction results a mixture of $Er_2O_2SO_4$ and Er_2O_3. In both air and nitrogen, the final reaction step above 1000°C is the formation of Er_2O_3.

INTRODUCTION

In the two preceding parts of this series (refs. 1, 2) we have reported structural and thermoanalytical data for the compounds $Ln_2(SO_3)_3 \cdot nH_2O$ (n = 3, 6 and Ln = Sm - Dy). It was found that after dehydration the thermal degradation is a complex process where disproportion and dissociation may simultaneously take place, their relative amounts depending on the experimental conditions and on the lanthanoid ion. The results obtained by Moskalenko et al. (Refs. 3 - 5) are generally in good agreement with our data although small differences due to experimental conditions may be noted (Ref. 6).

In order to further study the effects of experimental conditions and the role of the lanthanoid ion, the present investigation was undertaken.

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EXPERIMENTAL

Erbium sulphite trihydrate was prepared by dissolving Er_2O_3 into aqueous solution of SO_2 at room temperature. Subsequently the temperature was raised to 70°C which caused the microcrystalline $Er_2(SO_3)_3\cdot3H_2O$ to precipitate (Ref. 1). X-ray diffraction technique was used to characterize the precipitate.

A Mettler thermoanalyzer TA-1 was used to obtain simultaneous recording of the TG, DTG and DTA curves. The furnace was supplied with either a dynamic air or dynamic nitrogen atmosphere, with flow rate of 95 cm^3/min. The sample size varied between 20 and 200 mg and heating rate between 2 and 15°C/min. The highest temperature reached was 1600°C. Standard platinum crucibles were employed and alumina was used as reference material in the DTA measurements.

In addition, the Perkin-Elmer TGS-2, DTA 1700 and DSC-4 instruments were used to obtain in some cases the TG, DTA and DSC curves, respectively. A Netzsch STA 429 thermoanalyzer with Balzers QMG 511 mass spectrometer was used in one measurement. The sample size was 25.6 mg, heating rate 10°C/min and atmosphere static air. Crucible material was aluminium oxide. In mass spectrometer the vacuum was 2.5 10^{-5} mbar and following mass numbers were recorded: 16, 18, 34, 48, 64, 80.

RESULTS

Simultaneous TG, DTG and DTA study

Figures 1a and 1b give the overall decomposition scheme of $Er_2(SO_3)_3\cdot3H_2O$ when a small sample size (20 mg) and a slow heating rate ($2^oC min^{-1}$) are employed. The first reaction (1) both in air and nitrogen is the release of water in a single-step process. The anhydrous sulphite formed around 250°C is not stable in air, however, but starts to decompose slowly until 450°C where the reaction rate increases.

The exothermic reaction (2) in air leads to a clear plateau between 615 and 770°C; the weight change does not correspond to any simple process, however. The remaining steps (3 and 4) are endothermic and lead to the formation of the oxysulphate and oxide, respectively.

In nitrogen the degradation leads also to the sesquioxide as the final product above 1000°C but the intermediate reactions are different. Especially noteworthy is the fact that the degradation of anhydrous sulphite goes beyond the oxysulphate level as seen in Fig. 1b (step 2).

Effect of experimental conditions

As the experimental conditions obviously had a significant effect on the reaction mechanism, a series of experiments was planned where the effects of sample weight, heating rate and atmosphere were studied.

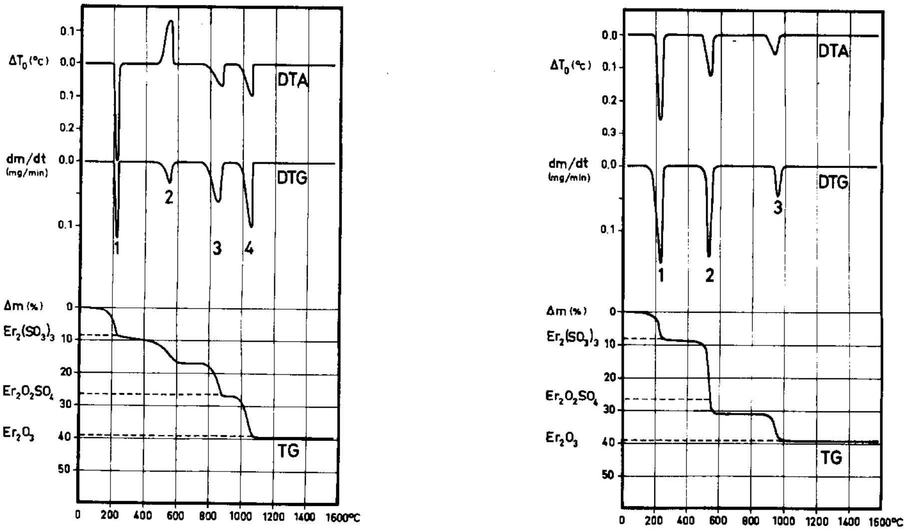

Fig. 1. TG, DTG and DTA curves of $Er_2(SC_3)_3\cdot 3H_2O$ in a) air (left) and b) nitrogen (right). The instrument is Mettler TA-1. For other details, see the text.

The effect of sample weight (20 - 200 mg) and heating rate (2 - 10 °C min^{-1}) on the TG curves in air is shown in Figure 2. Besides having the expected effect on the decomposition temperatures, these factors influence greatly the reaction mechanism when the anhydrous sulphite is decomposed to oxysulphate (steps 2 and 3 of Fig. 1). When a suitable sample weight / heating rate combination is used (e.g. 20 mg/10°C min^{-1}) the intermediate step (3) is not visible in the curves but the reaction proceeds directly from $Er_2(SO_3)_3$ to $Er_2O_2SO_4$.

In all experiments the dehydration reaction appeared as a single step process but a separate DSC study showed that at least under some experimental conditions it consists of several steps in the temperature range 130 - 300 °C (Fig. 3).

Further experiments using a separate TG apparatus confirmed the findings summarized in Fig. 2. By changing the sample weight / heating rate combination the reaction $Er_2(SO_3)_3 \rightarrow Er_2O_2SO_4$ in air may take quite different routes (cf. Fig. 4b). In nitrogen (Fig. 4a) the variations due to experimental conditions are smaller but on the other hand, the end product corresponds to a

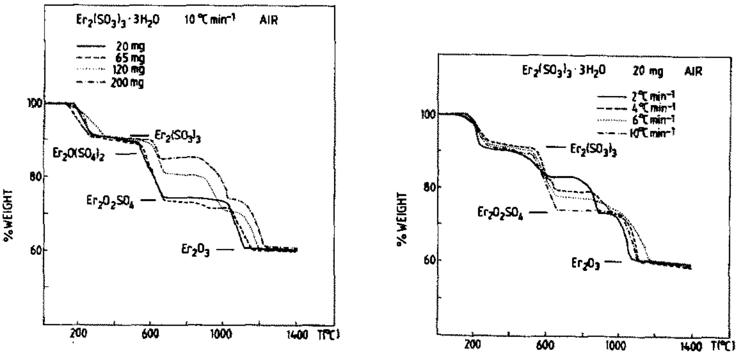

Fig. 2. The effect of sample weight and heating rate on the TG curves of $Er_2(SO_3)_3 \cdot 3H_2O$ in air.

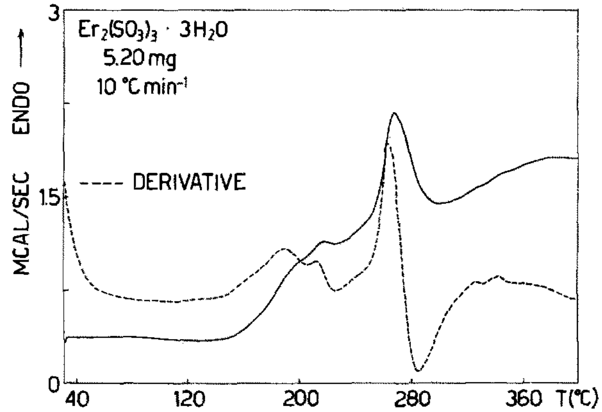

Fig. 3. DSC curve showing the dehydration of $Er_2(SO_3)_3 \cdot 3H_2O$.

weight loss larger than that calculated for $Er_2O_2SO_4$. In fact, the observed weight loss in the plateau extending over 200 degrees corresponds very closely to the formula Er_2S_3.

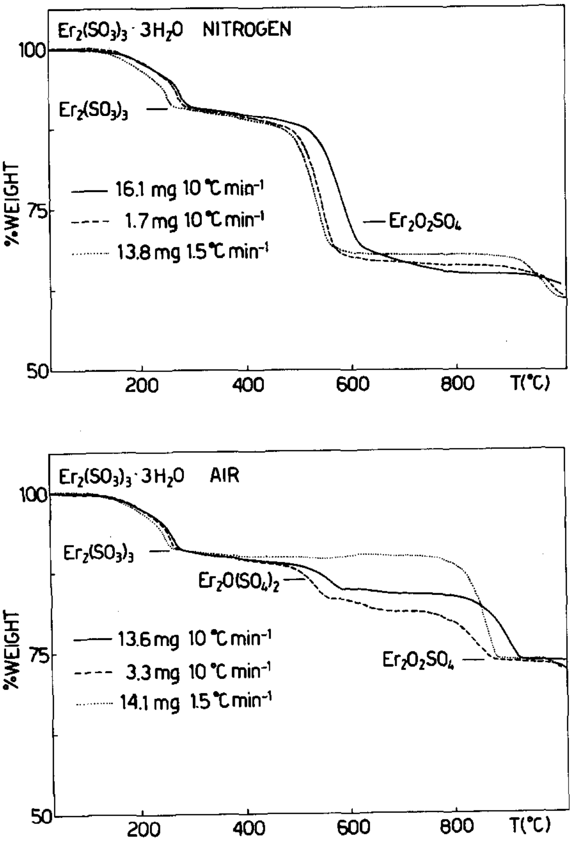

Fig. 4. TG curves of $Er_2(SO_3)_3\cdot 3H_2O$ recorded under various experimental conditions with a Perkin-Elmer TGS-2 instrument. Atmosphere: a) dynamic nitrogen (above) and b) dynamic air (below).

Reaction mechanism

As discussed earlier (Ref. 1), several competing reactions are possible during the thermal degradation of rare earth sulphites. In the case of erbium, these include (i) disproportionation: $4Er_2(SO_3)_3 \rightarrow 3Er_2(SO_4)_3 + Er_2S_3$, and (ii) dissociation: $Er_2(SO_3)_3 \xrightarrow{(O)} Er_2O(SO_4)_2 + SO_2$. Er_2S_3 and $Er_2O(SO_4)_2$ may react further in oxidative environment to form the (di)oxysulphate $Er_2O_2SO_4$; $Er_2(SO_4)_3$ forms the same product through the release of SO_3. Finally, the sesquioxide appears as stable end product at higher temperatures.

On the basis of the TG studies in air as well as EGA measurements (Ref. 7), it is obvious that SO_2 is being released already simultaneously with water indicating the instability of the anhydrous sulphite. The intermediate plateau which is then formed at 600 - 800 °C through the decomposition of the sulphite is a mixture of $Er_2(SO_4)_3$, $Er_2O(SO_4)_2$ and $Er_2O_2SO_4$; the composition is very sensitive to experimental conditions. Only at 900 - 1000°C the first stable phase $Er_2O_2SO_4$ is formed.

In nitrogen, the position of the intermediate level before the oxide corresponds very closely to Er_2S_3 but X-ray diffraction study showed it to contain $Er_2O_2SO_4$ and Er_2O_3. The oxide level is reached in nitrogen somewhat earlier than in air where it appears first around 1100°C.

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