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STUDIES ON LANTHANOID SULPHITES. V. THERMAL DECOMPOSITION OF CERIUM AND NEODYMIUM SULPHITES*

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ABSTRACT

The preparation and thermal behaviour of $Ce_2(SO_3)_3 \cdot 3H_2O$, $Nd_2(SO_3)_3 \cdot 6H_2O$ and $Nd_2(SO_3)_3$ have been studied. Cerium sulphite undergoes first dehydration which is followed by decomposition to CeO_2 in the temperature range 500 - 850 °C. The decomposition involves two intermediate phases both in air and nitrogen. According to the TG curves the phases in air are $Ce_2(SO_3)_2SO_4$ and $Ce_2SO_3(SO_4)_2$. In nitrogen, $Ce_2O_2SO_4$ was identified and this provides a synthetic route to cerium oxysulphate.

Neodymium sulphite decomposes to $Nd_2O_2SO_4$ when heated in air or in nitrogen up to 950°C. The intermediate levels observed do not correspond to single phases, and the reaction mechanism depends strongly on the experimental conditions.

INTRODUCTION

Among the lanthanoid sulphite hydrates, the compounds formed by trivalent cerium and neodymium are difficult to prepare as stoichiometric crystalline phases. This has probably been the reason for their incomplete thermoanalytical characterization as compared to other sulphites.

The literature on cerium sulphites is very limited; it has been recently reviewed in the Gmelin Handbook (Ref. 2). Even the water content of solid $Ce_2(SO_3)_3$ hydrate seems to be uncertain. Detailed data on neodymium sulphites are also lacking in the literature where only the hexahydrate has been reported (Ref. 3).

The present work is a continuation of our studies on the preparation, thermoanalytical characterization and structural chemistry of the lanthanoid sulphites.

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*For part IV, see ref. 1.

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EXPERIMENTAL

The sulphites were synthesized by passing SO_2 through aqueous suspensions of $CeOHCO_3$ and Nd_2O_3. The SO_2 excess was removed by passing nitrogen through the solution, resulting in the precipitation of sulphite hydrates. In the case of cerium the product was trihydrate regardless of the precipitation temperature (10 - 95 °C). Under hydrothermal conditions under a prolonged stay in a closed vessel cerium was found to form also the $Ce_2(SO_3)_2SO_4 \cdot 4H_2O$ phase which has been previously described by Peterson et al. (Ref. 4). Neodymium sulphite contained six water molecules when precipitated at room temperature. At higher temperatures (95°C) the product was anhydrous sulphite.

The sulphite hydrates obtained were analyzed for the lanthanoid content by firing to oxide or oxysulphate; sulfur analyses were performed also in some cases. X-ray diffraction patterns were recorded for every sample and the results showed that the cerium sulphite trihydrate is not isomorphous with the known trihydrate structures of the heavier lanthanoids (Refs. 5, 6). Neodymium sulphite hexahydrate was nearly completely amorphous whereas the anhydrous phase was crystalline and its diffraction pattern was different from those of the other lanthanoid sulphites (Ref. 7).

In the thermoanalytical measurements a Perkin-Elmer set of instruments was employed. For experimental details, see Ref. 1.

RESULTS AND DISCUSSION

Cerium sulphite trihydrate

According to the DTG and DSC curves cerium sulphite trihydrate is dehydrated in air and nitrogen in three stages between 80 and 250°C. The small intermediate levels correspond to 2.5 and 0.5 hydrates. In air the anhydrous sulphite is stable up to 500°C after which it starts to oxidize. The oxidation occurs in two stages having the DTG maxima at about 520 and 570°C (10 mg, 10°C min^{-1}, Fig. 1). The weight gains observed correspond to formulas $Ce_2(SO_3)_2SO_4$ and $Ce_2SO_3(SO_4)_2$. Closest agreement to the latter phase is obtained with small mass and slow heating rate: The disulphite sulphate phase is stable and can be easily prepared by other methods, too (Ref. 8). The existence of the latter phase, sulphite disulphate, is somewhat uncertain because we have not succeeded in preparing it by an independent method.

The oxidized phase begins to decompose below 700°C and pure CeO_2 is obtained in a single step at 850°C when a heating rate of 10°C/min is used. Under the experimental conditions covered in the present study, the oxysulphate does not appear as an intermediate phase; cf. Peterson et al. (Ref. 4). The decomposition scheme of cerium sulphite in air appears also to be independent of the heating rate and amount of the sample.

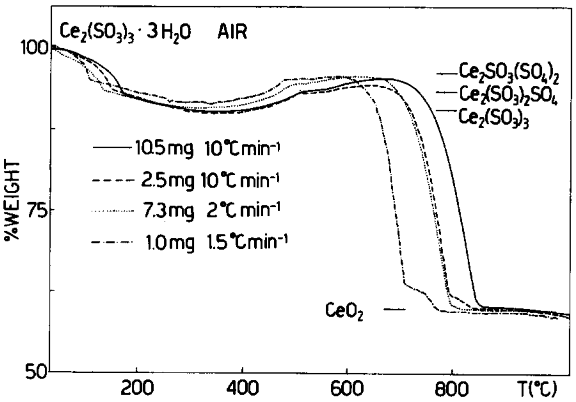

Fig. 1. TG-curves of $Ce_2(SO_3)_3 \cdot 3H_2O$ recorded in dynamic air atmosphere under various experimental conditions.

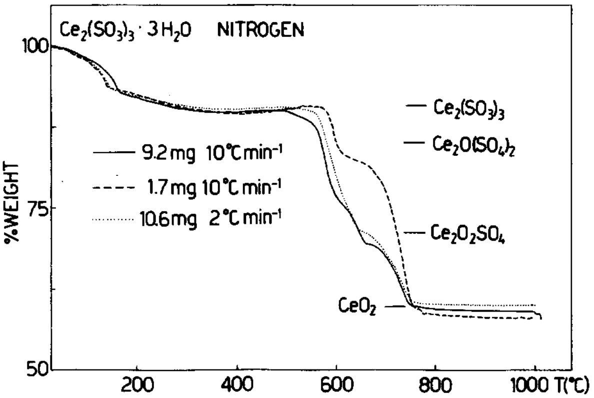

Fig. 2. TG-curves of $Ce_2(SO_3)_3 \cdot 3H_2O$ recorded in dynamic nitrogen atmosphere under various experimental conditions.

The behaviour of $Ce_2(SO_3)_3 \cdot 3H_2O$ in nitrogen is similar to that in air up to 500°C. However, in nitrogen the sulphite does not oxidize but decomposes between 500 and 750°C in two or three stages to CeO_2. The intermediate phases are quite unstable (Fig. 2). The weight of the latter phase (640°C) corresponds to $Ce_2O_2SO_4$ whereas the former plateau at 600°C is not a single phase. Thermal decomposition of cerium sulphite in an inert atmosphere offers thus an additional method of preparation for $Ce_2O_2SO_4$ which contrary to other oxysulphates is extremely difficult to prepare. For instance, Kay _et al._ (Ref. 9) have reported that cerium does not form oxysulphate at all, but never the less it has been found among the thermal decomposition products of $Ce_2(SO_3)_2SO_4 \cdot 4H_2O$ and Ce_2O_2S (Refs. 4, 10). Larger scale batch experiments showed that the product obtained by the present method is very pure while the oxidation of Ce_2O_2S produces always mixed phases.

Neodymium sulphites

Neodymium sulphite hexahydrate begins to loose the water molecules already at 40°C and the process continues slowly to 550°C. No intermediate level corresponding to the trihydrate could be observed, in contrast to $Gd_2(SO_3)_3 \cdot 6H_2O$ (Ref. 11). There is also no plateau corresponding to the anhydrous sulphite but the TG curve goes down rather linearly with increasing temperature (Figs. 3 and 4). It is obvious that H_2O and SO_2 are being released simultaneously, _cf._ the TG curves of anhydrous sulphite in N_2 (Fig. 5). A characteristic step in the decomposition process under some experimental conditions is the abrupt weight loss at 550°C. The weight loss does not correspond to any known single phase. In nitrogen the decomposition is slightly slower and the level reached in the TG curve corresponds to $Nd_2O_2SO_4$. In air the slow decomposition of $Nd_2(SO_3)_3$ continues with other experimental conditions up to 800°C after which the reaction to oxysulphate occurs. The unknown intermediate phase mentioned above decomposes also to $Nd_2O_2SO_4$ after 750°C. In nitrogen the experimental conditions have less effect on the reaction temperatures than in air.

The anhydrous neodymium sulphite begins to decompose immediately above room temperature and the behaviour is quite similar as observed with hexahydrate above 230°C (Figs. 4 and 5). The abrupt decomposition occurs at 530 - 630 °C depending on the experimental conditions both in air and nitrogen. In air there is usually only one step and the level reached is below that calculated for $Nd_2O_2SO_4$. According to the X-ray diffraction pattern oxysulphate is the main phase, however. In nitrogen the fast decomposition of sulphite has often two stages, the intermediate level being above the level of oxysulphate.

The overall thermal degradation of neodymium sulphite seems to be a result of at least two competing reactions, _viz._ a slow reaction which may be disproportion, and a fast one which is the normal decomposition to oxysulphate.

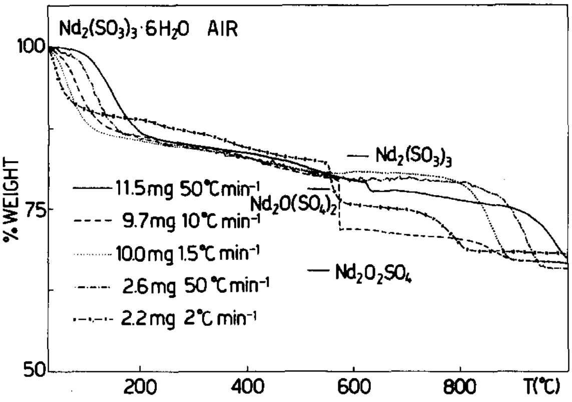

Fig. 3. TG curves of $Nd_2(SO_3)_3 \cdot 6H_2O$ in air.

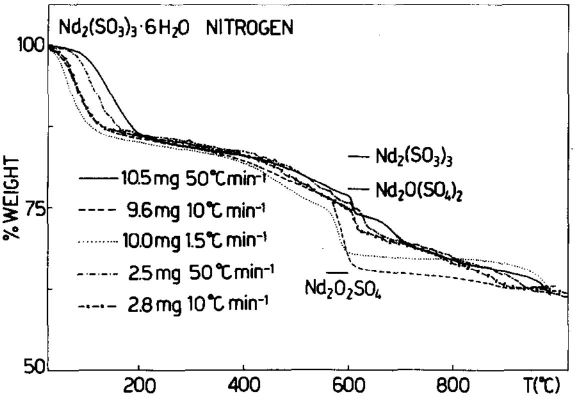

Fig. 4. TG curves of $Nd_2(SO_3)_3 \cdot 6H_2O$ in nitrogen.

The experimental conditions have a profound effect on the kinetics of these reactions so that each case is different. The reaction temperatures and the degree of reaction depend on the ratio of these competing reactions which is affected by the experimental conditions.

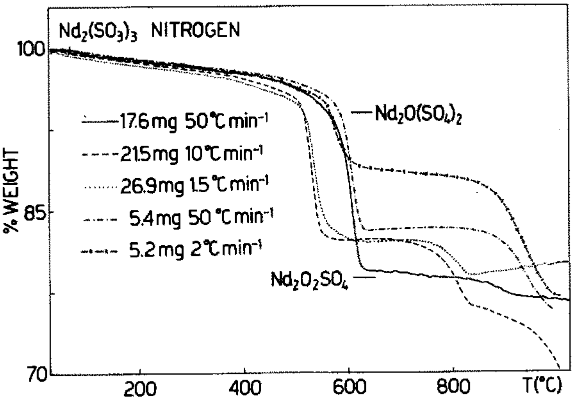

Fig.5. TG curves of anhydrous $Nd_2(SO_3)_3$ in nitrogen.

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