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THERMAL STUDIES ON YTTRIUM, NEODYMIUM AND HOLMIUM OXALATES

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ABSTRACT

The thermal decomposition patterns of $Y_2(C_2O_4)_3 \cdot 9\ H_2O$, $Nd_2(C_2O_4)_3 \cdot 10\ H_2O$ and $Ho_2(C_2O_4)_3 \cdot 5.5\ H_2O$ have been studied using TG and DTG. The hydrated neodymium oxalate loses all the water of hydration in one step to give the anhydrous oxalate while $Y_2(C_2O_4)_3 \cdot 9\ H_2O$ and $Ho_2(C_2O_4)_3 \cdot 5.5\ H_2O$ involve four or more dehydration steps to yield the anhydrous oxalates. Further heating of the anhydrous oxalates results in the loss of CO_2 and CO to give the stable metal oxides.

INTRODUCTION

Because rare earth oxalates are sparingly soluble, the oxalate precipitation is extensively used in the analysis of rare earth elements to separate them from minor amounts of many other elements and to determine them gravimetrically.

Scandium, yttrium and rare earth metal oxalates have been investigated for their thermal behavior by several workers [1–5]. However, few investigators have studied the kinetics of the thermal decomposition [4,5]. Since the thermal decomposition patterns of the oxalates described by Nair et al. [5] are in disagreement with those of Wendlandt [2,3], the present study was undertaken to reinvestigate the type of thermal decomposition and the kinetics of decomposition of yttrium and some oxalates of rare earths.

EXPERIMENTAL

$Y_2(C_2O_4)_3 \cdot 9\ H_2O$, $Nd_2(C_2O_4)_3 \cdot 10\ H_2O$ and $Ho_2(C_2O_4)_3 \cdot 10\ H_2O$ were obtained from Alfa Chemical Co., and were used as received. The degree of hydration of the first two compounds was established by TG studies.

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Analysis of the holmium compound by TG showed that this compound had only 5.5 molecules of water as water of hydration and should, therefore, be formulated as $Ho_2(C_2O_4)_3 \cdot 5.5\ H_2O$.

TG studies were carried out in a nitrogen atmosphere using a Perkin-Elmer thermogravimetric system, model TGS-2. The procedures used were similar to those described previously [6].

TG data were analysed to determine kinetic parameters by means of both the Coats–Redfern equations [7] and the Reich–Stivala method [8]. The equations used in the analysis by the Coats–Redfern method were

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln\frac{AR}{E\beta}\left[1-\frac{2RT}{E}\right] - \frac{E}{RT} \tag{1}$$

and for the case where $n = 1$

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\frac{AR}{E\beta}\left[1-\frac{2RT}{E}\right] - \frac{E}{RT} \tag{2}$$

where α is the fraction of the reaction completed, E is the activation energy, β is the heating rate, T is the temperature (K), A is the frequency factor, and R is the molar gas constant. Calculations for the Coats–Redfern method and the Reich–Stivala iterative method were carried out by computer using programs written in FORTRAN.

RESULTS AND DISCUSSION

The TG and DTG curves for the thermal decomposition of $Y_2(C_2O_4)_3 \cdot 9\ H_2O$, $Nd_2(C_2O_4)_3 \cdot 10\ H_2O$ and $Ho_2(C_2O_4)_3 \cdot 5.5\ H_2O$ and shown in Figs. 1–3. From the TG curves, it can be seen that the decomposition of neodymiun oxalate decahydrate takes place in two distinct steps while that of $Y_2(C_2O_6)_3 \cdot 9\ H_2O$ and $Ho_2(C_2O_4)_3 \cdot 5.5\ H_2O$ takes place in five or more steps. The reactions involved in those decompositions can be represented by eqns. (3)–(15).

$$Nd_2(C_2O_4)_3 \cdot 10\ H_2O_{(s)} \rightarrow Nd_2(C_2O_4)_{3(s)} + 10\ H_2O_{(g)} \tag{3}$$

$$Nd_2(C_2O_4)_{3(s)} \rightarrow Nd_2O_{3(s)} + 3\ CO_{2(g)} + 3\ CO_{(g)} \tag{4}$$

$$Y_2(C_2O_4)_3 \cdot 9\ H_2O_{(s)} \rightarrow Y_2(C_2O_4)_3 \cdot 6\ H_2O_{(s)} + 3\ H_2O_{(g)} \tag{5}$$

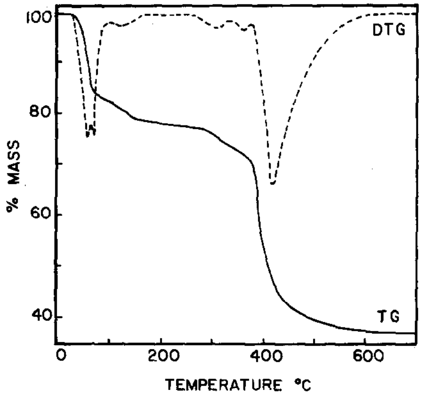
$$Y_2(C_2O_4)_3 \cdot 6\ H_2O_{(s)} \rightarrow Y_2(C_2O_4)_3 \cdot 4\ H_2O_{(s)} + 2\ H_2O_{(g)} \tag{6}$$

$$Y_2(C_2O_4)_3 \cdot 4\ H_2O_{(s)} \rightarrow Y_2(C_2O_4)_3 \cdot 2\ H_2O_{(s)} + 2\ H_2O_{(g)} \tag{7}$$

$$Y_2(C_2O_4)_3 \cdot 2\ H_2O_{(s)} \rightarrow Y_2(C_2O_4)_3 \cdot H_2O_{(s)} + H_2O_{(g)} \tag{8}$$

$$Y_2(C_2O_4)_3 \cdot H_2O_{(s)} \rightarrow Y_2(C_2O_4)_{3(s)} + H_2O_{(g)} \tag{9}$$

$$Y_2(C_2O_4)_{3(s)} \rightarrow Y_2O_{3(s)} + 3\ CO_{2(g)} + 3\ CO_{(g)} \tag{10}$$



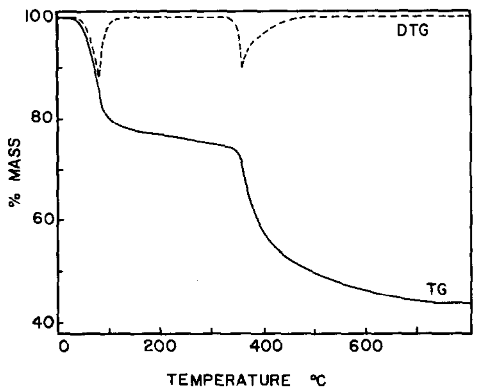


Fig. 1. TG and DTG curves for $Y_2(C_2O_4)_3 \cdot 9\ H_2O$.

Fig. 2. TG and DTG curves for $Nd_2(C_2O_4)_3 \cdot 10\ H_2O$.

$$Ho_2(C_2O_4)_3 \cdot 5.5\ H_2O_{(s)} \rightarrow Ho_2(C_2O_4)_3 \cdot 4.5\ H_2O_{(s)} + H_2O_{(g)} \tag{11}$$

$$Ho_2(C_2O_4)_3 \cdot 4.5\ H_2O_{(s)} \rightarrow Ho_2(C_2O_4)_3 \cdot 2\ H_2O_{(s)} + 2.5\ H_2O_{(g)} \tag{12}$$

$$Ho_2(C_2O_4)_3 \cdot 2\ H_2O_{(s)} \rightarrow Ho_2(C_2O_4)_3 \cdot H_2O_{(s)} + H_2O_{(g)} \tag{13}$$

$$Ho_2(C_2O_4)_3 \cdot H_2O_{(s)} \rightarrow Ho_2(C_2O_4)_{3(s)} + H_2O_{(g)} \tag{14}$$

$$Ho_2(C_2O_4)_{3(s)} \rightarrow Ho_2O_{3(s)} + 3\ CO_{2(g)} + 3\ CO_{(g)} \tag{15}$$

The dehydration reaction of $Nd_2(C_2O_4)_3 \cdot 10\ H_2O$ begins at 30°C and is completed in one step at 130°C. The resulting anhydrous oxalate decomposes losing both CO_2 and CO near 335°C and yields stable Nd_2O_3 at 730°C.

As described by eqns. (5)–(9) and (11)–(14), $Y_2(C_2O_4)_3 \cdot 9\ H_2O$ and $Ho_2(C_2O_4)_3 \cdot 5.5\ H_2O$ dehydrate in several steps to give the anhydrous oxalates which further lose CO_2 and CO in one step to give the stable metal oxides. In these two oxalates, the water of hydration begins to come off at 30°C, resulting in the anhydrous oxalates around 350°C. Above this temper-

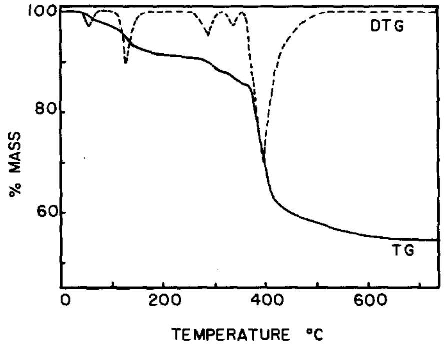


Fig. 3. TG and DTG curves for $Ho_2(C_2O_4)_3 \cdot 5.5\ H_2O$.

ature, the anhydrous oxalates of yttrium and holmium start losing CO_2 and CO to yield the stable oxides, Y_2O_3 and Ho_2O_3. The processes are complete at about 730°C.

According to previous studies on oxalates of scandium, yttrium and rare earth metals [2,4], they begin to dehydrate near 40°C. The resulting anhydrous oxalates decompose in one step to give the stable metal oxides around 735°C with the exception of $La_2(C_2O_4)_3$. The results obtained in the present study are in good agreement with those results. But the investigation of oxalates of yttrium and rare earth metals by Nair et al. [5] contradicts our results and those obtained previously [2–4]. According to Nair et al., $Y_2(C_2O_4)_3 \cdot 9\ H_2O$ and all the rare earth oxalates are stable up to 100°C and they begin to dehydrate in the range of 100–150°C. All these oxalates, including $Nd_2(C_2O_4)_3 \cdot 10\ H_2O$, lose water in multiple steps. After complete dehydration, the anhydrous oxalates with the exception of $Ce_2(C_2O_4)_3$, decompose in two or three steps via oxycarbonate intermediates to give stable oxides as final products.

The only difference between the present work and the work by Nair et al. is that a dynamic nitrogen atmosphere was used in the present study while the decompositions were carried out in a static air medium by Nair et al. Therefore, in order to see the effect of medium, in the present work the hydrated oxalate samples were also studied in a static air atmosphere. Both the TG and DTG curves obtained were almost identical to those obtained in a dynamic nitrogen atmosphere. However, it was observed that in the static air atmosphere, the decomposition of the anhydrous oxalates was rapid. This could be due to the fact that in an oxidizing atmosphere the oxidation of oxalates to oxides can be facilitated.

Table 1 shows the average percentage mass loss and the temperature range for each decomposition reaction and kinetic parameters for some reactions. The linear regression analysis of the TG data obtained from several individual samples were carried out using the Coats–Redfern method [eqns. (1) and (2)] and the Reich–Stivala method. Analysis of the kinetic parameters for the dehydration reactions in $Ho_2(C_2O_4)_3 \cdot 5.5\ H_2O$ and $Y_2(C_2O_4)_3 \cdot 9\ H_2O$ was not carried out because either the decomposition steps were not resolved adequately or the mass losses were too small to carry out an accurate analysis. However, the dehydration step in $Nd_2(C_2O_4)_3 \cdot 10\ H_2O$ was studied and found to be a second-order reaction with an activation energy of 89.4 ± 6.2 kJ $mole^{-1}$.

The TG data obtained for the decomposition of anhydrous oxalates of yttrium, neodymium and holmium were also analysed using the Coats–Redfern method and the Reich–Stivala method. The results obtained in these analyses were found to be contrary to each other. In the former method, the correct order of reaction is assumed to be the order of reaction which corresponds to the highest correlation coefficient. Based on this fact, the results obtained by the former method showed that the order of reactions

TABLE 1

Thermal decomposition data for $Y_2(C_2O_4)_3 \cdot 9\ H_2O$, $Nd_2(C_2O_4)_3 \cdot 10\ H_2O$ and $Ho_2(C_2O_4)_3 \cdot 5.5\ H_2O$

Eqn.	Temp. range (°C)	Mass loss	
		Obsd. (%)	Calcd. (%)
$Nd_2(C_2O_4)_3 \cdot 10\ H_2O$			
(3) *	30–130	24.2	24.6
(4)	335–730	30.7	29.5
$Y_2(C_2O_4)_3 \cdot 9\ H_2O$			
(5)	30– 56	10.0	9.0
(6)	56– 83	6.7	6.0
(7)	90–150	5.2	6.0
(8)	250–310	3.0	3.0
(9)	320–357	2.7	3.0
(10)	360–730	35.3	35.8
$Ho_2(C_2O_4)_3 \cdot 5.5\ H_2O$			
(11)	30– 75	2.6	2.6
(12)	80–165	6.8	6.5
(13)	250–295	2.8	2.6
(14)	322–350	2.2	2.6
(15)	356–755	30.5	31.2

* The order of reaction and the activation energy for the reaction which is represented by eqn. (3) are 2 and 89.4±6.2 kJ mole^{-1}, respectively.

for the decomposition of the anhydrous oxalates of yttrium, neodymium and holmium lie between 20 and 40 with activation energies of several thousand kJ mole^{-1}. On the other hand, the Reich–Stivala method showed that the same processes were zero-order reactions with activation energy values less than 1000 kJ mole^{-1}. However, the intercepts obtained in this analysis were much too high since the best fits should have an intercept of zero. Comparison of the results obtained by both methods indicates that the decomposition of anhydrous rare earth oxalates does not follow the rate law used in the Coats–Redfern analysis.

These examples show further that for some reactions the TG data lead to unusual kinetic parameters when conventional analysis of the data is performed. It is likely that these cases do not follow the usual rate law, viz.

$$\frac{d\alpha}{dT} = \frac{A}{\beta}(1-\alpha)^n\, e^{-E/RT} \tag{16}$$

on which the analyses are based. We are currently developing computer methods to use more general rate laws in an effort to resolve these difficulties.

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