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Note

SOME OBSERVATIONS ON THE THERMAL DECOMPOSITION KINETICS OF GADOLINIUM(III), HOLMIUM(III) AND ERBIUM(III) NITRATE

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The thermal decomposition kinetics of some lanthanum(III) nitrates, M = La, Ce, Pr, Nd and Eu, have been described previously [1–3]. The decomposition reactions of $Nd(NO_3)_3$ and $Eu(NO_3)_3$ were shown to be accompanied by at least one reversible process, which seems to change the kinetic behaviour of the compound. The Arrhenius plots showed discontinuities at temperatures which correspond with those at which the reversible processes were observed. It has been postulated [3] that the decreasing ionic radius of the metal ion in the lanthanide series, influences the decomposition and kinetics.

It was therefore of interest to obtain additional data on the decomposition of the lanthanide(III) nitrates, especially on those of the latter part of the series, e.g. $Gd(NO_3)_3$, $Ho(NO_3)_3$ and $Eu(NO_3)_3$.

EXPERIMENTAL

Thermogravimetric studies

A Stanton Redcroft STA 780 simultaneous thermal analyser was used as described elsewhere [1,2]. Isothermal mass loss observations were made in the temperatures ranges 270–410 °C for $Gd(NO_3)_3$, 260–375 °C for $Ho(NO_3)_3$ and 250–370 °C for $Er(NO_3)_3$. The data collected were fitted to a variety of kinetic expressions [4]. The linearity of plots of the calculated values of $F(\alpha_i)$ against time for each kinetic expression was taken as a criterion for identification of the rate equation.

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Differential scanning calorimetry studies

A Du Pont 910 differential scanning calorimeter, controlled by a 1090 Thermal Analyser, was used for the DSC studies [1,2].

Sample preparation

The $Gd(NO_3)_3 \cdot 6H_2O$, $Ho(NO_3)_3 \cdot 6H_2O$ and $Er(NO_3)_3 \cdot 6H_2O$ were obtained from Fluka. The anhydrous lanthanide nitrates were prepared by heating the hydrated nitrate at a rate of 5 °C min^{-1} to maximum temperatures and constant mass in the thermobalance. The $Gd(NO_3)_3 \cdot 6H_2O$ was heated to 230 °C, the $Ho(NO_3)_3 \cdot 6H_2O$ to 240 °C, and the $Er(NO_3)_3 \cdot 6H_2O$ to a maximum temperature of 210 °C.

RESULTS AND DISCUSSION

Gadolinium(III) nitrate

The anhydrous nitrate $Gd(NO_3)_3$ starts to decompose as 275 °C and decomposition was completed at 410 °C at a heating rate of 5 °C min^{-1}. An average mass loss of 30.5% was observed for the reaction $Gd(NO_3)_3 \rightarrow GdO(NO_3)$ + volatile products (theoretical value 31.47%). The oxynitrate starts to decompose at 420 °C.

Isothermal mass loss curves were recorded at selected temperatures between 270 and 410 °C. No single kinetic model seems to describe the rate

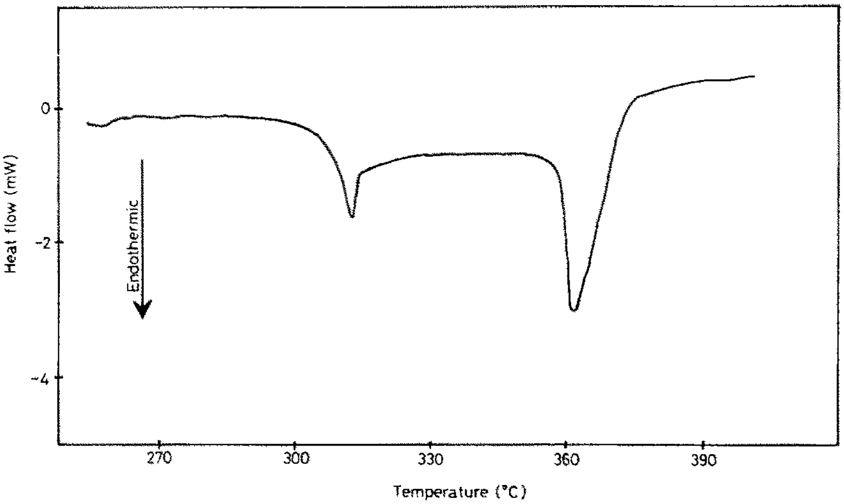

Fig. 1. DSC trace of the thermal decomposition of $Gd(NO_3)_3$.

data in this temperature range, judging by the linearity of the f(α) vs. t curves. It was observed that in the temperature range 270–315 °C, the Avrami-Erofe'ev equation, $[-\ln(1-\alpha)]^{1/2} = kt$ seems to describe the reaction ($\alpha = 0.02$–0.98). An apparent activation energy of 82.7 kJ mol^{-1} and $\ln A = 10.9$ min^{-1} were calculated for the reaction in this temperature range. In the temperature range 320–385 °C, the reaction conforms to the equation, $[-\ln(1-\alpha)]^{2/3} = kt$, with $E_a = 243.2$ kJ mol^{-1} and $\ln A = 43.2$ min^{-1}. The Prout-Tompkins equation, $\ln[\alpha/(1-\alpha)] = kt$, seems to describe the reaction in the temperature range 390–410 °C with an apparent activation energy, $E_a = 99.5$ kJ mol^{-1} and $\ln A = 17.8$ min^{-1}.

The DSC trace recorded at a heating rate of 5 °C min^{-1} shows two peaks, one with a maximum at 317 °C and the second with a maximum at 366 °C (Fig. 1). The enthalpy of the overall decomposition reaction of $Gd(NO_3)_3$ to $GdO(NO_3)$ was estimated as 138.1 kJ mol^{-1} $Gd(NO_3)_3$. The enthalpy of the process at 317 °C was roughly calculated to be 8.9 kJ mol^{-1} $Gd(NO_3)_3$.

Holmium(III) nitrate

Anhydrous holmium(III) nitrate starts to decompose at 250 °C and the decomposition is completed at 395 °C at a heating rate of 5 °C min^{-1}. An experimental mass loss of 31.5% was observed for the decomposition reaction which is in fair agreement with the theoretical value of 30.78% calculated for the formation of $HoO(NO_3)$. The oxynitrate started to decompose at 428 °C.

Isothermal rate data were recorded in the temperature range 260–375 °C and judged by the linearity of the f(α) vs. t curves: no single kinetic model

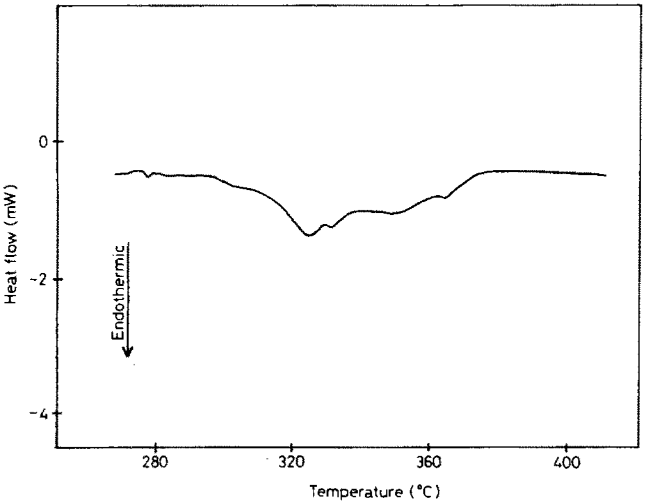

Fig. 2. DSC trace of the thermal decomposition of $Ho(NO_3)_3$.

TABLE 1

Kinetic data for the thermal decomposition reaction of $Ho(NO_3)_3$

Temperature range (°C)	Kinetic equation	Activation energy (kJ mol^{-1})	ln A (min^{-1})
260–285	$-\ln(1-\alpha)=kt$	96.2	15.6
290–305	$(-\ln(1-\alpha))^{3/2}=kt$	229.2	43.3
310–330	$1-(1-\alpha)^{1/3}=kt$	36.3	2.6
335–345	$(-\ln(1-\alpha))^{3/2}=kt$	480.2	91.2
350–375	$(-\ln(1-\alpha))^{1/2}=kt$	102.6	17.8

seems to describe the reaction. Table 1 summarizes the relevant kinetic data for the decomposition reaction.

The DSC trace for thermal decomposition reaction shows a broad peak, consisting of multiple overlapping peaks suggesting overlapping processes (Fig. 2). The enthalpy of decomposition was estimated as 119.9 kJ mol^{-1}.

Erbium(III) nitrate

The decomposition reaction $Er(NO_3)_3(s) \rightarrow ErO(NO_3)(s) + \text{gases}$ takes place in the temperature range 230–370 °C when heated at 5 °C min^{-1}. The theoretical mass loss should amount to 30.57%. The observed mass loss of 31.0% was in fair agreement with the theoretical value.

The isothermal rate data were recorded between 250 and 370 °C. Different kinetic models seem to describe the reaction in different temperature regions as summarized in Table 2. The enthalpy of decomposition was estimated from DSC measurements as 197.2 kJ mol^{-1}.

The above results indicate that the decomposition kinetics of the anhydrous lanthanide(III) nitrates are more complicated than expected. The DSC curves suggested that the decomposition reaction $M(NO_3)_3 \rightarrow MO(NO_3) + \text{gases}$ is accompanied by various other overlapping processes

TABLE 2

Kinetic data for the thermal decomposition reaction of $Er(NO_3)_3$

Temperature range (°C)	Kinetic equation	Activation energy (kJ mol^{-1})	ln A (min^{-1})
250–260	$(-\ln(1-\alpha))^{1/2}=kt$	84.2	12.1
263–278	$-\ln(1-\alpha)=kt$	124.9	22.2
280–290	$(-\ln(1-\alpha))^{1/4}=kt$	486.0	98.3
292–345	$(-\ln(1-\alpha))^{2/3}=kt$	155.6	28.5
350–370	$(-\ln(1-\alpha))^{1/3}=kt$	63.2	10.2

which seem to influence the kinetics. It is also clear that the decomposition kinetics of the anhydrous nitrates of the latter part of the lanthanide series, are much more complicated than the rest.

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