THE THERMAL DECOMPOSITION OF LANTHANUM(III), PRASEODYMIUM(III) AND EUROPIUM(III) NITRATES

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ABSTRACT

The thermal decomposition kinetics of some anhydrous lanthanide nitrates were investigated and compared with those of neodymium nitrate. The kinetics of the decomposition reaction of $La(NO_3)_3$ and $Pr(NO_3)_3$ are described by the contracting area and contracting volume mechanism, respectively. The enthalpy of decomposition amounts to 123.4 and 102.6 kJ mol^{-1}, respectively. No reversible changes were observed for these two nitrates. The decomposition reaction of $Eu(NO_3)_3$ is similar to that of $Nd(NO_3)_3$ in so far as a reversible change occurs simultaneously with the decomposition reaction, causing a change in the temperature dependence of the rate constant. The enthalpy of decomposition was estimated as 119.6 kJ mol^{-1}. Decreasing ionic size of the metal ions appears to decrease the thermal stability of the nitrate, as manifested by the values of the temperature of initiation of decomposition.

INTRODUCTION

The thermal decomposition of $Ce(NO_3)_3$ [1] and $Nd(NO_3)_3$ [2] are described and discussed elsewhere. The decomposition of $Ce(NO_3)_3$ was shown to be a single irreversible reaction with enthalpy of reaction 111.1 kJ mol^{-1} and the activation energy 104.4 kJ mol^{-1}. The thermal decomposition of $Nd(NO_3)_3$ to the oxynitrate was shown to be accompanied by at least two reversible processes, one of which takes place simultaneously with the decomposition reaction. The enthalpy of the overall reaction is 109.6 kJ mol^{-1}.

An investigation of the thermal behaviour of La(III), Pr(III) and Eu(III) nitrates was undertaken as a continuation of our study of the lanthanide nitrates. It was also of interest to determine whether other lanthanide nitrates would show the same behaviour as that which was described for $Nd(NO_3)_3$ [2].

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EXPERIMENTAL

The general experimental method which was followed and the apparatus used have been described previously [1,2].

Materials

The anhydrous nitrates were prepared from the hydrated species which were obtained from Fluka. $La(NO_3)_3 \cdot 6H_2O$ was heated in flowing nitrogen to 320°C and constant weight in the thermobalance: $Pr(NO_3)_3 \cdot 5H_2O$ was heated to 310°C and $Eu(NO_3)_3 \cdot 6H_2O$ to 300°C, respectively. The mass losses observed for the dehydration reactions agreed very well with the calculated values for the formation of the $M(NO_3)_3$ species (e.g. M = La, 24.1% obs. and 24.96% calc.; M = Pr, 22.0% obs. and 21.60% calc.; M = Eu, 24.8% obs. and 24.23% calc.).

RESULTS

Lanthanum nitrate

The TG trace obtained for the decomposition of $La(NO_3)_3 \cdot 6H_2O$, using a heating rate of 5°C min^{-1}, is given in Fig. 1. The trace indicates that, using this heating rate, $La(NO_3)_3$ starts to decompose at 375°C. The decomposition of the oxynitrate, $LaONO_3$, starts at ~ 415°C and overlaps with the decomposition reaction of the $La(NO_3)_3$. It was, however, possible to separate these two reactions if the data for the reaction

$$La(NO_3)_3(s) \rightarrow LaONO_3(s) + gases$$

were collected at isothermal temperatures below 410°C. An average mass loss of 32.9% was observed for the reaction, which is in good agreement with the calculated value of 33.24%. Isothermal decomposition curves of $La(NO_3)_3$ at some indicated temperatures are given in Fig. 2.

The rate data fitted the contracting area model, $1 - (1 - \alpha)^{1/2} = kt$, over the α-range 0.02–0.98. The activation energy parameters estimated from the Arrhenius plot Fig. 3, were $E_a = 226.8$ kJ mol^{-1} and ln $A = 35.5$ min^{-1}.

The DSC trace of the decomposition reaction is given in Fig. 4. At least two endothermic processes can be identified, none of which are reversible at indicated by the absence of any exothermic processes in the cooling curve. The peak with a maximum at 404°C, is assigned to the decomposition of the $La(NO_3)_3$ while the shoulder at ~ 420°C is ascribed to the decomposition of the oxynitrate. The enthalpy of the decomposition reaction studied was estimated as 123.4 kJ [mol $La(NO_3)_3$]$^{-1}$.

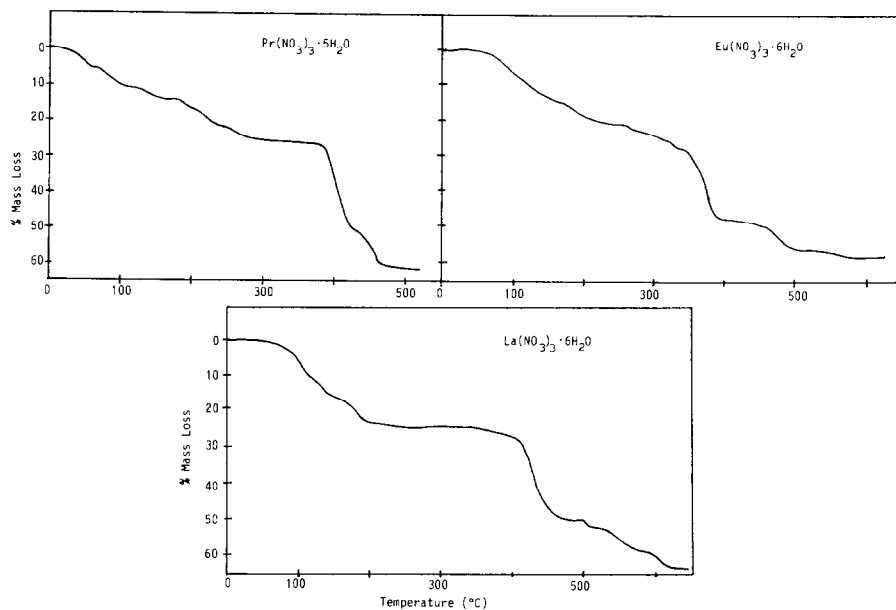Fig. 1. TG traces of $La(NO_3)_3 \cdot 6H_2O$, $Pr(NO_3)_3 \cdot 5H_2O$ and $Eu(NO_3)_3 \cdot 6H_2O$ at a heating rate of $5°C$ min^{-1} in flowing nitrogen.

Praseodymium nitrate

The TG trace (Fig. 1) of the decomposition of $Pr(NO_3)_3 \cdot 5H_2O$ recorded using a heating rate of $5°C$ min^{-1} indicates that the anhydrous nitrate starts to decompose at $\sim 365°C$ while the oxynitrate starts to decompose at
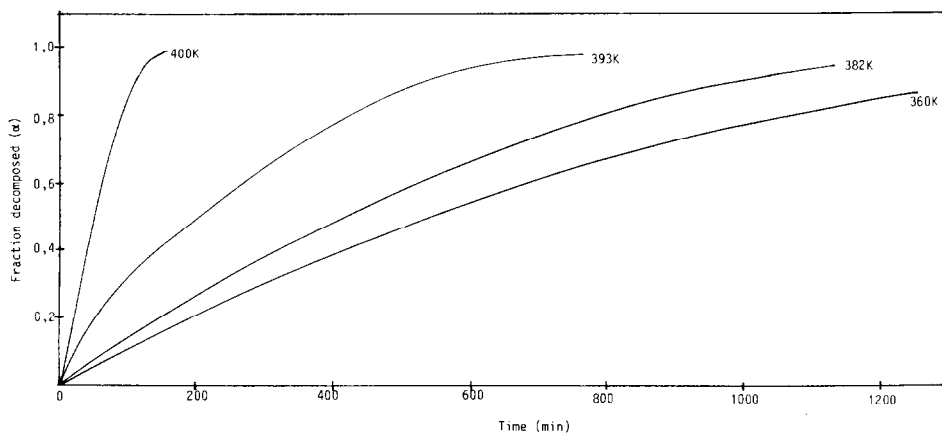

Fig. 2. Isothermal decomposition curves of $La(NO_3)_5$.

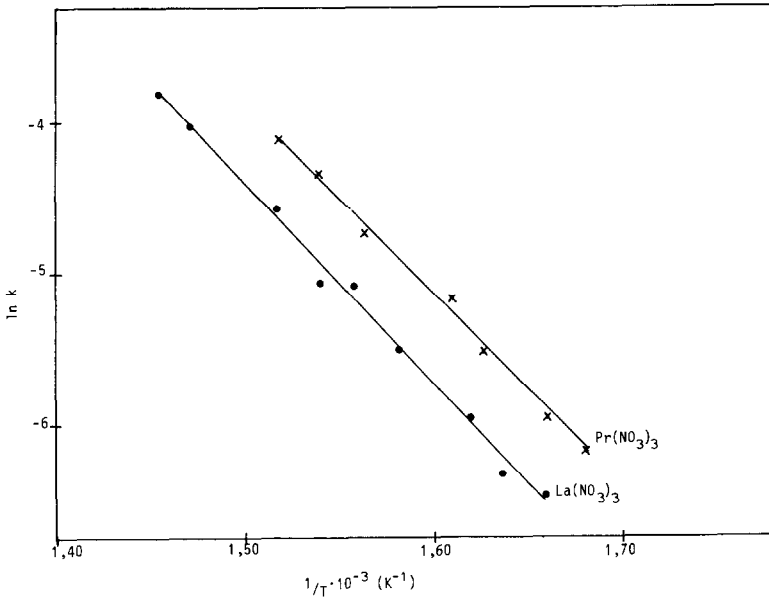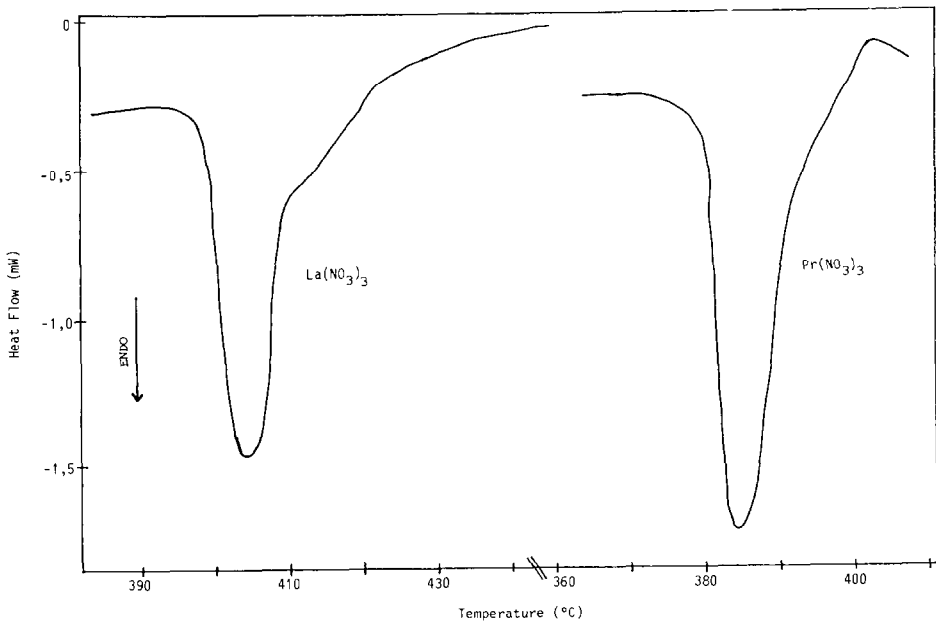Fig. 3. Arrhenius plots for the decomposition of $La(NO_3)_3$ and $Pr(NO_3)_3$ to their oxynitrates.

Fig. 4. DSC curves for the decomposition of $La(NO_3)_3$ and $Pr(NO_3)_3$.

~ 430 °C. The average mass loss observed for the reaction

$$Pr(NO_3)_3(s) \rightarrow PrONO_3(s) + gases$$

amounts to 32.7% whereas the calculated value is 33.04%.

Isothermal mass loss data were collected between 350 and 400 °C. The equation $1 - (1 - \alpha)^{1/3} = kt$ was found to describe the reaction over the α-range 0.02–0.99. The activation energy parameters were estimated from the Arrhenius plot and found to be $E_a = 206.2$ kJ mol^{-1} and ln $A = 32.3$ min^{-1}.

The DSC curve for the decomposition reaction is shown in Fig. 4. The trace suggests that only one endothermic process is taking place. The enthalpy estimated from the curve was 102.6 kJ [mol $Pr(NO_3)_3$]$^{-1}$. No reversible changes were detected upon cooling.

Europium nitrate

The TG trace of the decomposition of $Eu(NO_3)_3 \cdot 6H_2O$ (Fig. 1) indicates that, at a heating rate of 5 °C min^{-1}, the decomposition of the anhydrous nitrate starts at ~ 320 °C and is completed at ~ 410 °C, while decomposition to the oxynitrate starts only at ~ 425 °C. No overlapping of the two processes is therefore expected. An average mass loss of 31.0% was observed for the reaction

$$Eu(NO_3)_3(s) \rightarrow EuONO_3(s) + gases$$
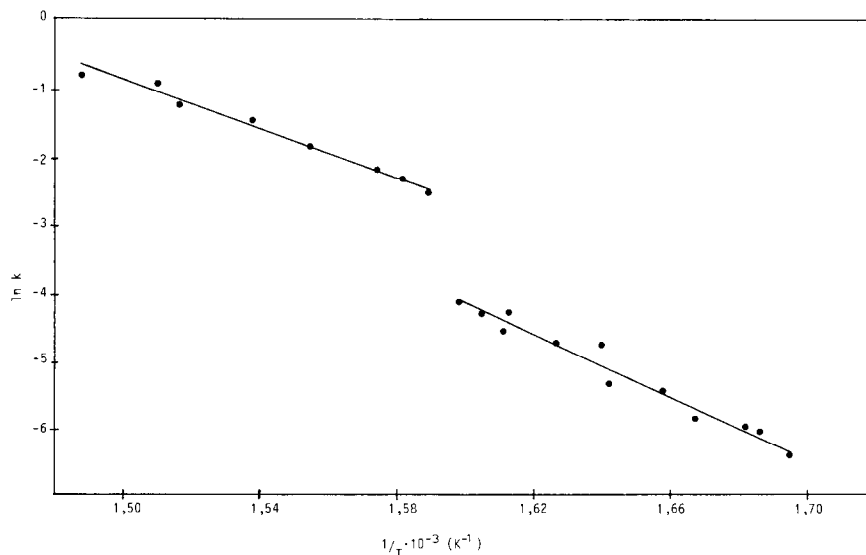
which compares favourably with the calculated value of 31.96%.

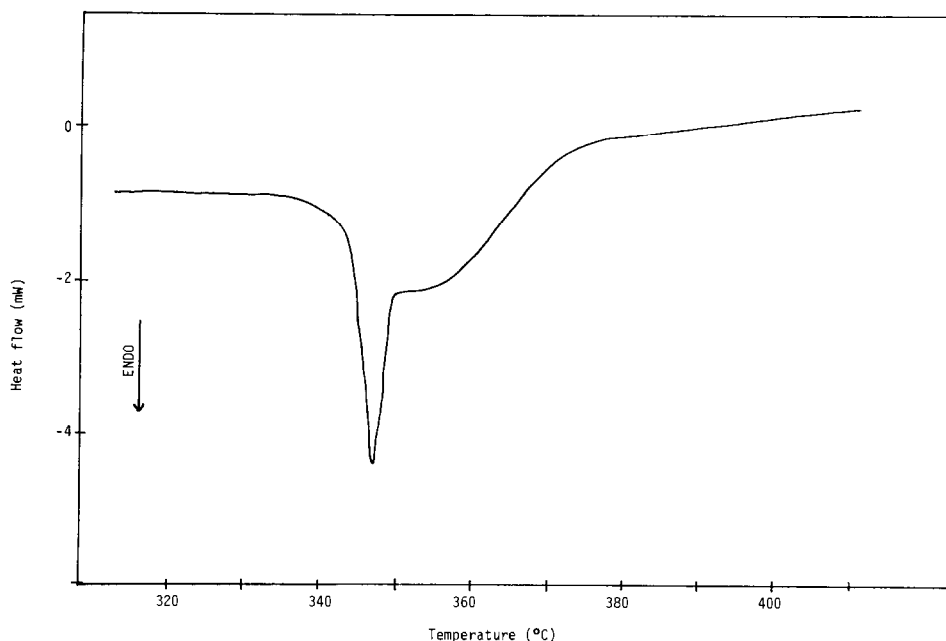Fig. 5. Arrhenius plot for the thermal decomposition of $Eu(NO_3)_3$ to $EuONO_3$.

Fig. 6. DSC trace for the decomposition of $Eu(NO_3)_3$.

The isothermal rate data collected between 310 and 400°C fitted the equation $[-\ln(1-\alpha)]^{2/3} = kt$ over the α-range 0.02–0.97. The Arrhenius plot for this decomposition reaction (Fig. 5) shows two straight lines, one between 355 and 400°C from which an activation energy of 139.9 kJ mol^{-1} and $\ln A = 24.3$ min^{-1} was estimated. The second straight line, in the temperature range 310–348°C, gave values of 189.6 kJ mol^{-1} and 32.3 min^{-1} for the activation energy and $\ln A$, respectively.

The DSC curve of the decomposition reaction (Fig. 6) shows an endothermic peak with a peak maximum at 348°C and a shoulder at ~ 350°C. On cooling a sample from 365°C, an exothermic peak was observed at 350°C which corresponds with the temperature at which the discontinuity in the Arrhenius plot occurs.

DISCUSSION

Important facts emerge from the results described above. It seems that the temperature of initiation of decomposition, T_i, measured at a heating rate of 5°C min^{-1}, for the decomposition reaction

$$M(NO_3)_3(s) \rightarrow MONO_3(s) + \text{gases}$$

where M = La, Pr, Nd and Eu, decreases with decreasing ionic radius of the

TABLE 1

Decomposition data and ionic radii of some anhydrous lanthanide nitrates

$M(NO_3)_3$	Ionic radius [a] (Å)	Temperature at which decomposition begins T_i (°C)	Enthalpy of decomposition ΔH (kJ mol^{-1})
$La(NO_3)_3$	1.14	375	123.4
$Pr(NO_3)_3$	1.06	365	102.6
$Nd(NO_3)_3$ [b]	1.04	360	109.6
$Eu(NO_3)_3$	0.98	320	119.6

[a] Ref. 3.
[b] Ref. 2.

metal ion. The decreasing ionic radii give rise to greater polarization of the nitrate ion and therefore greater instability of the ion. This in turn leads to the observed trend in T_i values. The values are given in Table 1. Tervalent cerium was excluded from this series, since the anhydrous nitrate decomposes without the formation of a stable oxynitrate [1] intermediate.

It appears that the decomposition reactions of some lanthanide nitrates, e.g. $Nd(NO_3)_3$ and $Eu(NO_3)_3$, are accompanied by reversible processes, the nature of which is not known at this stage. One would expect the decomposition enthalpy of the anhydrous nitrate (Table 1) to show a similar trend, i.e. decreasing values with decreasing ionic radius. Due to the overlapping reversible processes, this trend is not observed. Further, it appears that whenever a reversible process is observed, a change in the temperature dependence of the rate constant is observed. This could perhaps be linked to structural changes which occur in the anhydrous nitrate and/or the oxynitrate during the decomposition reaction. The lanthanide contraction would certainly influence such changes.

The above theory is under investigation at the moment by comparing the thermal decomposition of other anhydrous lanthanide nitrates.

REFERENCES

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