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THE THERMAL DECOMPOSITION OF NEODYMIUM NITRATE

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ABSTRACT

The thermal decomposition of $Nd(NO_3)_3$ was reinvestigated. The decomposition kinetics are described by a diffusion mechanism. The rate constant was found to be temperature dependent below 390°C with an apparent activation energy of 805 kJ mol^{-1} and almost temperature independent above 390°C with an apparent activation energy of 65 kJ mol^{-1}. The enthalpy of decomposition was estimated as 208.6 kJ mol^{-1} $Nd(NO_3)_3$ at atmospheric pressure and decreased to 187.3 kJ mol^{-1} $Nd(NO_3)_3$ at high pressure.

INTRODUCTION

The thermal decomposition of the rare-earth nitrates has been studied to some extent. Wendlandt [1] reported that, with the exception of cerium and samarium, the nitrates decomposed according to the general reaction: $M(NO_3)_3 \cdot 6H_2O(s) \rightarrow M(NO_3)_3(s) \rightarrow MONO_3(s)$ metal oxide. Differential thermal analysis of the rare-earth nitrate 4-hydrates indicated a series of endotherms over the temperature range 75–480°C. Rao and co-workers [2] reported the thermal decomposition of a series of rare-earth nitrates together with infrared data of the oxynitrate intermediate. The kinetics of decomposition of three rare-earth nitrates were also investigated but only first order rate constants, and activation energies were reported. The reported values of 33 kJ mol^{-1} for $Nd(NO_3)_3$, 23 kJ mol^{-1} for $Dy(NO_3)_3$ and 46 kJ mol^{-1} for $Yb(NO_3)_3$ seems to be very low.

In a previous study [3] it was postulated that the sequence of decomposition of $(NMe_4)_2U(NO_3)_6$ included an oxynitrate intermediate but no experimental evidence could have been produced for the formation of such an intermediate.

A kinetic investigation of the decomposition of $Nd(NO_3)_3$ was undertaken as a continuation of our study of the thermal decomposition of the actinide and lanthanide nitrates.

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EXPERIMENTAL

Thermogravimetric studies

A Stanton Redcroft STA 780 simultaneous thermal analyser was used to collect thermogravimetric data. Argon was used as a carrier gas at a flow rate of approximately 50 cm^3 min^{-1}. Platinum sample pans were used as sample holders. Temperature calibration of the equipment was achieved by using the ICTA recommended DTA temperature standards; GM 758, GM 759 and GM 760. Isothermal measurements were performed in the temperature range 380–410°C. Once the $Nd(NO_3)_3$ was formed in the thermobalance, the temperature was raised to the required experimental temperature for data collection. The data collected were fitted to a variety of kinetic expressions [4]. The linearity of plots of calculated values of $F(\alpha_i)$ against time for each kinetic expression was taken as a criterion for identification of the rate equation.

Differential scanning calorimetry studies

A DuPont 910 differential scanning calorimeter and high pressure cell which is controlled by a 1090 thermal analyser was used for the DSC studies. Peak integration and subsequent enthalpy calculations were performed by using the DuPont partial area integration data analysis program. The melting of pure indium metal ($\Delta H = 28.6$ J g^{-1}) was used as reference. $Nd(NO_3)_3 \cdot 6H_2O$ (puriss) was obtained from Fluka and used as such. The anhydrous $Nd(NO_3)_3$ was prepared by heating the $Nd(NO_3)_3 \cdot 6H_2O$ at a rate of 5°C min^{-1} to 370°C and constant mass in the thermobalance.

RESULTS AND DISCUSSION

The TG trace of the $Nd(NO_3)_3 \cdot 6H_2O$, Fig. 1, indicates that the anhydrous compound is formed at ±365°C. The observed mass loss of 24.8% is in good agreement with the theoretical value of 24.6%. The $Nd(NO_3)_3$ is stable over a very limited temperature range, i.e., 365–380°C. This stability region was, however, sufficient to facilitate the in situ preparation of the anhydrous material.

The reaction studied

$Nd(NO_3)_3(s) \rightarrow NdO(NO_3)(s)$ + oxides of nitrogen

takes place in the temperature range 380–430°C. The theoretical mass loss for the reaction

$Nd(NO_3)_3 \cdot 6H_2O(s) \rightarrow NdO(NO_3)(s)$ + volatile products

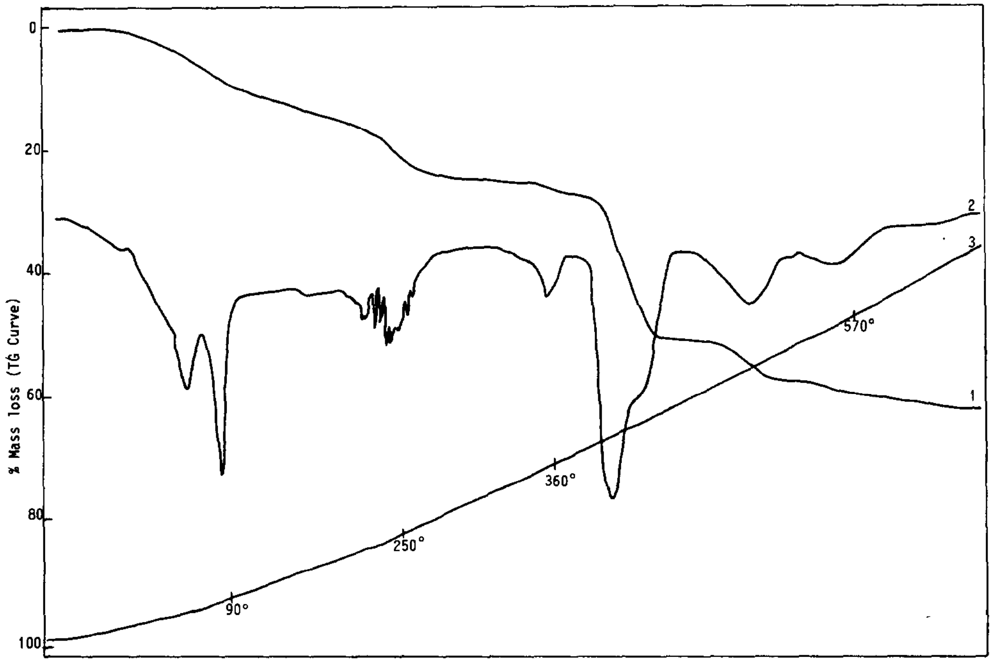

Fig. 1. TG and DTA traces of $Nd(NO_3)_3 \cdot 6H_2O$. Heating rate 5°C min^{-1} in Ar. (1) TG, (2) DTA, (3) temperature (°C).

should amount to 49.35%. The observed mass loss of 48.5% was in fair agreement with the theoretical value.

The isothermal decomposition curves at the indicated temperatures are given in Fig. 2. These rate data fitted the Ginstling–Brounshtein equation; $[1-(2\alpha/3)]-(1-\alpha)^{2/3}=kt$, as is shown in Fig. 3. The rate constants

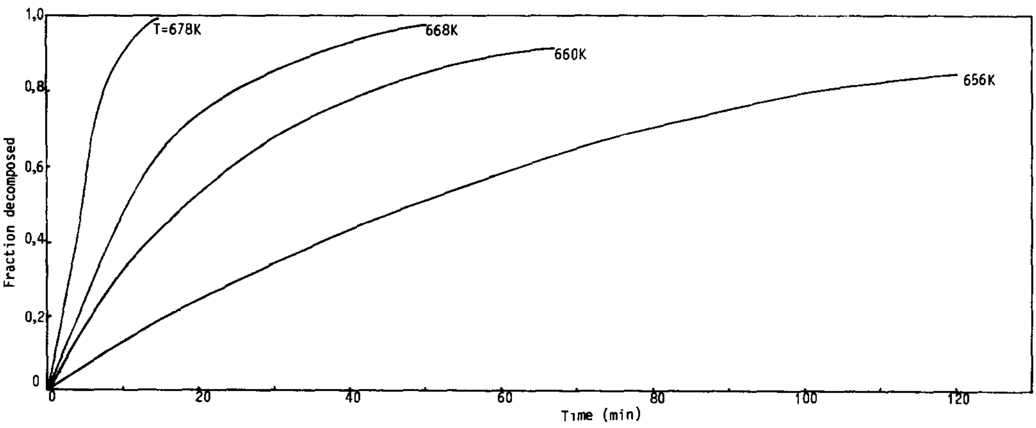

Fig. 2. Isothermal decomposition of $Nd(NO_3)_3$ in Ar (α vs. t curves); time (min).

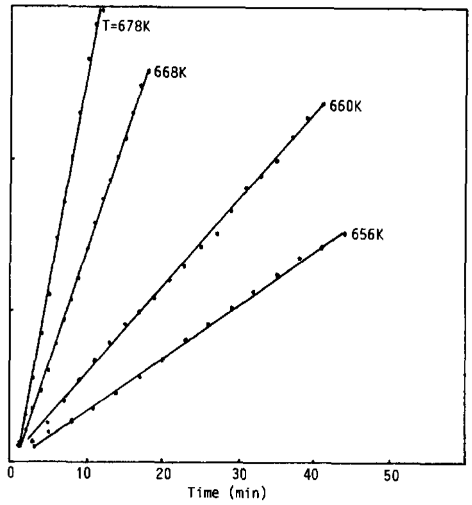

Fig. 3. Isothermal decomposition of $Nd(NO_3)_3$. Test of obedience to expression $[1-(^{2}/_{3}\alpha)]-(1-\alpha)^{2/3}=kt$.

which were estimated from the slopes of these curves, were found to be temperature dependent below 390°C and much less so above 390°C. This is illustrated in Fig. 4, which was used to estimate Arrhenius parameters. The

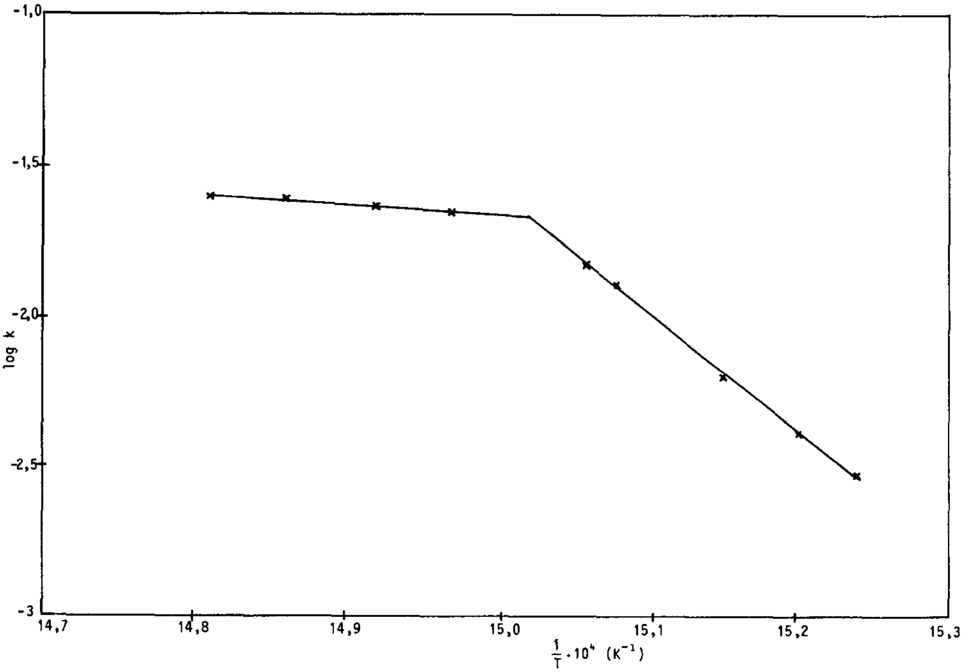

Fig. 4. Arrhenius plot for the decomposition of $Nd(NO_3)_3$.

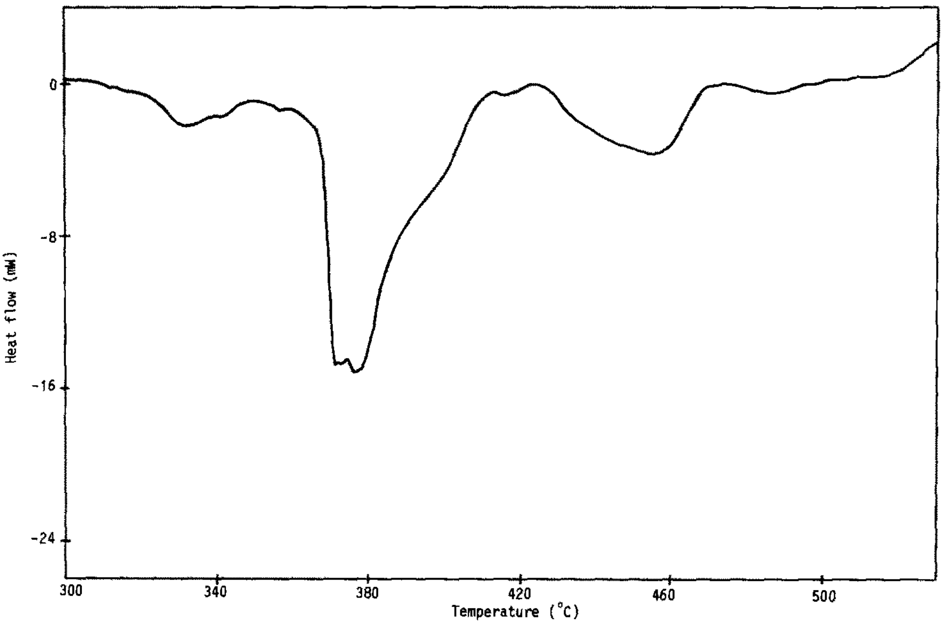

Fig. 5. DSC trace of the thermal decomposition of $Nd(NO_3)_3$ at atmospheric pressure.

values obtained below 390°C were; $E_a = 805$ kJ mol^{-1} and log(A/min^{-1}) = 61.48. Above 390°C, $E_a = 65.4$ kJ mol^{-1} and log(A/min^{-1}) = 3.46. Rao [2] reported a value, $E_a = 33$ kJ mol^{-1} but measurements were carried out at temperatures above 390°C.

The DTA trace for the decomposition (Figs. 1 and 5) suggested that the decomposition is not a straightforward reaction. The peak maximum is at 377°C with a shoulder at ±400°C. When a sample of $Nd(NO_3)_3 \cdot 6H_2O$ was heated at 5°C min^{-1} from room temperature to 400°C and then cooled at 5°C min^{-1}, two exothermic peaks were found at 390 and 335°C. The exothermic peak at 335°C was associated with the endotherm at 320°C in the heating curve. These exotherms suggested that at least two reversible processes were taking place.

The enthalpy of the reaction was estimated as 208.6 kJ mol^{-1} $Nd(NO_3)_3$. This value would contain contributions from both the reversible transition at 400°C and the reaction.

$Nd(NO_3)_3(s) \rightarrow NdO(NO_3)(s)$ + volatile products

The DSC trace of the decomposition at a pressure of 5×10^3 kPa is given in Fig. 6. It can be seen that the shape of the curve changed at this high pressure. The shoulder which was observed at 400°C under atmospheric pressure disappeared at this high pressure and the peak maximum shifted to higher temperature, at 442°C. The enthalpy was estimated as 187.3 kJ mol^{-1} $Nd(NO_3)_3$. It is suggested that the high pressure inhibited the process which

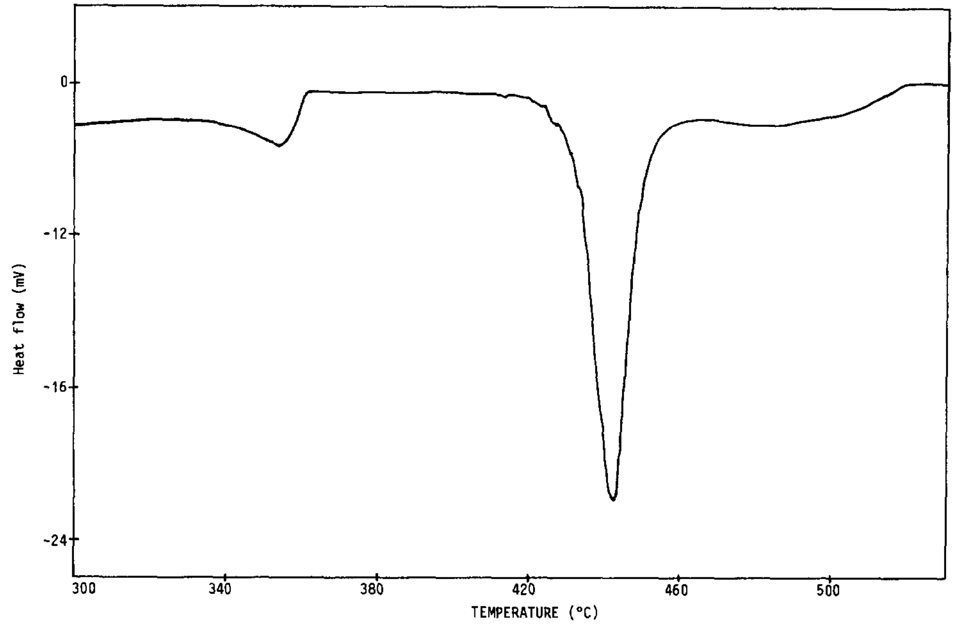

Fig. 6. DSC trace of the thermal decomposition of $Nd(NO_3)_3$ at 5×10^3 kPa.

occurred at 400°C and, therefore, the lower enthalpy value which was observed. It is suggested that this transition at ±400°C is also responsible for the change in temperature dependence of the rate constant at atmospheric pressure (see Fig. 4).

CONCLUSIONS

The thermal decomposition of $Nd(NO_3)_3(s)$ is more complex than previously reported. The decomposition reaction

$Nd(NO_3)_3(s) \rightarrow NdO(NO_3)(s)$ + volatile products

is accompanied by at least two reversible processes, one of which is taking place simultaneously with the decomposition reaction. The enthalpy change of the reaction at atmospheric pressure amounts to 208.6 kJ mol^{-1} $Nd(NO_3)_3$. The observed change in temperature dependence of the rate constant is probably due to this reversible process which is taking place during the course of the reaction. This phenomenon is being further investigated.

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