

## THE THERMAL DECOMPOSITION OF CERIUM(III) NITRATE

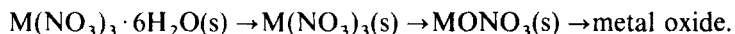
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The thermal decomposition of anhydrous  $\text{Ce}(\text{NO}_3)_3$  has been studied. The thermal decomposition reaction is described by the second order kinetic equation,  $[1/(1-\alpha)] - 1 = kt$ . The apparent activation energy was determined as  $E_a = 104 \text{ kJ mol}^{-1}$  while the enthalpy of the reaction was estimated as  $\Delta H_r = 111.1 \text{ kJ mol}^{-1}$ . The decomposition reaction differs from that observed for  $\text{Nd}(\text{NO}_3)_3$ .

Wendlandt [1] has shown that the rare-earth nitrates, with the exception of cerium and samarium, decompose according to the general reaction:



Anhydrous cerium nitrate decomposed directly to yield  $\text{CeO}_2$ . Patil and co-workers [2] observed that for the hydrated rare-earth nitrates the formation of the anhydrous nitrate was a definite stage in the thermal decomposition reactions. Apparent activation energies for the decomposition of the anhydrous nitrates are given as  $33 \text{ kJ} \cdot \text{mol}^{-1}$  for  $\text{Nd}(\text{NO}_3)_3$ ,  $23 \text{ kJ} \cdot \text{mol}^{-1}$  for  $\text{Dy}(\text{NO}_3)_3$  and  $46 \text{ kJ} \cdot \text{mol}^{-1}$  for  $\text{Yb}(\text{NO}_3)_3$  [2]. Since these activation energies were calculated from rate constants measured at only two temperatures, it was decided to reinvestigate the thermal decomposition of the anhydrous rare-earth nitrates as a continuation of our study of the decomposition of the actinide and lanthanide nitrates.

The results for the decomposition of anhydrous  $\text{Nd}(\text{NO}_3)_3$  are described and discussed elsewhere [3]. The temperature dependence of the rate constant as ( $\log k$  vs.  $1/T$ ) showed two straight lines, intersecting at  $390^\circ\text{C}$ . In addition, the DSC trace showed a peak which consisted of at least three different overlapping peaks. The enthalpy of the decomposition reaction was shown to be pressure dependent. This was explained in terms of a possible phase change which is inhibited by high pressures.

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As the decomposition of  $\text{Ce}(\text{NO}_3)_3$  differs from that of anhydrous  $\text{Nd}(\text{NO}_3)_3$  it was of interest to study in more detail this reaction and to compare observations with those for the decomposition of anhydrous  $\text{Nd}(\text{NO}_3)_3$  [1].

## Experimental

A Stanton Redcroft STA 780 simultaneous thermal analyser was used. Platinum sample pans were used in an argon atmosphere at a flow of  $50 \text{ cm}^3 \text{ min}^{-1}$ .

Isothermal mass loss observations were performed at temperatures between  $222^\circ$  to  $350^\circ$ . Once the  $\text{Ce}(\text{NO}_3)_3$  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.

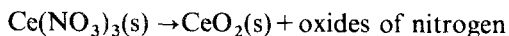
A DuPont 910 differential scanning calorimeter controlled by a 1090 Thermal Analyser was used with a high pressure cell for the DSC studies. Peak integration and subsequent enthalpy calculations were performed by using the DuPont Partial Area Integration Data analysis program. The calibration constant of the cell which is used to calculate enthalpy values, was determined over the pressure range ambient to  $5 \times 10^3 \text{ kPa}$  [5] and found to be constant. The melting of pure indium metal ( $\Delta H_f = 28.4 \text{ J g}^{-1}$ ) and pure zinc metal ( $\Delta H = 102.0 \text{ J g}^{-1}$ ) were used as reference materials.

The anhydrous  $\text{Ce}(\text{NO}_3)_3$  was prepared in situ by heating at a rate of  $10 \text{ deg min}^{-1}$  to  $210^\circ$  in flowing Ar,  $15 \text{ mg Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (puriss) (Fluka). The sample was held at  $210^\circ$  until a constant mass was observed. The observed mass loss was  $23.6 \pm 1.0\%$  (Cf  $24.9\%$  theoretical for dehydration).

## Results and discussion

The observed TG curve of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  is represented in Fig. 1 and indicated that  $\text{Ce}(\text{NO}_3)_3$  is only stable over a limited temperature range i.e. between  $210^\circ$  to  $220^\circ$ . Even so, it was still possible to prepare the anhydrous material as described above.

The decomposition of  $\text{Ce}(\text{NO}_3)_3$  as reflected by mass loss observed over the temperature range  $230^\circ$  to  $360^\circ$  was considered to be a redox reaction written overall as:



(observed mass loss  $47.6\%$ , theory  $47.2\%$ ).

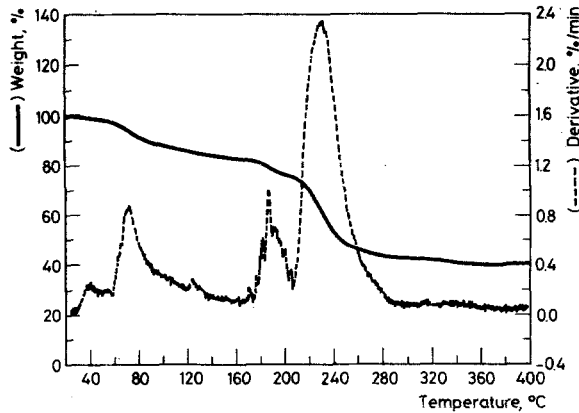


Fig. 1 TG trace of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ . Heating rate  $3 \text{ deg min}^{-1}$  in flowing Ar ( $50 \text{ cm}^3 \text{ min}^{-1}$ )

Isothermal mass loss curves at identified temperatures between  $230^\circ$  and  $360^\circ$  were recorded (Fig. 2). The data at each temperature fitted the equation for a second order solid state reaction;  $[1/(1-\alpha)] - 1 = kt$ . The activation parameters for the reaction were estimated from the rate coefficients in an Arrhenius plot and found to be;

$$E_a = 104 \text{ kJ mol}^{-1} \text{ and } \ln(A/\text{min}^{-1}) = 21.7.$$

The enthalpy of the reaction was estimated as  $111.1 \text{ kJ mol}^{-1}$  and it was found to be pressure independent up to the maximum experimental pressure of  $5 \times 10^3 \text{ kPa}$ . The symmetrical shape of the DSC peak, suggested that the decomposition reaction is not accompanied by any other changes, e.g. phase changes. The decomposition of  $\text{Ce}(\text{NO}_3)_3$  is considered to be a single irreversible step in contrast to that of  $\text{Nd}(\text{NO}_3)_3$  in which at least one reversible phase change was observed during the decomposition reaction [3].

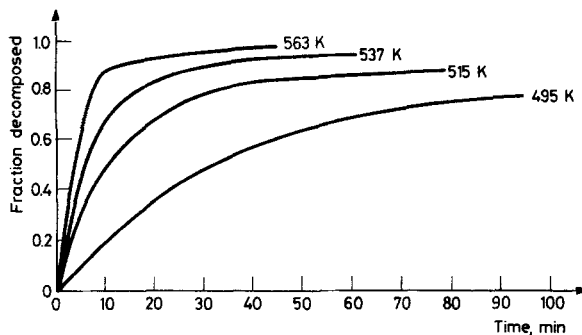


Fig. 2 Isothermal decomposition of  $\text{Ce}(\text{NO}_3)_3$  in flowing Ar ( $\alpha$  vs.  $t$  curves)

## Conclusions

The decomposition of  $\text{Ce}(\text{NO}_3)_3$  differs from that of  $\text{Nd}(\text{NO}_3)_3$  in so far that no reversible changes or intermediate stages were detected. The reaction can be considered as an oxidation of the Ce(III) by the nitrate ion and the concurrent isothermal mass loss can be described by  $[1/(1-\alpha)]-1 = kt$ . The apparent activation energy of  $104 \text{ kJ mol}^{-1}$  for the isothermal mass losses is in good agreement with the observed endothermal enthalpy observed in temperature programmed DSC ( $\Delta H_r = 111.1 \text{ kJ mol}^{-1}$ ).

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## References

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**Zusammenfassung** — Die thermische Zersetzung von wasserfreiem  $\text{Ce}(\text{NO}_3)_3$  wurde untersucht. Die thermische Zersetzung wird durch die Geschwindigkeitsgleichung zweiter Ordnung  $[1/(1-\alpha)]-1 = kt$ , beschrieben. Für die scheinbare Aktivierungsenergie wurde ein Wert von  $104 \text{ kJ} \cdot \text{mol}^{-1}$  und für die Enthalpie der Reaktion ein Wert von  $111,1 \text{ kJ} \cdot \text{mol}^{-1}$  ermittelt. Die Zersetzungsreaktion unterscheidet sich von der für  $\text{Nd}(\text{NO}_3)_3$ .

**Резюме** — Изучено термическое разложение безводного нитрата церия. Реакция термического разложения описывается кинетическим уравнением второго порядка:  $[1/(1-\alpha)]-1 = kt$ . Определены кажущаяся энергия активации  $E_a$ , равная  $104 \text{ кдж} \cdot \text{моль}^{-1}$ , и энтальпия реакции  $\Delta H_r$ , равная  $111,1 \text{ кдж} \cdot \text{моль}^{-1}$ . Реакция разложения отличается от наблюдаемой для нитрата неодима.