Journal of Thermal Analysis, Vol. 35 (1989) 347–353

THERMAL DECOMPOSITION AS A PREPARATIVE ROUTE TO ANHYDROUS RARE EARTH NITRATES

M. Karppinen, P. Kyläkoski, L. Niinistö and *C. Rodellas*

LABORATORY OF INORGANIC AND ANALYTICAL CHEMISTRY, HELSINKI UNIVERSITY OF TECHNOLOGY, SF-02150 ESPOO, FINLAND

Thermal decomposition of rare earth pentanitrato complexes has been studied by TG and DTA. $M_2Ln(NO_3)_5 \cdot nH_2O$ ($M = NH_4$, Ln = La, Nd, Pr) decomposes in air through anhydrous $(NH_4)_2Ln(NO_3)_5$ to $Ln(NO_3)_3$, $LnONO_3$ and finally to Ln_2O_3 above 600°C. When M = K and Ln = La, the intermediate $K_2La(NO_3)_5$ is remarkably stable and $KLaO_2$ is formed at 800°C. Except for Nd, the nonanitrato complex $M_3Ln_2(NO_3)_9$ was detected during the degradation process in both air and nitrogen but its stability range is too narrow to allow its preparative isolation as single phase. For comparison, the TG and DSC curves were recorded for $La(NO_3)_3 \cdot 6H_2O$ where $La(NO_3)_3$ and especially $LaONO_3$ appear as stable intermediates.

Because rare earth nitrates are possible starting materials for the preparation of superconducting $LnBa_2Cu_3O_{7-x}$ phases (Ln = Y, for instance), there has been lately a renewed interest to study their thermal decomposition mechanisms and temperatures. The earlier investigations into the structural and thermal properties of rare earth nitrates have been recently reviewed [1]. The thermal degradation of the trinitrate hydrates, $Ln(NO_3)_3 \cdot nH_2O$, were first systematically studied by Wendlandt and Bear [2, 3]. Later studies have confirmed their finding that the decomposition proceeds via the anhydrous phase to the oxonitrate $LnONO_3$ and finally to the sesquioxide Ln_2O_3. Cerium and scandium behave exceptionally as they form the Ce(IV) oxonitrate or complex scandium oxonitrates, respectively [4, 5].

The decomposition of rare earth nitrato complexes containing alkali, ammonium or hydroxo ions is more complicated than that of the simple nitrates and several intermediates are possible [1]. In this study we shall discuss the possibility of preparing various anhydrous nitrates by isolating the intermediates formed during the thermal decomposition of complex nitrate hydrates. These results will be compared to thermoanalytical data obtained for a simple nitrate, *viz.* $La(NO_3)_3 \cdot 6H_2O$.

Experimental

The starting materials, $La(NO_3)_3 \cdot 6H_2O$ and $M_2Ln(NO_3)_5 \cdot nH_2O$ ($M = NH_4$, K; Ln = La,Nd, Pr), were prepared by slow crystallization from

John Wiley & Sons. Limited, Chichester
Akadémiai Kiadó, Budapest

aqueous solution [6]. TG experiments were performed in a Perkin-Elmer TGS–2 or TGA–7 equipment using a dynamic nitrogen or air atmosphere and heating rates from 2 to 15 deg min^{-1}. The sample size was 10–20 mg. Simultaneous TG/DTA curves were recorded with a MOM Q-derivatograph using 100–200 mg samples. DSC curves were recorded in a Perkin-Elmer equipment in air using Al crucibles having a small hole in their lid to allow the evolved gases to escape.

Results and discussion

The pentanitrato complexes used as starting materials may contain a variable amount of water. In the case of the ammonium complexes this has been verified by an X-ray crystallographic study [7]. Regardless of the degree of hydration, the anhydrous $M_2Ln(NO_3)_5$ phase is formed around 200°. Figures 1–3 depict the thermoanalytical curves for the lanthanum compounds. It appears that the anhydrous $K_2La(NO_3)_5$ phase is much more stable than the corresponding ammonium compound. Its stability range extends up to 400° while the ammonium compounds starts to decompose already at 200°. The decomposition is completed and La_2O_3 is formed at much lower temperature (600°) for the ammonium compound than for the potassium complex which forms the thermally very stable $KLaO_2$ first at 800°.

There seem to be no significant differences between the decomposition patterns of $(NH_4)_2Ln(NO_3)_5 \cdot 4H_2O$ (Ln = La, Nd, Pr) as shown by the

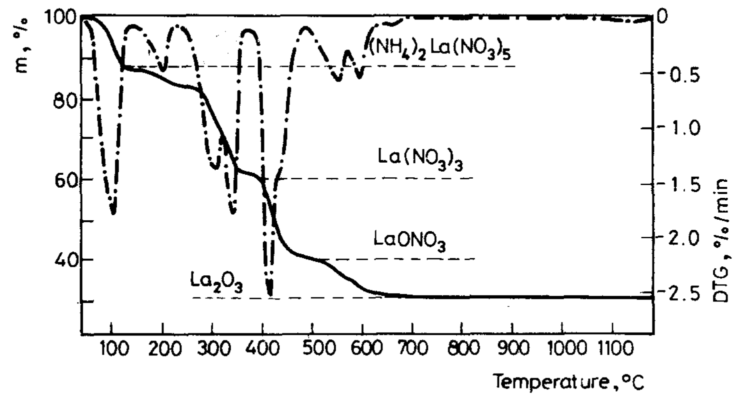

Fig. 1 TG and DTG curves of $(NH_4)_2La(NO_3)_5 \cdot nH_2O$ in nitrogen. Sample weight is 19.8 mg and the heating rate is 5 deg min^{-1}.

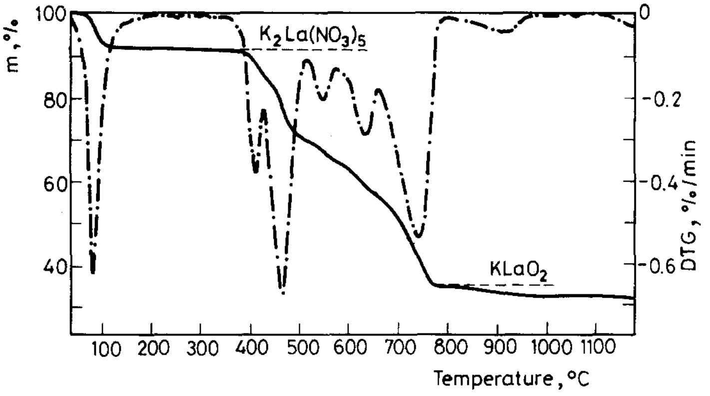

Fig. 2 TG and DTG curves of $K_2La(NO_3)_5 \cdot nH_2O$ in air. Sample weight is 20.6 mg and heating rate 2 deg min^{-1}.

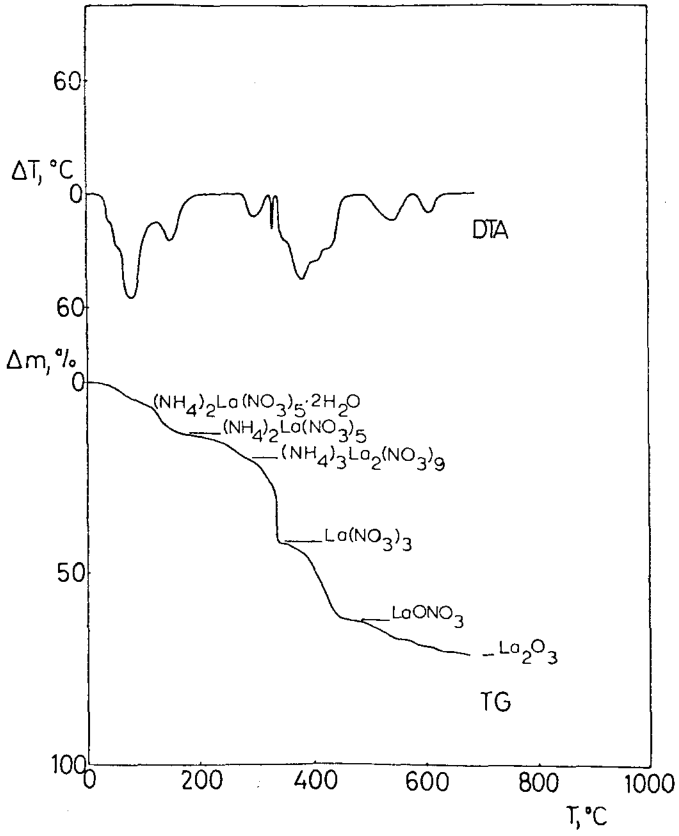

Fig. 3 TG and DTA curves of $(NH_4)_2La(NO_3)_5 \cdot 4H_2O$ in air. Sample weight is 200 mg and heating rate 5 deg min^{-1}.

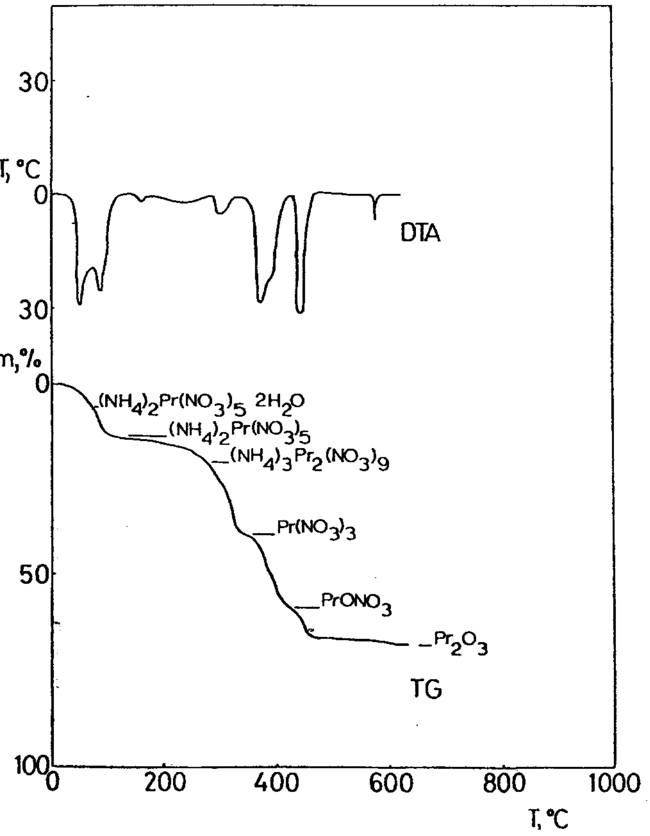

Fig. 4 TG and DTA curves of $(NH_4)_2Pr(NO_3)_5 \cdot 4H_2O$ in air. Sample weight is 100 mg and heating rate 5 deg min^{-1}.

TG/DTA curves (Figs. 3–5). These curves, recorded with relatively large samples and a low heating speed, allow us to examine the possibility to utilize thermal decomposition as a preparative method for the synthesis of anhydrous nitrates $(NH_4)_2Ln(NO_3)_5$, $(NH_4)_3Ln_2(NO_3)_9$, $Ln(NO_3)_3$ and $LnONO_3$ of which especially the cubic nonanitrato complex would be of interest for spectroscopic studies [8].

The formation of $M_3Ln_2(NO_3)_9$ can be seen in the TG curves for the La and Pr complexes but not for the Nd compound. Unfortunately, the stability range of the nonanitrato intermediate appears too low for separation. On the other hand, thermal decomposition could be used for the synthesis of $M_2Ln(NO_3)_5$, $Ln(NO_3)_3$ and $LnONO_3$ in case of all rare earths studied including neodymium. The atmosphere (nitrogen or air) or the

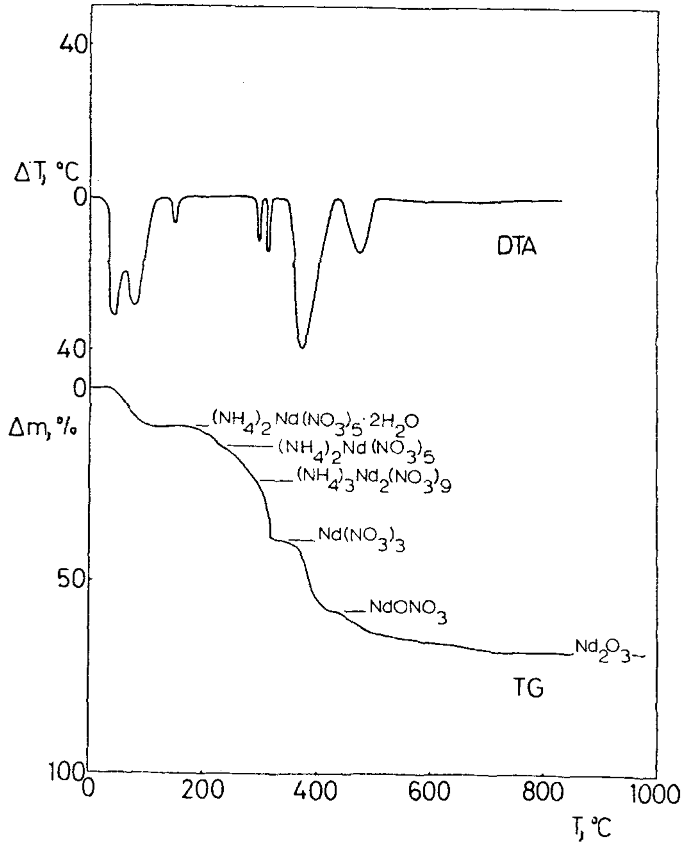

Fig. 5 TG and DTA curves of $(NH_4)_2Nd(NO_3)_5 \cdot 4H_2O$ in air. Experimental conditions as in Fig. 4.

sample weight do not seem to have a significant effect on the decomposition mechanism as seen when comparing the intermediates and temperatures in Figs. 1 and 3.

For comparison, the TG and DSC curves were recorded for $La(NO_3)_3 \cdot 6H_2O$ (Fig. 6). It has a crystal structure where the nitrate groups and all but one of the water molecules are coordinated to lanthanum [9]. Accordingly one could expect the pentahydrate to appear as an intermediate during heating but this phase and other intermediate hydrates appear only transiently according to the TG and DSC data. DSC curve, with an endotherm at 50°, gives an indication that the sample melts before the dehydration in accordance with the results of Dabkowska [10]. A comparison of the calculated and observed weight losses shows that the anhydrous phase $La(NO_3)_3$ is formed above 250° and its decomposition starts at 400°

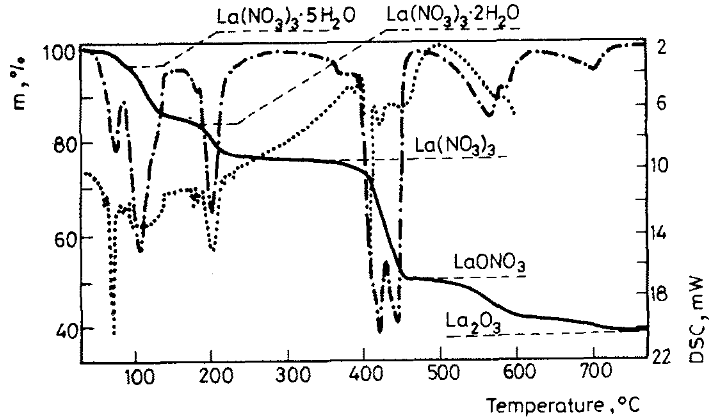

Fig. 6 TG (solid line) and DTG (broken line) curves of La(NO$_3$)$_3$·6H$_2$O in air. Sample weight is 30.6 mg and the heating rate 5 deg min^{-1}. The DSC curve, recorded separately with a 2.2 mg sample, is also depicted (dotted line).

LaONO$_3$ appears stable, too, and its stability range extends over 100 degrees allowing separation. It should be noted, however, that the TG and DSC curves were recorded separately with different sample sizes but the temperatures for various decomposition steps coincide quite well.

References

1 M. Leskelä and L. Niinistö, Handbook of the Physics and Chemistry of the Rare Earths, K. A. Gscheidner Jr. and L. Eyring (Eds.), Vol. 8, North-Holland, Amsterdam 1986, p. 203.

2 W. W. Wendlandt, Anal. Chim. Acta, 15 (1956) 439.

3 W. W. Wendlandt and J. L. Bear, J. Inorg. Nucl. Chem., 12 (1960) 276.

4 S. Pajakoff, Monatsh. Chem., 95 (1964) 1108.

5 L. N. Komissarova, G. Yu. Puskhina and V. I. Spitsyn, Zh. Neorg. Khim., 8 (1963) 1884; Russ. J. Inorg. Chem., (Engl. transl.) 8 (1963) 719.

6 P. Riikonen, M. Sc. Thesis, Helsinki University of Technology, Espoo 1978, 134 p.

7 B. Eriksson, L. O. Larsson and L. Niinistö, Acta Chem. Scand., Ser. A, 36 (1982) 465.

8 W. T. Carnall, S. Siegell, J. R. Ferraro, B. Tani and E. Gebert, Inorg. Chem., 12 (1973) 560.

9 B. Eriksson, L. O. Larsson, L. Niinistö and J. Valkonen, Inorg. Chem., 19 (1980) 1207.

10 M. Dabkowska, Atlas of Thermoanalytical Curves, G. Liptay (Ed.), Akadémiai Kiadó, Budapest 1976, Vol. V, p. 305.

Zusammenfassung — Mittels TG und DTA wurde die thermische Zersetzung der Pentanitratokomplexe von Seltenerden untersucht. Oberhalb 600°C zersetzt sich M$_2$Ln(NO$_3$)$_5$·nH$_2$O (M = NH$_4$, Ln = La, Nd, Pr) in Luft über die Zwischenstufen wasserfreies (NH$_4$)$_2$Ln(NO$_3$)$_5$, Ln(NO$_3$)$_3$ und LnONO$_3$ zu Ln$_2$O$_3$. Mit M = K und Ln = La ist das Zwischenprodukt K$_2$La(NO$_3$)$_5$ äußerst stabil und bei 800°C bildet sich KLaO$_2$. Mit Ausnahme von Nd konnten während der Abbauprozesse sowohl in Luft als auch in Stickstoff die Nonanitratokomplexe $M_3Ln_2(NO_3)_9$ beobachtet werden, deren Stabilitätsbereich jedoch für eine präparative Isolierung in Form einer einzigen Phase zu klein ist. Zum Vergleich wurden die TG- und DSC-Kurven von $La(NO_3)_3 \cdot 6H_2O$ aufgenommen, wobei sich $La(NO_3)_3$ und besonders $LaONO_3$ als stabile Zwischenprodukte erwiesen.

Резюме – Методом ТГ и ДТА изучено термическое разложение пентанитрато-комплексов редкоземельных элементов. Комплексы типа $M_2Ln/NO_3/_5 \cdot nH_2O$ /M=NH$_4$, Ln= La, Nd, Pr/ разлагаются в атмосфере воздуха сначала до безводных солей, а затем до $Ln/NO_3/_3$, $LnONO_3$, а при температуре выше 600° до конечного продукта Ln_2O_3. В случае комплексов с M=K и Ln= La об-образующийся промежуточный продукт $K_2La/NO_3/_5$ чрезвычайно устойчив и только при температуре 800° разлагается до $KLaO_2$. В процессе разложения всех комплексов в атмосфере воздуха и азота, за исключением неодима, было обнаружено образование нонанитратных комплексов $M_3Ln_2/NO_3/_9$, но область их устойчивости была настолько узкой, что не позволило выделить их в качестве единственной фазы. С целью сравнения были измерены ТГ и ДСК кривые гексагидрата тринитрата лантана, показавшие образование стабильных соединений безводного нитрата лантана и $LaONO_3$ в качестве промежуточных соединений.