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TG-DTA STUDY ON THE LANTHANOID TRIFLUOROMETHANESULFONATE COMPLEXES

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Abstract

The thermal decomposition of the lanthanoid trifluoromethanesulfonate (triflate) complexes $\{Ln(CF_3SO_3)_3\cdot 9H_2O; Ln=La–Lu\}$ was studied by TG and DTA methods. From the endothermic and exothermic data of $Ln(CF_3SO_3)_3\cdot 9H_2O$ complexes, pyrolysis behavior of the complexes is classified into three groups: 1) La–Nd salts, 2) Sm–Ho salts, 3) Er–Lu salts. It has also shown that all the final decomposition products were found to result in the formation of LnF_3.

Keywords: lanthanoid trifluoromethanesulfonate complexes, pyrolysis behavior, TG-DTA, thermal decomposition

Introduction

As compared with 3d-transition elements, lanthanoids are known to form complexes of higher coordination numbers ranging from 7 to 12 due to the large size of ions and the ionic nature of the metal–ligand bonding [1]. Until now there have been some thermal studies on the lanthanoid complexes [2–7]. Recently, much attention has been directed to the lanthanoid complexes containing trifluoromethanesulfonate (triflate) [8] because of its unique properties [9–11]. Lanthanoid triflates are also now widely used as a catalyst in various organic reactions [12].

Yanagihara *et al*. [5] have studied thermal decomposition of lanthanum trifluoromethanesulfonate. They stated that the general reaction scheme for the decomposition process can be shown as follows:

$$La(CF_3SO_3)_3 \rightarrow LaF_3+3SO_2+CO_2+CF_3OCF_3$$

However, systematic studies including all lanthanoid members have been still lacking. It is well known that the various data, such as thermodynamic and transport

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properties [13–15], complex formation constants [16], Raman peak frequencies [17] etc., of lanthanoid electrolyte solutions show irregular variations across the series. These irregular variations are explained by the coordination number change of lanthanoid ions in the middle of the series [17, 18]. It is then very interesting to determine the thermal decomposition processes of the lanthanoid triflates of all lanthanoid members. Some new insights could be obtained from the pyrolysis behavior of the complexes.

In this study, we have investigated the thermal decomposition of the lanthanoid trifluoromethanesulfonate (triflates) complexes {$Ln(CF_3SO_3)_3\cdot 9H_2O$; Ln=La–Lu} by TG-DTA measurements.

Experimental

Sample preparation

The lanthanoid triflates {$Ln(CF_3SO_3)_3$; Ln=La–Lu} were prepared from Ln_2O_3 (Santoku Metals, 99.9%) and trifluoromethanesulfonic acid (HCF_3SO_3; Wako Pure Chemicals, 98%>). The oxide was mixed with the slightly excess trifluoromethanesulfonic acid at room temperature and then heated on a hot plate at about 80–90°C to synthesize the $Ln(CF_3SO_3)_3$ and evaporate excess water. The resulting white salt was recrystallized from aqueous solution. The composition of the triflate as precipitated from the solution corresponds to the formula of $Ln(CF_3SO_3)_3\cdot 9H_2O$. The crystals were preserved in a dessicator before use as samples.

TG-DTA measurements

The theromogravimetric (TG) and differential thermal analysis (DTA) measurements were carried out with a Mac Science WS-002 TG-DTA system in static air. About 15 mg of the sample was taken for each run. The sample pan was an open aluminum type. An α-Al_2O_3 powder was used as a reference material. TG and DTA curves were obtained up to ~550°C. The heating rate was 5°C min^{-1}.

Results and discussion

Figures 1–3 show the typical TG and DTA curves of lanthanoid triflates {Fig. 1; La-triflate, Fig. 2; Gd-triflate, Fig. 3; Lu-triflate}. For a convenience, the peak temperatures revealed on the DTA curve are designated to T_{nx} for the onset endothermic temperature and T_{dx} for the onset exothermic temperature (x=1, 2,..), respectively. As seen in Figs 1–3, there are clear differences in the decomposition processes. The DTA curve for lanthanum triflate (Fig. 1) gives two large endothermic peaks and one sharp exothermic peak, but that for gadolinium triflate (Fig. 2) composed of three endothermic peaks and two small exothermic peaks. The DTA trace for lutetium triflate (Fig. 3} shows two large endothermic peaks and two exothermic peaks. The several

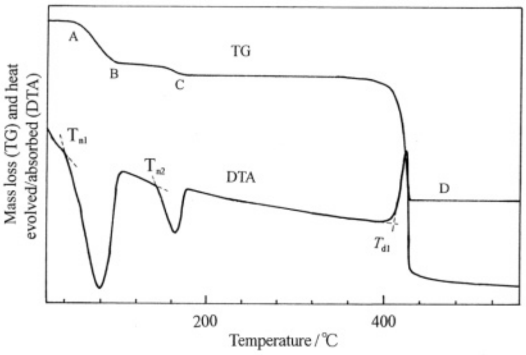

Fig. 1 The TG-DTA trace of the lanthanum triflate. The respective mass loss steps on the TG curve are designated to A, B, C, D. The onset endothermic temperatures revealed on the DTA curve are indicated as T_{nx}. The onset exothermic temperatures are denoted as T_{dx} (x=1, 2..)

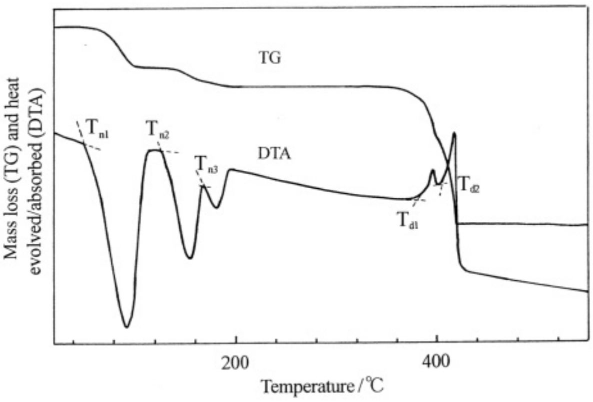

Fig. 2 The TG-DTA trace of the gadolinium triflate

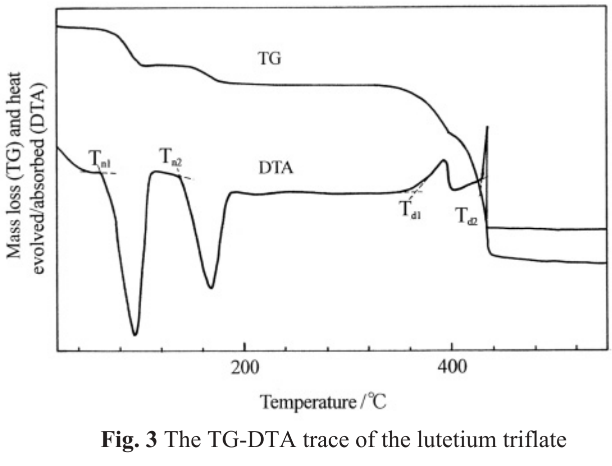

Fig. 3 The TG-DTA trace of the lutetium triflate

peaks on the DTA curve correspond to the successive steps on the gravimetric change on the TG curve. The entire TG curve shows various decomposition steps.

Figure 4 shows the temperatures of all endothermic peaks (T_{nx}) appeared in the DTA curves of lanthanoid triflates across the series. The value of the temperature of the first endothermic peak (T_{n1}) rises gradually from La to Lu complexes. The second endothermic peak (T_{n2}) for La–Nd salts appears to be nearly constant, but that for Sm–Lu salts increases with the increase in the atomic number of lanthanoid. In the case of Sm–Ho salts, the third endothermic peak (T_{n3}) is observed.

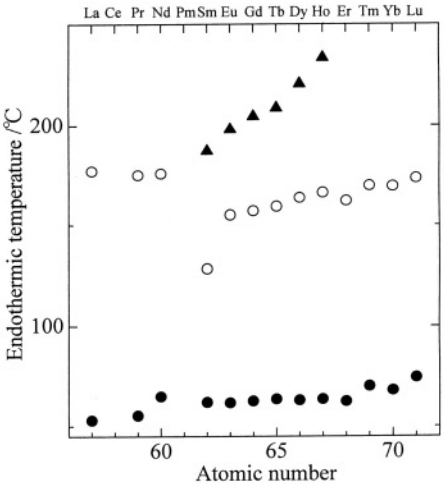

Fig. 4 The series behavior of the temperatures of the endothermic peaks; ● – T_{n1}, ○ – T_{n2}, ▲ – T_{n3}

Figure 5 shows the temperatures of all exothermic peaks (T_{dx}) appeared in the DTA curves of lanthanoid triflates. The first exothermic temperature (T_{d1}) decreases with the increase in the atomic number of lanthanoid. For Sm–Lu triflate salts, the second exothermic temperature (T_{d2}) is observed and the temperature increases with the increase in the atomic number.

The mass loss at the end of the decomposition, expressed in percent of the initial mass, is denoted with ● in Fig. 6. It is noticeable that the values of gravimetric change are almost constant across the series. If the complex is converted completely into LnF_3 at the end of its decompositions, the value of gravimetric change can be calculated by the Eq. (1), and is shown as Δ in Fig. 6.

$$\Delta(\%)=100\frac{\mathrm{Ln(CF_3SO_3)_3{\cdot}9H_2O-LnF_3}}{\mathrm{Ln(CF_3SO_3)_3{\cdot}9H_2O}} \tag{1}$$

As can be seen in Fig. 6, the calculated value is in good agreement with the experimental value within the experimental uncertainty. In addition, in order to confirm that the final decomposition products were not Ln_2O_3, we dissolved the final decom-

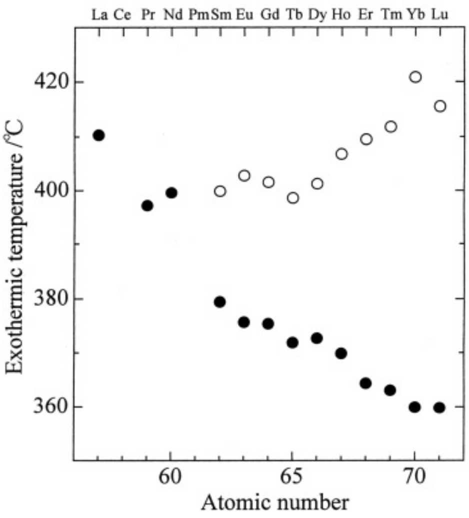

Fig. 5 The series behavior of temperatures of the exothermic peaks; ● – T_{d1}, ○ – T_{d2}

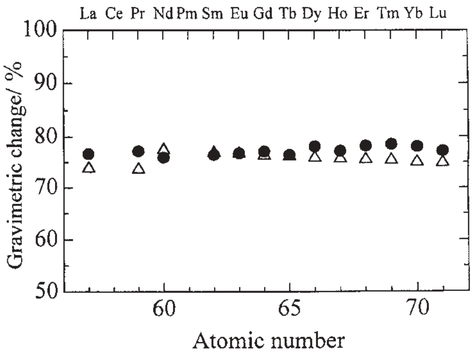

Fig. 6 The relative mass of the final product of the lanthanoid triflates plotted *vs*. the atomic number of Ln; ● – experimental values, △ – calculated values

position products into the nitric acid. It is found that the decomposition products do not dissolve in the nitric acid. It should be pointed out that Yanagihara *et al*. [5] examined the product remaining after thermal decomposition of the $La(CF_3SO_3)_3$ by XRD study. They reported that the lanthanum trifluoride (LaF_3), which has the crystal structure of a hexagonal form, was obtained as the final product. Therefore, in view of these results it is most likely that the lanthanoid triflate complexes were converted into the LnF_3 at the end of their decomposition.

From all the data obtained in this study, the pyrolysis behavior of the complexes can be classified into three groups, i.e., (1) La–Nd salts, (2) Sm–Ho salts, (3) Er–Lu salts. Considering the TG data for the complexes, the reaction scheme for each group of the lanthanoid triflates can be expressed as follows:

$$Ln(CF_3SO_3)_3{\cdot}9H_2O \rightarrow Ln(CF_3SO_3)_3{\cdot}H_2O \rightarrow Ln(CF_3SO_3)_2(CF_3SO_2) \rightarrow LnF_3 \quad (1)$$

The complex begins to lose $8H_2O$ molecules when heated to a certain temperature (step AB in the TG curve) in Fig. 1. Then comes another step BC. The TG change of the step BC is gentler than that of the step AB. Finally comes the decomposition of the $Ln(CF_3SO_3)_2(CF_3SO_2)$ rather rapidly with the rise of temperature, up to a point D where the mass of the residue becomes nearly constant.

$$\begin{aligned}&Ln(CF_3SO_3)_3{\cdot}9H_2O \rightarrow Ln(CF_3SO_3)_3{\cdot}3H_2O \rightarrow Ln(CF_3SO_3)_3 \rightarrow\\ &\rightarrow Ln(CF_3SO_3)_2(CF_3SO_2) \rightarrow Ln(CF_3SO_3)_2{\cdot}F \rightarrow LnF_3 \quad (2)\end{aligned}$$

Taking the occurrence of one more set of endothermic and exothermic peaks in the DTA curve and the corresponding TG curve into account, the decomposition process for the Sm–Ho complexes is different from that for the La–Nd complexes. As compared with the process (1), the main difference in the pyrolysis behavior is that the intermediate decomposition products such as $Ln(CF_3SO_3)_3$ and $Ln(CF_3SO_3)_2\ {\cdot}F$ should exist in the course of decomposition process. The number of water molecules released at the first step in this process is fewer than that in the process (1).

$$\begin{aligned}&Ln(CF_3SO_3)_3{\cdot}9H_2O \rightarrow Ln(CF_3SO_3)_3{\cdot}3H_2O \rightarrow \quad (3)\\ &\rightarrow Ln(CF_3SO_3)_2(CF_3SO_2) \rightarrow Ln(CF_3SO_3)_2{\cdot}F \rightarrow LnF_3\end{aligned}$$

The differences in the pyrolysis behavior between the process (2) and (3) are present in that the $3H_2O$ molecules and an O atom of the CF_3SO_3 molecule are lost simultaneously and $Ln(CF_3SO_3)_3$ is not the intermediate substance in the course of the decomposition.

These differences in the pyrolysis behavior are possibly due to the size differences between lanthanoid ion and its ligands. The complexes of the lighter lanthanoid members with larger ionic radii of Ln^{3+}, will have weaker Ln–H_2O bonds. The crystal structure of $Ln(CF_3SO_3)_3{\cdot}9H_2O$ was determined by X-ray diffraction technique [19]. It was reported that the crystal structure has the hexagonal space group ($P6_3/m$) and the basic coordination sphere around Ln^{3+} ion involves nine water molecules in a tricapped trigonal-prismatic array. There should be the mismatch between the size of lanthanoid ion and that of the coordination sphere of water molecules and the triflate ions. Thus, their coordination spheres are not perfectly packed with $9H_2O$ molecules, so that the interactions will be relatively weaker than those in the complexes with smaller Ln^{3+} ions.

Rillings and Roberts [20] reported the thermal studies on several lanthanide salts of trifluoroacetic acid ($Ln(CF_3CO_2)_3{\cdot}3H_2O$; Ln=Pr, Sm, Er). As like in our results in this study, the compounds, which have isomorphous structures within the series, dehydrate in definite steps and a variety of intermediates are formed depending on the lanthanoid ion. The respective trifluoroacetate shows 1-, 1.5- and 2-hydrate intermediates for the first step of dehydration. The procedural decomposition temperature of the salts increases with increasing the atomic number of the lanthanide. Rillings and Roberts stated that the lanthanide contraction and decreasing base strength of the elements are major causes of the results. It is to be noted that there is a difference in the pyrolysis behavior between the lanthanoid triflates and trifluoroacetate salts; The number of water molecules released per step increases with an increase in atomic number. They suggested the general reaction scheme for the trifluoroacetates to proceed as follows:

$$Ln(CF_3CO_2)_3 \rightarrow LnF_3 + (CF_3CO)_2O + CO_2 + CO$$

Secondary decomposition of the anhydride also occurred.

$$(CF_3CO)_2O \rightarrow CF_3COF + COF_2 + CO$$

Wendlandt [21, 22] studied the thermal decomposition of the hydrated oxalates of lanthanoid ($Ln_2(C_2O_4)_3 \cdot 10H_2O$; Ln=La–Er). As like in our results, he concluded that the thermal decomposition curves of the lanthanoid oxalates can be classified into three groups. The first group includes the oxalates of La–Nd. The formation of intermediate hydrates was not observed and the 10-hydrates decomposed directly to the anhydrous oxalates; the second group consists of the oxalates of Sm–Dy. The formation of 6- and 2-intermediate hydrates was observed; the third group contains Ho and Er. The 2-hydrates appeared to be stable complex.

Conclusions

In conclusion, the present TG-DTA data provides previously unreported information concerning the thermal stability and thermal decomposition of the $Ln(CF_3SO_3)_3 \cdot 9H_2O$ complexes. An important point is that the thermal decomposition behavior of the lanthanoid complexes, as well as thermodynamic properties observed in aqueous lanthanoid salt solutions, is not the same throughout the series and is considerably dependent on the size of the lanthanoid ion. That is, the $Ln(CF_3SO_3)_3 \cdot 9H_2O$ complexes decompose in definite steps and a variety of intermediates are formed depending on the lanthanoid ion. It is found that the pyrolysis behavior of the $Ln(CF_3SO_3)_3 \cdot 9H_2O$ complexes can be classified into three groups as La–Nd salts, Sm–Ho salts, and Er–Lu salts, though all the final decomposition products are LnF_3.

References

1 V. Alexander, Chem. Rev., 95 (1995) 273.
2 R. C. Paul, M. S. Bains and J. S. Ghotra, Indian J. Chem., 7 (1964) 514.
3 G. A.-H. Hussen and H. M. Ismail, Bull. Chem. Soc. Jpn., 67 (1994) 2634.
4 A. M. Soto, N. Yanagihara and T. Ogura, Anal. Chem., 63 (1991) 1170.
5 N. Yanagihara, S. Nakamura and M. Nakayama, Chem. Lett., (1995) 555.
6 H. Aono, M. Tsuzaki, A. Kawaura, M. Sakamoto, E. Traversa and Y. Sasaoka, Chem. Lett., 11 (1999) 1175.

7 M. A. Carvalho Filho, N. S. Fernandes, M. I. G. Leles, R. Mendes and M. Ionashiro, J. Therm. Anal. Cal., 59 (2000) 669.
8 R. D. Howells and J. D. McCown, Chem. Rev., 77 (1977) 69.
9 G. A. Lawrance, Chem. Rev., 86 (1986) 17.
10 F. Pilloud and J.-C. G. Bünzli, Inorg. Chim. Acta, 139 (1987) 153.
11 J.-C. G. Bünzli and A. Milicic-Tang, The Handbook on the Physics and Chemistry of Rare Earths, Vol. 21, Chap. 145, Elsevier Science (1995).
12 S. Kobayashi, Chem. Lett., 2187 (1991); S. Kobayashi and I. Hachiya, Tetrahedron Lett., 33 (1992) 1625; S. Kobayashi, I. Hachiya, K. Takahori and H. Ishitani, Tetrahedron Lett., 33 (1992) 6815.
13 F. H. Spedding, P. F. Cullen and A. Habenschuss, J. Chem. Phys., 78 (1974) 1106.; F. H. Spedding, M. J. Pikal and B. O. Ayers, J. Phys. Chem., 70 (1966) 2440.
14 F. H. Spedding and M. J. Pikal, J. Phys. Chem., 70 (1966) 2430; J. A. Rard and F. H. Spedding, J. Phys. Chem., 79 (1975) 257.
15 H. Kanno and Y. Akama, J. Phys. Chem., 91 (1987) 1263.
16 S. P. Sinha, Struct. Bonding, 30 (1976) 1.
17 H. Kanno and J. Hiraishi, Chem. Phys. Lett., 75 (1980) 553; J. Phys. Chem., 86 (1982) 1488.
18 A. Habenshuss and F. H. Spedding, J. Phys. Chem., 70 (1979) 2797, 3758; 73 (1980) 442.
19 J. M. Harrowfield, D. L. Kepert, J. M. Patrick and A. H. White, Aust. J. Chem., 36 (1983) 483.
20 K. W. Rillings and J. E. Roberts, Thermochim. Acta, 10 (1974) 285.
21 W. W. Wendlandt, Anal. Chem., 30 (1958) 58.
22 W. W. Wendlandt, Anal. Chem., 31 (1959) 408.