Journal of Alloys and Compounds 408–412 (2006) 573–576

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Thermochemical studies on the lanthanoid complexes of trifluoroacetic acid

Y. Yoshimura[*], K. Ohara

Department of Applied Chemistry, National Defense Academy, 1-10-20 Hashirimizu, Yokosuka, Kanagawa 239-8686, Japan

Received 30 July 2004; received in revised form 21 October 2004; accepted 15 December 2004
Available online 17 June 2005

Abstract

The thermal decomposition of the lanthanoid complexes of trifluoroacetic acid ($Ln(CF_3COO)_3·3H_2O$; Ln = La–Lu) was studied by TG and DTA methods. The $Ln(CF_3COO)_3·3H_2O$ complexes decompose in several stages; first dehydrate to the anhydrous state, then followed by decomposition of the anhydrous salt to a stable product of LnF_3. From the endothermic and exothermic data of $Ln(CF_3COO)_3·3H_2O$ complexes, pyrolysis behavior of the complexes is classified into three groups: (1) La–Pr salts; (2) Nd–Gd salts; (3) Tb–Lu salts. It has been shown that all the final decomposition products were found to result in the formation of LnF_3.

Keyword: Thermal analysis

---

1. Introduction

It is well known that lanthanoids form a variety of complexes of higher coordination numbers ranging from 7 to 12 because of the large size of ions [1,2]. Many thermal studies on the lanthanoid complexes have been reported so far [3–8]. Recently, we have reported the thermal decomposition of the lanthanoid trifluoromethanesulfonate (triflate) complexes ($Ln(CF_3SO_3)_3·9H_2O$) [9]. From the endothermic and exothermic data of $Ln(CF_3SO_3)_3·9H_2O$ 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 been shown that all the final decomposition products were found to result in the formation of LnF_3.

In this study, as an extension of the previous work [9], the techniques of thermogravimetry (TG) and differential thermal analysis (DTA) were applied to the study of the thermal decomposition of the lanthanoid complexes of trifluoroacetic acid. It is to be noted that Rillings and Roberts [10] have already performed on powder X-ray diffraction and thermal studies about the trifluoroacetates of praseodymium, samarium and erbium. According to their results, the compounds are isomorphous within their respective series and decompose in several stages. However, systematic studies including all lanthanoid members have been still lacking. It is of importance to determine the thermal decomposition processes of all the series, since new insights could be obtained from the pyrolysis behavior of the complexes.

2. Experimental

2.1. Sample preparation

The lanthanoid complexes of trifluoroacetic acid ($Ln(CF_3COO)_3$; Ln = La–Lu) used in this study were prepared from Ln_2O_3 (Santoku Metals, 99.9%) and trifluoroacetic acid (CF_3COOH; Wako Pure Chemicals, 98%>). The oxide was mixed with the slight excess of dilute trifluoroacetic acid at room temperature and then heated on a hot plate at about ∼50 °C to synthesize the $Ln(CF_3COO)_3$ and evaporate the solution to dryness. The resulting salt was recrystallized from aqueous solution followed by drying in vacuum. The composition of all the complexes as

---

[*] Corresponding author. Tel.: +81 46 841 3810x3583;
fax: +81 46 844 5901.
E-mail address: muki@nda.ac.jp (Y. Yoshimura).

0925-8388/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2004.12.082

precipitated from the solution revealed to exist as trihydrates ($Ln(CF_3COO)_3{\cdot}3H_2O$). The crystals were preserved in a dessicator before use as samples.

2.2. *TG–DTA measurements*

The thermogravimetric (TG) and differential thermal analysis (DTA) measurements were carried out with a Mac Science WS-002 TG–DTA system in static air. About 20 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.

3. Results and discussion

As examples of the typical TG and DTA curves of lanthanoid complexes of trifluoroacetic acid, Figs. 1 and 2 show the results for lanthanum complex of trifluoroacetic acid ($La(CF_3COO)_3{\cdot}3H_2O$) and thulium complex of trifluoroacetic acid ($Tm(CF_3COO)_3{\cdot}3H_2O$), respectively. As seen in Fig. 1, the DTA curve for $La(CF_3COO)_3{\cdot}3H_2O$ gives three endothermic peaks and two exothermic peaks, whereas that for $Tm(CF_3COO)_3{\cdot}3H_2O$ (Fig. 2) is composed of two endothermic peaks and one sharp exothermic peak. The respective peaks on the DTA curve correspond to the successive steps on the gravimetric change on the TG curve.

$La(CF_3COO)_3{\cdot}3H_2O$ compound began to lose hydrate water at ~94 °C giving a small broad peak in the DTA curve, i.e. this stage corresponds to the dihydrate ($La(CF_3COO)_3{\cdot}2H_2O$), whereas the second small peak at around 135 °C appeared to be the monohydrate ($La(CF_3COO)_3{\cdot}H_2O$). Finally, when the temperature reached the third large sharp peak of ~162 °C, the anhydrous state ($La(CF_3COO)_3$) was probably formed. According to Rillings and Roberts [10], there is the “solution effect”, when the complex loses hydrated water molecules. The “solution” here is not a result of melting but a result of the anhydrous compound dissolving in its own evolved water of hydration. The large sharp exotherm at ~287 °C is due to the decomposition of the compound. It is clear that no weight change is indicated in an air atmosphere between ~300 and ~550 °C.

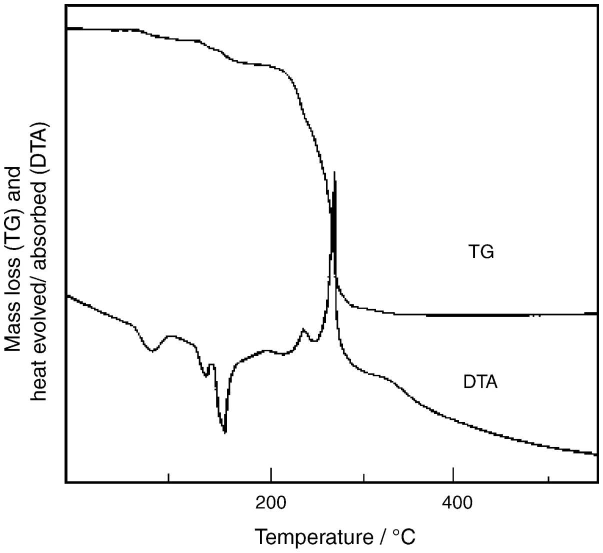

Fig. 1. The TG–DTA trace of the $La(CF_3COO)_3{\cdot}3H_2O$.

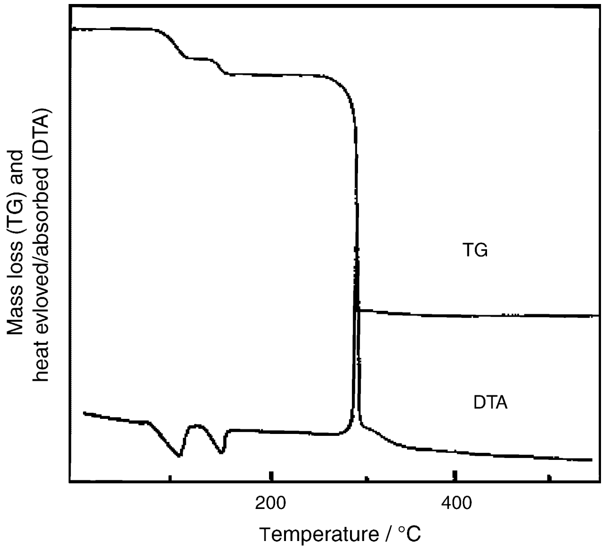

Fig. 2. The TG–DTA trace of the $Tm(CF_3COO)_3{\cdot}3H_2O$.

In the case of $Tm(CF_3COO)_3{\cdot}3H_2O$ (Fig. 2), hydrate waters began to lose at ~108 °C giving two breaks in the TG curve. The first break at 108 °C corresponds to the loss of two water molecules with the resultant formation of the monohydrate ($Tm(CF_3COO)_3{\cdot}H_2O$), while the second break at ~153 °C is due to the anhydrous state ($Tm(CF_3COO)_3$). The anhydrous compound is stable up to a temperature of ~300 °C.

Fig. 3 compiles the temperatures of all endothermic peaks (T_{nx}; $x = 1$–3) appeared in the DTA curves of

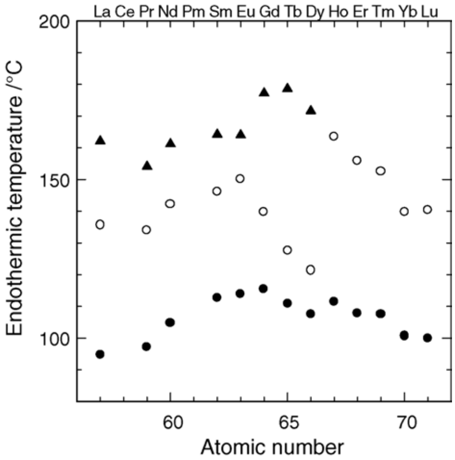

Fig. 3. The series behavior of the temperatures of the endothermic peaks. The peak temperatures revealed on the DTA curve are designated to T_{nx} ($x = 1$–3, ●: T_{n1}, ○: T_{n2}, ▲: T_{n3}) for the onset endothermic temperatures.

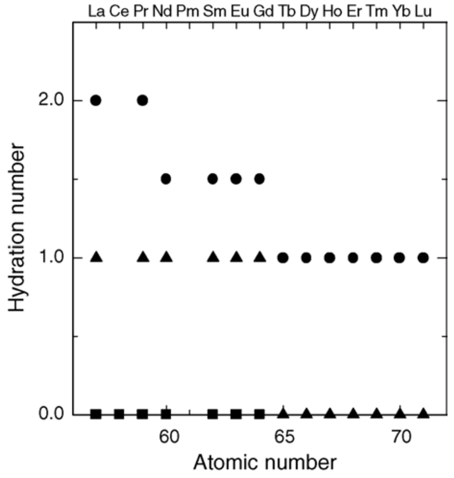

Fig. 4. A schematic diagram for the dehydration processes of $Ln(CF_3COO)_3{\cdot}3H_2O$. Ln = La–Lu (●) shows the hydration number (n) of the $Ln(CF_3COO)_3{\cdot}nH_2O$ ($n = 0$–3) at first dehydration step. (▲) and (■) denote the hydration numbers of second and third dehydration processes, respectively.

$Ln(CF_3COO)_3{\cdot}3H_2O$ across the series. In case of the La–Dy trifluoroacetate salts, the third endothermic peak (▲: T_{n3}) is observed. After Ho salts in the series, first (●: T_{n1}) and second (○: T_{n2}) endothermic peaks are observed. These values revealed rather complex behavior in the temperature region at which dehydration takes place in that three distinct endotherms are present.

The $Ln(CF_3COO)_3{\cdot}3H_2O$ release an appreciable amount of hydrate water depending on the lanthanoid ions. Fig. 4 is a schematic representation on the hydration number of $Ln(CF_3COO)_3{\cdot}3H_2O$ complexes in the course of dehydration processes upon heating. Y axis indicates the hydration number (n) of the $Ln(CF_3COO)_3{\cdot}nH_2O$ ($n = 0$–3) at each step, that is (●) denotes the total hydration number of the complexes at first dehydration process, and (▲) and (■) correspond to the numbers of the second and third dehydration processes, respectively.

Fig. 5 shows the temperatures of all exothermic peaks (T_{dx}; $x = 1,2$) appeared in the DTA curves of lanthanoid complexes of trifluoroacetic acid. The trifluoroacetates of La–Gd are observed to show two exothermic peaks(●: T_{d1}, ○: T_{d2}), but for Tb–Lu acetates, only one exothermic temperature (T_{d1}) is observed. T_{d1} values show extended s-shaped behavior with the increase in the atomic number, which is common behavior for thermodynamic and transport properties [11–13] of lanthanoid electrolyte solutions.

The weight loss at the end of the decomposition (final weight) is in good agreement with the formation of LnF_3. In addition, in order to confirm that the final decomposition products were not Ln_2O_3, we dissolved the final decomposition products into the nitric acid. It is found that the decomposition products do not dissolve in the nitric acid.

From all the data obtained in the present study, the pyrolysis behavior of the lanthanoid trifluoroacetate complexes can be classified into three groups, i.e. (1) La–Pr salts; (2) Nd–Gd salts; (3) Tb–Lu salts. Considering the TG data for the complexes, the reaction scheme for each group of the lanthanoid trifluoroacetates can be expressed as follows:

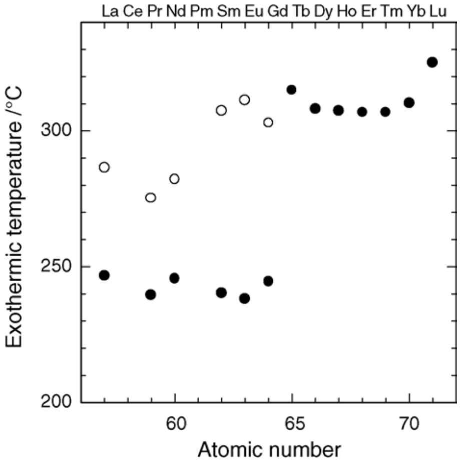

Fig. 5. The series behavior of the temperatures of the exothermic peaks. The peak temperatures revealed on the DTA curve are designated as T_{dx} ($x = 1$–2, (●) Td_1, (○) T_{d2}) for the onset exothermic temperatures.

$$\begin{aligned}&Ln(CF_3COO)_3{\cdot}3H_2O \rightarrow Ln(CF_3COO)_3{\cdot}2H_2O\\ &\quad\rightarrow Ln(CF_3COO)_3{\cdot}H_2O \rightarrow Ln(CF_3COO)_3\\ &\quad\rightarrow Ln(CF_2COO)_3 \rightarrow LnF_3 \qquad (1)\end{aligned}$$

The complex begins to lose one H_2O molecule when heated to a certain temperature. Then comes another dehydration step and two remaining H_2O molecules are released completely. In addition to the "solution effect" mentioned above, the decomposition of $Ln(CF_3COO)_3$ to $Ln(CF_2COO)_3$ may occur considering the TG data for the complexes. However, this assignment is rather speculative. We suspect that the decomposition product of $Ln(CF_2COO)_3$ is not stable, if it exists. On further heating, finally comes the decomposition to LnF_3 rather rapidly with the rise of temperature.

$$\begin{aligned}&Ln(CF_3COO)_3{\cdot}3H_2O \rightarrow Ln(CF_3COO)_3{\cdot}1.5H_2O\\ &\quad\rightarrow Ln(CF_3COO)_3{\cdot}H_2O \rightarrow Ln(CF_3COO)_3\\ &\quad\rightarrow Ln(CF_2COO)_3 \rightarrow LnF_3 \qquad (2)\end{aligned}$$

The differences in the pyrolysis behavior between the process (1) and (2) are present in the number of H_2O molecules at each dehydration process.

$$\begin{aligned}&Ln(CF_3COO)_3{\cdot}3H_2O \rightarrow Ln(CF_3COO)_3{\cdot}H_2O\\ &\quad\rightarrow Ln(CF_3COO)_3 \rightarrow LnF_3 \qquad (3)\end{aligned}$$

Taking the occurrence of one less set of endothermic and exothermic peaks in the DTA curve and the corresponding TG curve into account, the decomposition process for the Tb–Lu complexes is different from those for the groups of (1) La–Pr complexes and (2) Nd–Gd complexes. The characteristic difference in the pyrolysis behavior is mainly present in that the $Ln(CF_2COO)_3$ 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. There should be the mismatch between the size of lanthanoid ion and that of the coordination sphere of water molecules and the trifluoroacetate ions. Their coordination spheres are not perfectly packed with three H_2O molecules, so that the interactions will be relatively weaker than those in the complexes with smaller Ln^{3+} ions.

As mentioned briefly in the introduction section, Rillings and Roberts [10] carried out thermal studies on only three lanthanide salts (Pr, Sm, Er) of trifluoroacetic acid. They heated the compounds to higher temperature of ∼1200 °C. It was reported that slow decomposition was observed from 680 to 890 °C resulting in the formation of PrOF as an unstable intermediate. Further heating in the wet atmosphere produced additional hydrolysis until ∼1100 °C. In general, all of the anhydrous compounds decomposed initially to the LnF_3 and then the LnOF and Ln_2O_3 products were formed upon further decomposition under the conditions described in their paper. They also stated that the compounds, which have isomorphous structures within the series with similar d spacings and line intensities [10,14], dehydrate in definite steps.

They suggested the general decomposition 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.

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

There have been a number of thermal decomposition studies on rare earth acetates [15–21]. Adachi and Secco [15] reported the thermal transformation in anhydrous acetates. The anhydrous acetates ($Ln(CH_3COO)_3$) prepared from the decomposition of the hydrated rare earth acetates were stable and decomposed only above 400 °C. The anhydrous acetates also show two stages of decomposition; At the first stage between 420 and 460 °C, anhydrous acetates decompose to $Ln_2O_3{\cdot}CO_2$ and at the second stage to the formation of the Ln_2O_3. General decomposition paths are as follows:

$$2Ln(CH_3CO_2)_3 \rightarrow Ln_2O_3{\cdot}CO_2 + 2CO_2 + 3CH_3COCH_3$$

$$Ln_2O_3{\cdot}CO_2 \rightarrow Ln_2O_3 + 2CO_2$$

As compared with the results of trifluoroacetates ($Ln(CF_3COO)_3$), the anhydrous $Ln(CH_3COO)_3$ complexes decompose at relatively lower temperatures. This might be due to the effect of the charge diminution at oxygen of the acetate ion by fluorine substitution [22]. Electron-withdrawing groups such as F produce significant changes in the electron density distribution of a molecule or molecular ion.

In conclusion, the present TG–DTA data provides detailed information concerning the thermal stability and thermal decomposition of the $Ln(CF_3COO)_3{\cdot}3H_2O$ complexes across all the rare earth series. The $Ln(CF_3COO)_3{\cdot}3H_2O$ complexes decompose in several stages; first dehydrate to the anhydrous state, then followed by decomposition of the anhydrous salt to a stable product of LnF_3. Both TG and DTA analyses revealed the decomposition of the salts to be highly exothermic. An important point is that the pyrolysis behavior of the $Ln(CF_3COO)_3{\cdot}3H_2O$ complexes can be classified into three groups as (1) La–Pr salts; (2) Nd–Gd salts; and (3) Tb–Lu salts, though all the final decomposition products are LnF_3 up to ∼550 °C. This means 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.

References

[1] V. Alexander, Chem. Rev. 95 (1995) 273–342.
[2] M. Leskelä, L. Niinistö, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, Elsevier, 1986 (chapter 56).
[3] R.C. Paul, M.S. Bains, J.S. Ghotra, Indian J. Chem. 7 (1964) 514–519.
[4] G.A.-H. Hussen, H.M. Ismail, Bull. Chem. Soc. Jpn. 67 (1994) 2634–2638.
[5] A.M. Soto, N. Yanagihara, T. Ogura, Anal. Chem. 63 (1991) 1178.
[6] N. Yanagihara, S. Nakamura, M. Nakayama, Chem. Lett. (1995) 555–556.
[7] H. Aono, M. Tsuzaki, A. Kawaura, M. Sakamoto, E. Traversa, Y. Sasaoka, Chem. Lett. 11 (1999) 1175–1176.
[8] M.A. Carvalho Filho, N.S. Fernandes, M.I.G. Leles, R. Mendes, M. Ionashiro, J. Therm. Anal. Calorim. 59 (2000) 669–674.
[9] K. Egashira, Y. Yoshimura, H. Kanno, Y. Suzuki, J. Therm. Anal. Calorim. 71 (2003) 501–508.
[10] K.W. Rillings, J.E. Roberts, Thermochim. Acta 10 (1974) 285–298.
[11] F.H. Spedding, M.J. Pikal, B.O. Ayers, J. Phys. Chem. 70 (1966) 2440–2447.
[12] J.A. Rard, F.H. Spedding, J. Phys. Chem. 79 (1975) 257–262.
[13] H. Kanno, Y. Akama, J. Phys. Chem. 91 (1987) 1263–1266.
[14] J.E. Roberts, J. Am. Chem. Soc. 83 (1961) 1087–1088.
[15] G. Adachi, E.A. Secco, Can. J. Chem. 50 (1972) 3100–3103.
[16] K.C. Patil, G.V. Chandrashekhar, M.V. George, C.N.R. Rao, Can. J. Chem. 46 (1968) 257–265.
[17] K. Manabe, M. Ogawa, Nihonkagakukaishi (1982) 694–696.
[18] K. Manabe, M. Ogawa, Y. Eizuka, Nihonkagakukaishi (1983) 450–453.
[19] K. Manabe, M. Ogawa, Nihonkagakukaishi (1983) 1092–1095.
[20] D.D. Ensor, G.R. Choppin, J. Inorg. Nucl. Chem. 42 (1980) 1477–1480.
[21] I. Mayer, F. Kassierer, J. Inorg. Nucl. Chem. 28 (1966) 2430–2432.
[22] J. Barthel, H.-J. Gores, L. Kraml, J. Phys. Chem. 100 (1996) 1283–1287.