Thermochimica Acta, 208 (1992) 181–190
Elsevier Science Publishers B.V., Amsterdam

Thermal decomposition process of some rare-earth–nitrilotriacetic acid–serine mixed complexes

W.M. Sun, C.J. Niu and Y.Q. Jia

Changchun Institute of Applied Chemistry, Academia Sinica Changchun, Jilin (People's Republic of China)

(Received 6 January 1992)

Abstract

Thermal decomposition processes of the mixed complexes of nitrilotriacetates of Pr, Sm, Tb, Ho and Tm with 2-amino-3-hydroxypropionic acid have been investigated. The results indicate that serine may coordinate to the rare earth ion via its hydroxyl group, not by means of its carboxyl group. From the thermogravimetric and the derivative thermogravimetric curves it can be deduced that there may be six or seven steps in the thermal decomposition process of these mixed complexes, and that not all thermal decomposition processes in these mixed complexes are the same. Some possible thermal decomposition reactions have been proposed, and the differences between the thermal decomposition processes of these complexes are also discussed.

INTRODUCTION

The complexation reactions of rare earth ions with nitrilotriacetic acid in aqueous solution or in aqueous–ethanol solution have been studied [1–3]. Work on the mixed complexes of the rare earth ions with nitrilotriacetic acid and other ligands has also been published [3–6]. It is found that the rare-earth–bi(nitrilotriacetate) complexes of 3,6-di-di(dimethylamino)dibenzopyriodonium are biologically active and possess some antitumor activity [6].

The amino acid is one of the most important biological substances. Therefore, to investigate the mixed complexes of rare earth ions with nitrilotriacetic acid and amino acids will be very interesting. We have therefore synthesized the solid mixed complexes of some rare earths with nitrilotriacetic acid and serine and measured the thermogravimetric and derivative thermogravimetric curves of these mixed complexes. We found that serine may coordinate directly to the rare earth ion by means of its hydroxyl group but not its carboxyl group, and that the thermal

---

Correspondence to: Y.Q. Jia, Changchun Institute of Applied Chemistry, Academia Sinica, Changchun, Jilin, People's Republic of China.

0040-6031/92/$05.00 © 1992 – Elsevier Science Publishers B.V. All rights reserved

decomposition process of these mixed complexes is rather complicated; there may perhaps be six or seven steps in the thermal decomposition process. In addition, not all thermal decomposition processes are the same for the mixed complexes of these rare earth ions.

EXPERIMENTAL

All the chemicals used in the synthetic process were of analytical reagent grade.

The aqueous solution of the rare earth chloride was prepared by dissolving the rare earth oxide (purity >99.9%) in dilute hydrochloric acid. The concentration of the rare earth ion was determined by means of an EDTA titration. The carbonates of the rare earths were obtained by adding an aqueous solution of ammonium carbonate (8%) to the aqueous solution of the corresponding rare earth chloride $[(1.0–1.5) \times 10^{-3} M]$ mentioned above. The solid rare earth carbonate was separated from the solution by filtration and the solid product was washed with distilled water. The freshly prepared rare earth carbonate was dissolved by an aqueous solution of nitrilotriacetic acid (NTA) in an 1:1 stoichiometric ratio. Then 2-amino-3-hydroxypropionic acid (serine or Ser), in an equivalent proportion of rare earth to serine of 1:1, was added to the solution of the rare earth nitrilotriacetate. The resultant solution was filtered and the clear filtrate was placed in a thermostated bath at 40°C

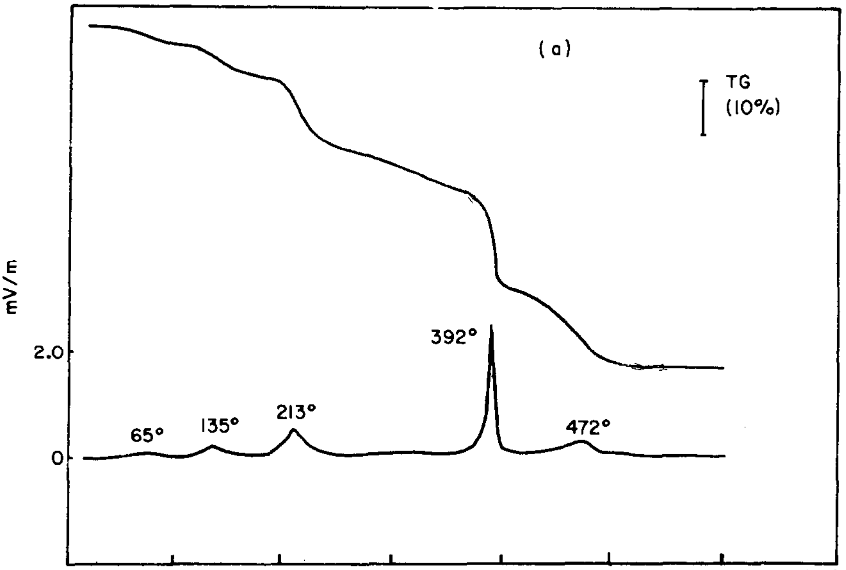


Fig. 1. The TG and DTG curves of the mixed complexes of some rare earth nitrilotriacetates and serine (a) Pr(NTA) · (Ser) · H_2O, $W = 3.10$ mg; (b) Sm(NTA) · (Ser) · H_2O, $W = 3.12$ mg; (c) Tb(NTA) · (Ser) · H_2O, $W = 4.10$ mg; (d) Ho(NTA) · (Ser), $W = 3.89$ mg; (e) Tm(NTA) · (Ser), $W = 3.58$ mg.

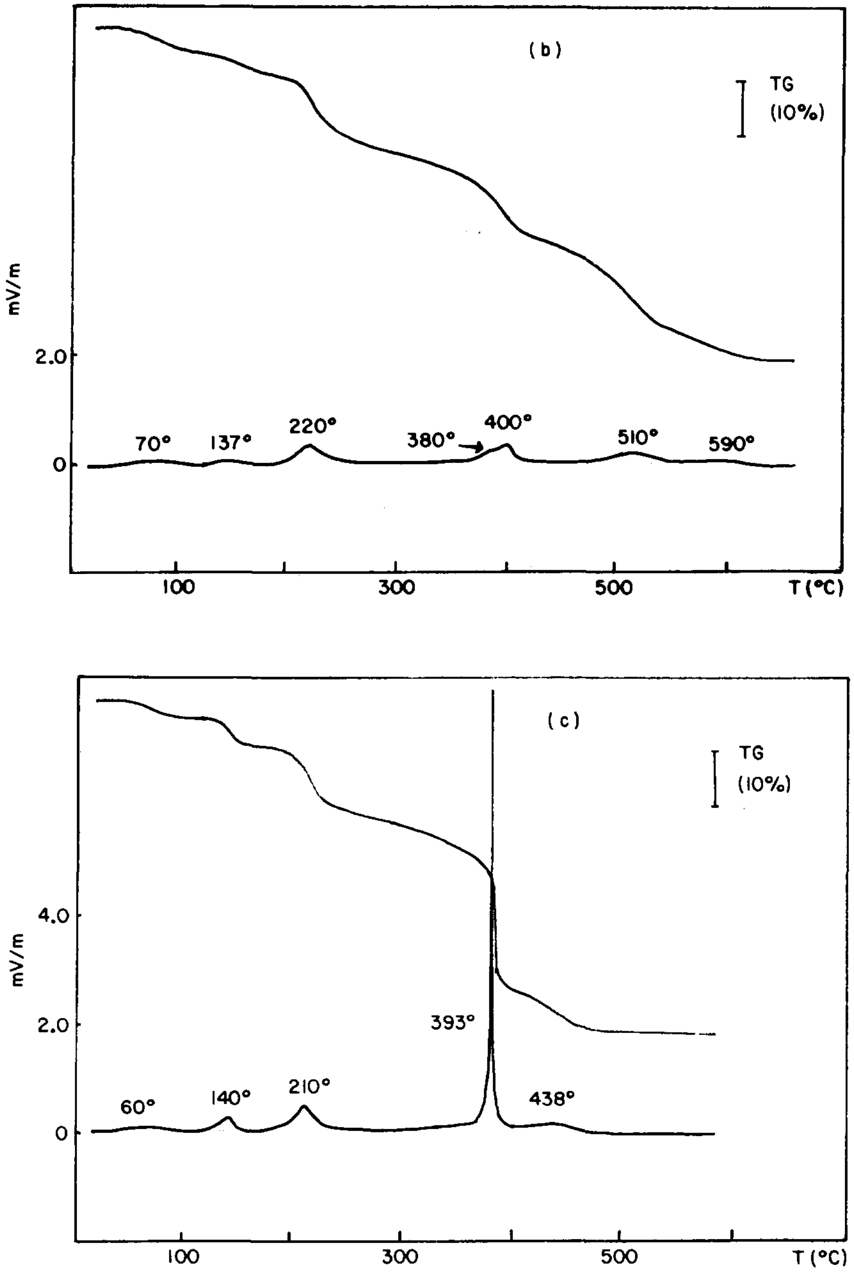
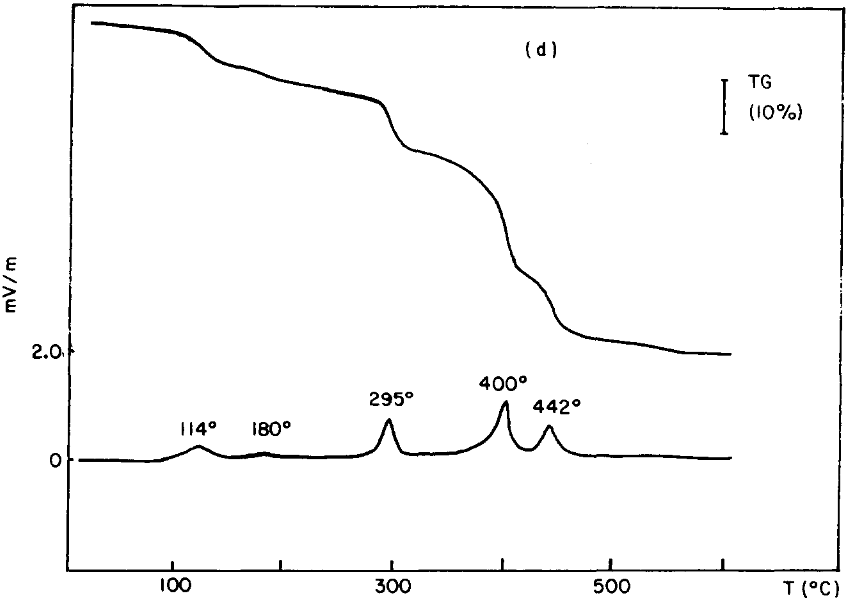


Fig. 1—contd.

and continuously stirred for 12 h. The obtained solid compound was collected by filtration and washed with ether. Finally, the solid compound was dried in a vaccum desiccator over P_2O_5. The results of elemental analyses for these solid compounds indicate that these solid compounds are the mixed complexes of the rare earth nitrilotriacetate and serine. The general formula is $RE(N(CH_2COO)_3) \cdot (HOCH_2CH(NH_2)COOH) \cdot nH_2O$



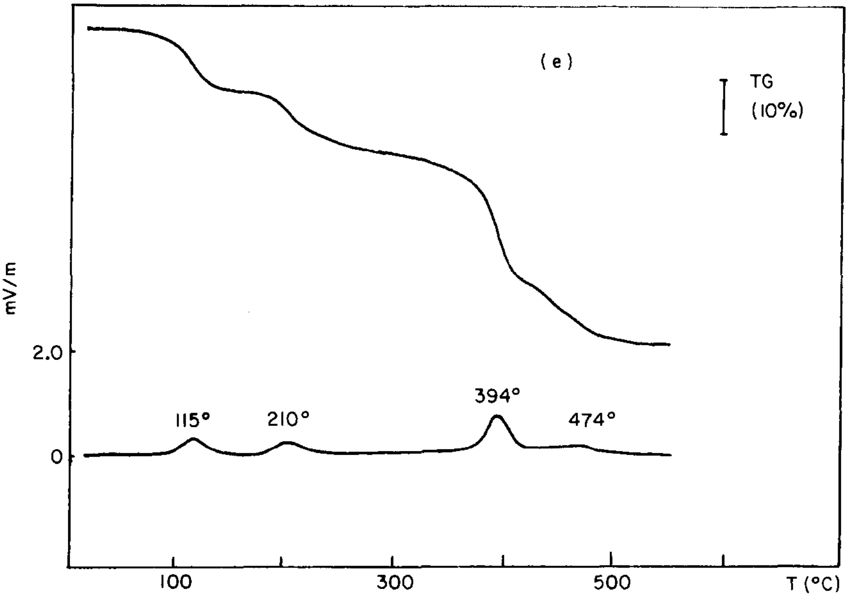


Fig. 1—contd.

or RE(NTA) · (Ser) · nH$_2$O ($n = 1$ for RE = Pr, Sm and Tb; $n = 0$ for RE = Ho and Tm).

Thermal studies were carried out on a Shimadzu DT-30 thermal analyzer. The thermogravimetric and derivative thermogravimetric curves were registered in dynamic conditions using an air flow rate of 60 ml min^{-1} and a heating rate of 5°C min^{-1}, and with sample masses between 3 and

5 mg. The thermogravimetric and derivative thermogravimetric curves of the mixed complexes are shown in Fig. 1.

RESULTS AND DISCUSSION

In the TG and DTG curves of the Pr, Sm and Tb mixed complexes, the first weight loss can be observed when the temperature is below 80°C (see also Table 1). The experimental percentage weight losses of 4, 4 and 3.5% are in good agreement with the water contents of 4, 4 and 3.8% in Pr(NTA) · (Ser) · H_2O, Sm(NTA) · (Ser) · H_2O and Tb(NTA) · (Ser) · H_2O, respectively. However, neither the TG curves nor the DTG curves of the Ho and Tm mixed complexes show any considerable weight loss until the temperature is above 90°C. The fact that the dehydration temperature is not very low may perhaps indicate that the water molecule in the Pr, Sm and Tb mixed complexes may not be an absorbed one, but water of hydration. Whether there is a water molecule in the mixed complexes of different rare earth ions will be related to the ionic radius of the rare earth ion. The ionic radius of the heavy rare earths (Ho, Tm) is smaller than that of the light rare earths (Pr, Sm). Possibly a water molecule can exist only in a mixed complex of a rare earth of larger ionic radius.

After dehydration, the second weight loss in the TG curves of the Pr, Sm and Tb mixed complexes corresponds to the peak at 135–140°C in the DTG curves. The total weight loss is about 10%. In consideration of all the possible pyrolytic reactions, we can assume that this weight loss is caused by the pyrolysis of serine. Serine can coordinate to the rare earth ion via either a hydroxyl group or a carboxyl group. We surmise that the serine in the mixed complexes of the rare earth nitrilotriacetates and serine coordinates directly to the rare earth ion by means of its hydroxyl group but not its carboxyl group. This is not only because the association of the carboxyl group with the adjacent amino group in serine will reduce the ability of the carboxyl group to coordinate to the rare earth ion, but also because the large NTA molecule in the inner coordination sphere will sterically hinder the bigger carboxyl grop from coordinating directly to the central rare earth ion. Based on this assumption, we can consider that the second weight loss of the Pr, Sm and Tb mixed complexes may be related to the pyrolysis of the carboxyl group and the amino group in serine. Because, in serine, an oxygen atom of the carboxyl group can link to the nitrogen atom by a hydrogen bond, a β-elimination reaction can occur in the pyrolysis. If an oxygen atom and an NH group are lost in this pyrolytic reaction, the theoretical weight loss will be 6.9%, 6.7% and 6.6% for the mixed complexes of Pr, Sm and Tb, respectively. This correlates very well with the experimental weight loss of 6–7%. Because some aldehydes can be prepared by heating a carboxylic acid [7], after the above mentioned

TABLE 1

Thermal decomposition data for the mixed complexes of some rare earth nitrilotriacetates and serine

Reaction	T_{max} in DTG (°C)	Total weight loss (%)	
		W(exp.)	W(theor.)
$Pr(NTA) \cdot (Ser) \cdot H_2O \rightarrow Pr(NTA) \cdot (Ser) + H_2O$	65	4	4
$Pr(NTA) \cdot (Ser) \rightarrow Pr(NTA) \cdot (HOCH_2CH_2CHO)$ + d.p. [a]	135	10	10.9
$Pr(NTA) \cdot (HOCH_2CH_2CHO) \rightarrow Pr(NTA) \cdot (HOCH_3)$ + d.p.	213	21	20.2
$Pr(NTA) \cdot (HOCH_3) \rightarrow Pr(NTA)$ + d.p.		29	27.3
$Pr(NTA) \rightarrow Pr(HCOO)_3$ + d.p. } [b]			39
$Pr(HCOO)_3 \rightarrow Pr_2(CO_3)_3$ + d.p. }	392	48	48.9
$Pr_2(CO_3)_3 \rightarrow Pr_4O_{11}$ + d.p.	472	63	62.4
$Sm(NTA) \cdot (Ser) \cdot H_2O \rightarrow Sm(NTA) \cdot (Ser) + H_2O$	70	4	4
$Sm(NTA) \cdot (Ser) \rightarrow Sm(NTA) \cdot (HOCH_2CH_2CHO)$ + d.p.	137	10	10.7
$Sm(NTA) \cdot (HOCH_2CH_2CHO) \rightarrow Sm(NTA) \cdot (HOCH_3)$ + d.p.	220	20	19.8
$Sm(NTA) \cdot (HOCH_3) \rightarrow Sm(NTA)$ + d.p.	380	28	26.7
$Sm(NTA) \rightarrow Sm(HCOO)_3$ + d.p. } [b]		40	38.2
$Sm(HCOO)_3 \rightarrow Sm_2(CO_3)_3$ + d.p. }	400	50	47.9
$Sm_2(CO_3)_3 \rightarrow Sm_2O_3 \cdot 0.5CO_2$ + d.p.	510	57	57.5
$Sm_2O_3 \cdot 0.5CO_2 \rightarrow Sm_2O_3 + 0.5CO_2$	590	63	62.2

$Tb(NTA) \cdot (Ser) \cdot H_2O \rightarrow Sm(NTA) \cdot (Ser) + H_2O$	60	3.5	3.8
$Tb(NTA) \cdot (Ser) \rightarrow Tb(NTA) \cdot (HOCH_2CH_2CHO)$ + d.p.	140	10	10.4
$Tb(NTA) \cdot (HOCH_2CH_2CHO) \rightarrow Tb(NTA) \cdot (HOCH_3)$ + d.p.	210	20	19.3
$Tb(NTA) \cdot (HOCH_3) \rightarrow Tb(NTA)$ + d.p.		27	26.2
$Tb(NTA) \rightarrow Tb(HCOO)_3$ + d.p. \} [b]			37.5
$Tb(HCOO)_3 \rightarrow Tb_2(CO_3)_3$ + d.p.	394	51	46.7
$Tb_2(CO_3)_3 \rightarrow Tb_4O_7$ + d.p.	438	60	60.2
$Ho(NTA) \cdot (Ser) \rightarrow Ho(NTA) \cdot (HOCH_2CH_2CHO)$ + d.p.	114	6.5	6.8
$Ho(NTA) \cdot (HOCH_2CH_2CHO) \rightarrow Ho(NTA) \cdot (HOCH_2CH_3)$ + d.p.	180	12.5	12.9
$Ho(NTA) \cdot (HOCH_2CH_3) \rightarrow Ho(NTA)$ + d.p.	295	22	23
$Ho(NTA) \rightarrow Ho(HCOO)_3$ + d.p. \} [b]		35	34.6
$Ho(HCOO)_3 \rightarrow Ho_2(CO_3)_3$ + d.p.	400	45	44.4
$Ho_2(CO_3)_3 \rightarrow Ho_2O_3$ + d.p.	442	59	58.8
$Tm(NTA) \cdot (Ser) \rightarrow Tm(NTA) \cdot (HOCH_2CH_3)$ + d.p.	115	12	12.8
$Tm(NTA) \cdot (HOCH_2CH_3) \rightarrow Tm(NTA)$ + d.p.	210	21	22.8
$Tm(NTA) \rightarrow Tm(HCOO)_3$ + d.p. \} [b]			34.3
$Tm(HCOO)_3 \rightarrow Tm_2(CO_3)_3$ + d.p.	394	44	44
$Tm_2(CO_3)_3 \rightarrow Tm_2O_3$ + d.p.	474	58	58.3

[a] d.p. indicates decomposition product(s).

[b] $RE(NTA) \rightarrow RE(HCOO)_3$ and $RE(HCOO)_3 \rightarrow RE_2(CO_3)_3$ may occur sequentially or RE(NTA) may be converted directly to $RE_2(CO_3)_3$.

reaction serine may become a β-hydroxy-aldehyde through a molecular rearrangement. The hydroxyl group still coordinates directly to the rare earth ion. Then the above mentioned β-hydroxypropionaldehyde will undergo pyrolysis at about 200°C and lose a –CHCHO group. In this case, the theoretical total weight loss for Pr(NTA) · (Ser) · H_2O, Sm(NTA) · (Ser) · H_2O and Tb(NTA) · (Ser) · H_2O will be 20.2%, 19.8% and 19.3%, respectively. This closely agrees with the experimentally total weight losses of 21, 20 and 20%. The loss of CH_3OH coordinated directly to the rare earth ion is a slow process. In this step, the theoretical total weight loss of the Pr, Sm an Tb mixed complexes is 27.3%, 26.7% and 26.2%, respectively. From the TG curves of the Pr, Sm and Tb mixed complexes, we can evaluate the experimental total weight loss at 360°C. This is about 29%, 28% and 27%, respectively, and is very close to the theoretical total weight loss.

The thermal decomposition process of serine in the anhydrous complexes Ho(NTA) · (Ser) and Tm(NTA) · (Ser) is apparently different from that in the Pr, Sm and Tb mixed complexes. The Ho(NTA) · (Ser) will lose an oxygen atom and an NH group, like Pr(NTA) · (Ser), Sm(NTA) · (Ser) and Tb(NTA) · (Ser), but the corresponding peak in the DTG curve is at 114°C, not at 135–140°C. The experimental weight loss is about 6.5% and agrees with the theoretical weight loss of 6.8%. However, in the next step, the mixed complex will lose a CO group at 180°C instead of a –CHCHO group at 210–220°C. The corresponding theoretical weight loss of 6.1% is close to the experimental weight loss of 6%. The pyrolytic reaction in this step is similar to the decarbonylation of an aldehyde [7]. Like the loss of the CH_3OH coordinated directly to Pr, Sm and Tb, the loss of the CH_3CH_2OH coordinated to Ho is also a slow process. The theoretical total weight loss is 23%. The approximate total weight loss at 300°C evaluated from the experimental TG curve of Ho(NTA) · (Ser) is about 22%. As for Tm(NTA) · (Ser), the serine in the mixed complex will lose not only a nitrogen atom and but also a carboxyl group simultaneously in the first weight loss at about 115°C. This is very similar to the decarboxylation reaction of a β-hydroxy carboxylic acid in organic chemistry [7]. The theoretically calculated weight loss is 12.8% and the experimental weight loss is about 12%. After the first pyrolysis step, the CH_3CH_2OH coordinated directly to the Tm will slowly be lost. However, the decomposition temperature (about 210°C) is much below that (about 300°C) for the mixed complexes of other rare earths.

We have also noted that the thermal decomposition temperature in each pyrolytic step of serine in these rare earth mixed complexes decreases gradually from Pr to Tm. This may perhaps, be because the chemical bond between the central rare earth ion and the oxygen atom of the hydroxyl group in serine becomes weaker and weaker from Pr to Tm, and this will result in a different effect on the other chemical bonds in the serine molecule owing to the inductive effect.

Therefore, from the above discussion, we can conclude that the thermal decomposition process of the mixed complexes of rare earth nitrilotriacetates with serine is mainly dehydration, and the process of pyrolysis of serine in RE(NTA) · (Ser) · nH_2O. The fact that the carboxyl group and the amino group in serine undergo pyrolysis first may demonstrate that serine coordinates directly to the rare earth ion via its hydroxyl group but not its carboxyl group. In addition, we want to point out that the thermal decomposition process of free serine must be very different from that of serine in this mixed complex [8], because the coordination of serine to the rare earth ion must influence the thermal behavior of the serine.

At first, the thermal decomposition of the rare earth nitrilotriacetate is very slow when the temperature is below 380°C. However, when the temperature is over 390°C, the pyrolytic reaction becomes very fast. All the rare earth nitrilotriacetates will become rare earth carbonates above 400°C. In this case, the theoretical total weight loss of these complexes is 48.9%, 47.9%, 46.7%, 44.4% and 44.0% for the Pr, Sm, Tb, Ho and Tm mixed complex, respectively. The approximate value of the experimental weight loss evaluated from the TG curves of these mixed complexes is 48%, 50%, 51%, 45% and 44%, respectively. We find that the rare earth nitrilotriacetate seems to undergo two steps when it becomes a rare earth carbonate. First the rare earth nitrilotriacetate becomes the rare earth formate, then the rare earth formate is decomposed to the rare earth carbonate. Of course, it is possible that the two processes occur simultaneously. Afterwards, like all the rare earth carbonates, the final product at a high temperature is the corresponding rare earth oxide. Pr_6O_{11}, Sm_2O_3, Tb_4O_7, Ho_2O_3 or Tm_2O_3, respectively. In this step, the theoretically calculated total weight loss of the mixed complex is 62.4%, 62.2%, 60.2%, 58.8% and 58.3%, respectively. The experimental total weight loss of the sample determined from the TG curve is 63%, 63%, 60%, 59% and 58%, respectively.

CONCLUSION

The thermal decomposition process of the rare earth nitrilotriacetate–serine complexes is rather complicated. When the temperature is below 360°C, the main pyrolytic reaction is the dehydration of Pr(NTA) · (Ser) · H_2O, Sm(NTA) · (Ser) · H_2O and Tb(NTA) · (Ser) · H_2O and pyrolysis of serine in the anhydrous rare earth mixed complexes. The hydroxyl group of serine coordinates directly to the central rare earth ion, and the carboxyl group of serine and the amino group in the side chain will undergo continuous pyrolysis. Finally, the thermal decomposition results in the dissociation of the hydroxyl group in the pyrolysis residue of serine from the rare earth ion. Not all the decomposition processes for these mixed complexes are the same because of differences between the chemical bonding of different rare earth ions with serine. However, the thermal decomposition process of all the rare earth nitrilotriacetates is the same.

REFERENCES

1 W. Noddack and G. Oertel, Z. Elektrochem., 61 (1957) 1216.
2 H.G. Brittain and J.P. Jasinske, J. Coord. Chem., 18 (1988) 279.
3 P.C. Pant, D.P. Bhatt and M. Chandra, Trans. SAEST., 21 (1986) 189.
4 N.A. Dobrynina, I.E. Svetlova, N.S. Smirnova, L.I. Martynenko and A.M. Evseeva, Zh. Neorg. Khim., 35 (1990) 1216.
5 I.E. Svetlova, N.A. Dobrynina, N.S. Smirnova, L.I. Martynenko and A.M. Evseeva, Zh. Neorg. Khim., 33 (1988) 1429.
6 Chen Shuying, Lin Zhanliang, Hou Zijie, Li Du, Wang Xin, Fu Ping and Zhang Peiyan, Huaxue Xuebao, 47 (1989) 428.
7 J. March, Advanced Organic Chemistry. Reactions, Mechanisms, and Structure, 3rd edn., Wiley, New York, 1985.
8 M.L. Rodriguez-Mendez, F.J. Rey, J. Martin-Gil and F.J. Martin-Gil, Thermochim. Acta, 134 (1988) 73.