Thermal decomposition of solid state compounds of lanthanide and yttrium benzoates in CO$_2$ atmosphere

J. R. Locatelli[1], A. B. Siqueira[2], C. T. Carvalho[2], M. Ionashiro[2]*

[1]*Academia da Força Aérea, AFA. Estrada de Aguaí; s/n, CEP 13630-000 Pirassununga, SP, Brazil.*
[2]*Instituto de Química, UNESP, C. P. 355, CEP 14801 – 970 Araraquara, SP, Brazil*
*massaoi@yahoo.com.br

Abstract: Solid-state Ln-Bz compounds, where Ln stands for trivalent lanthanides and Bz is benzoate have been synthesized. Simultaneous thermogravimetric and differential thermal analysis in a CO$_2$ atmosphere were used to study the thermal decomposition of these compounds.

Keywords: lanthanides; benzoate; thermal decomposition; CO$_2$ atmosphere.

Introduction

Benzoic acid and some of its derivatives are used as conservant, catalyst polymers precursors, in pharmaceutical industries, etc. A survey of literature shows that the complexes of rare earth elements with benzoic acid and some of their derivatives have been investigated in aqueous solutions [1-5] and in solid state [6-25].

In the present study, as an extension of the work of ref. 25, benzoates of trivalent lanthanides and yttrium (III) were investigated by using simultaneous thermogravimetry and differential thermal analysis (TG-DTA) in a CO$_2$ atmosphere. The results of this study are discussed in connection with those found for previously study involving these compounds in an air atmosphere.

Experimental

The preparation of the solid state compounds of trivalent lanthanides and yttrium (III) with Bz, as well as, the determination of hydration water, metal-lic ions and ligand contents, the same procedure were used as previously described in Ref. 25.

The Simultaneous TG-DTA curves were obtained with thermal analysis system model SDT 2960 from TA Instruments. The purge gas was a CO$_2$ with flow of 100 mL min^{-1}. A heating rate of 20 ºC min^{-1} was adopted with samples weighing about 7 mg. Alumina crucibles were used for TG-DTA.

Results and Discussion

The analytical and thermoanalytical (TG) data were obtained in air atmosphere, Table 1 Ref. 25. These results establish the stoichiometry of these compounds, which are in agreement with the Ln(Bz)$_3$.nH$_2$O general formula, where Ln represents trivalent lanthanides or yttrium, Bz is benzoate and n= 2.5 (Nd), 2 (La, Ce, Pr, Sm), 1.5 (Eu, Gd), 1(Tb), 0.5 (Dy) and 0 (Ho to Lu and Y).

The simultaneous TG and DTA curves of the compounds are shown in Fig. 1. These curves exhibit mass loss in steps and endothermic peaks
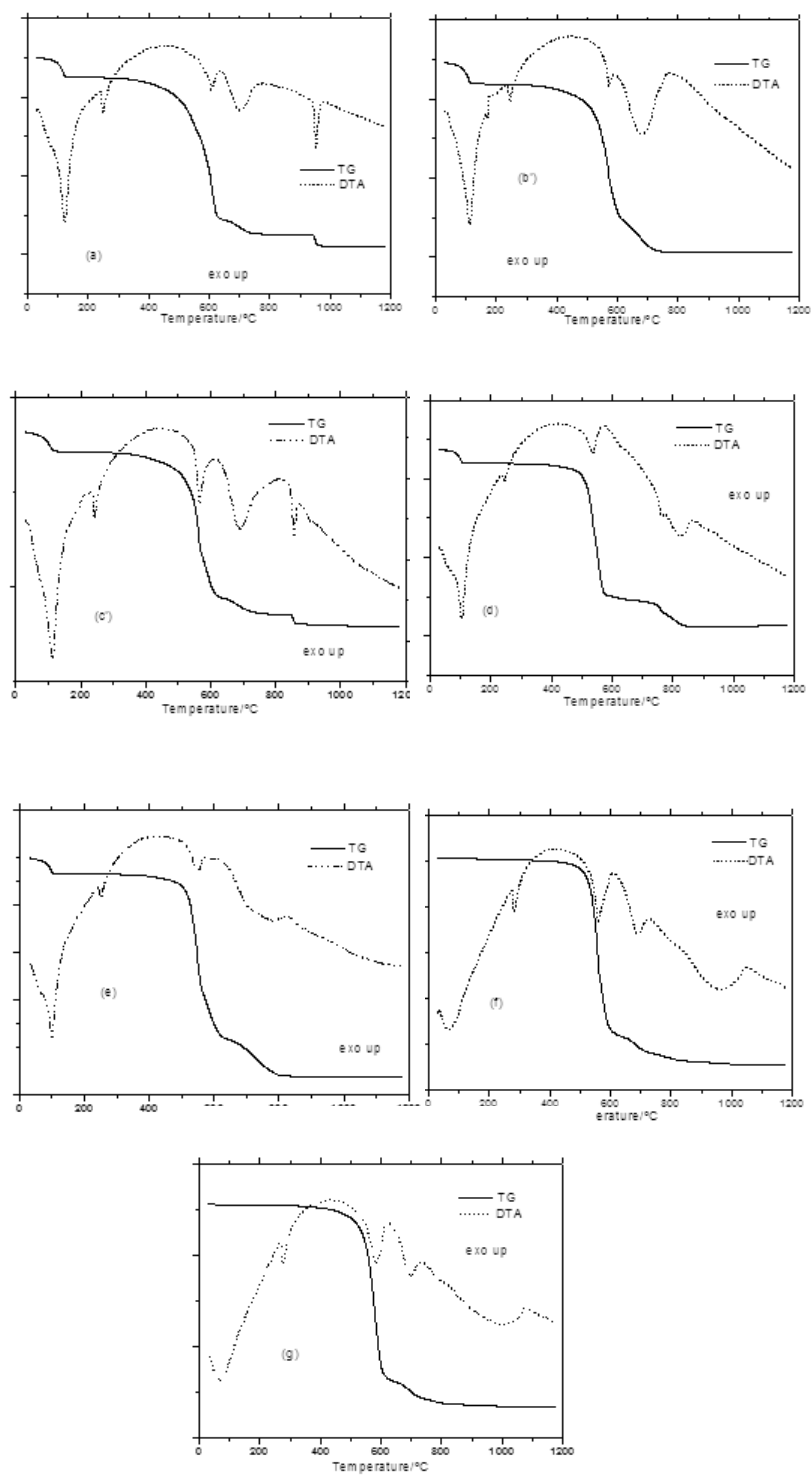
Figure 1. TG-DTA curves of the compounds: (a) La(L)$_3$.2H$_2$O (m = 7.014 mg), (b) Ce(L)$_3$.2H$_2$O (m = 6.937 mg), (c) Pr(L)$_3$.2H$_2$O (m = 7.156 mg), (d) Eu(L)$_3$.1.5H$_2$O (m = 6.806 mg), (e) Gd(L)$_3$.1.5H$_2$O (m = 7.022 mg), (f) Ho(L)$_3$ (m = 7.062mg), (g) Yb(L)$_3$ (m = 7.108 mg). L= benzoate.

corresponding to these losses or due to physical phenomenon, Table 2.

For the lanthanum to dysprosium compounds, the first mass loss (range: 130 – 90ºC), associated to endothermic peaks at 120 – 80 ºC, is ascribed to the dehydration, which occurs in a single step. No influence of the atmosphere (CO_2 or air) was observed in the dehydration process of these compounds.

Once dehydrated, the anhydrous compounds are stable up to 350 ºC (La to Sm), 375 ºC (Eu), 385 ºC (Er, Tm) and 400 ºC (Gd to Ho, Yb, Lu, Y), showing that the anhydrous compounds are more stable in CO_2 than in an air atmosphere. Above these temperatures the TG – DTA curves show mass losses in steps characteristic of each compound and the general aspect of these curves allows the division into the four groups; first group: La, Pr, Nd; second group: Ce, Sm, Gd, Tb; Third group: Eu and fourth group: Dy to Lu and Y. Thus the feature of each of these compounds are discussed on the base of their similar thermal profiles.

Lanthanum, praseodymium and neodymium compounds

The TG-DTA curves of the lanthanum and praseodymium as representative of these compounds are shown in Fig. 1. The first mass loss up to 130 ºC (La) and 120 ºC (Pr, Nd) with the corresponding endothermic peaks at 120 ºC (La) and 110 ºC (Pr, Nd) is due to the release of $2.5H_2O$ (Nd) and $2H_2O$ (La, Pr).

After their dehydration the anhydrous compounds are stable up to 350 ºC, and the endothermic peaks at 250 ºC (La), 245 ºC (Pr) and 240 ºC (Nd) are atributed to the reversible crystalline phase transition, in agreement with the thermal decomposition of these compounds in an air atmosphere [25].

The thermal decomposition of the anhydrous compounds occurs in three (La, Pr) and four (Nd) steps. The first one corresponding to endothermic peaks is attributed to thermal decomposition of these compounds and tests with hydrochloric acid solution on samples heated up to the final temperature of this step, showed in all

Table 1. Analytical and thermoanalytical (TG) data of the compounds.

Compound	Metal oxide (%)			Δ(L) (%)		H_2O (%)		C(%)		H (%)		Final Residue
	Calcd.	TG	EDTA	Calcd.	TG	Calcd.	TG	Calcd.	AE	Calcd.	AE	
La(Bz)$_3$.2 H_2O	30,26	29,79	30,35	63,04	63,48	6,70	6,73	46.85	47.06	2.81	2.82	La$_2$O$_3$
Ce(Bz)$_3$.2 H_2O	31,90	32,00	31,76	61,42	61,30	6,68	6,70	46.75	46.69	2.81	2.80	CeO$_2$
Pr(Bz)$_3$.2 H_2O	31,51	31,40	31,74	61,82	61,76	6,67	6,84	46.68	46.65	2.80	2.80	Pr$_6$O$_{11}$
Nd(Bz)$_3$.2,5 H_2O	30,44	30,55	30,03	61,41	61,55	8,15	7,90	45.64	45.70	2.74	2.73	Nd$_2$O$_3$
Sm(Bz)$_3$.2 H_2O	31,71	31,86	31,62	61,73	61,49	6,56	6,65	45.87	45.75	2.76	2.74	Sm$_2$O$_3$
Eu(Bz)$_3$.1,5 H_2O	32,45	32,35	32,21	62,57	62,50	4,98	5,15	46.50	46.47	2.79	2.81	Eu$_2$O$_3$
Gd(Bz)$_3$.1,5 H_2O	33,10	33,19	32,88	61,96	61,78	4,94	5,03	46.05	46.13	2.77	2.80	Gd$_2$O$_3$
Tb(Bz)$_3$.1 H_2O	34,60	34,46	34,60	62,06	62,14	3,34	3,40	46.65	46.69	2.80	2.81	Tb$_4$O$_7$
Dy(Bz)$_3$.0,5 H_2O	34,87	35,00	34,55	63,45	63,28	1,68	1,72	47.15	47.07	2.83	2.80	Dy$_2$O$_3$
Ho(Bz)$_3$	35,76	35,82	35,57	64,24	64,18			47.74	47.71	2.87	2.85	Ho$_2$O$_3$
Er(Bz)$_3$	36,04	36,17	36,01	63,96	63,83			47.53	47.47	2.86	2.85	Er$_2$O$_3$
Tm(Bz)$_3$	36,24	36,35	36,58	63,75	63,65			47.38	47.33	2.85	2.83	Tm$_2$O$_3$
Yb(Bz)$_3$	36,73	36,66	36,85	63,27	63,34			47.02	47.10	2.82	2.83	Yb$_2$O$_3$
Lu(Bz)$_3$	36,90	37,14	36,71	63,10	62,86			46.84	46.73	2.81	2.81	Lu$_2$O$_3$
Y(Bz)$_3$	24,97	25,01	24,90	75,03	74,99			55.76	55.78	3.35	3.34	Y$_2$O$_3$

Table 2. Temperature ranges θ, mass losses (Δm) and peak temperatures observed for each step of the TG-DTA curves of the compounds $Ln(Bz)_3.H_2O$, where Ln = lanthanides; Bz = benzoate.

Compound		Steps				Crystalline transition
		1ª	2ª	3ª	4ª	
La(Bz)₃.2 H₂O	θ°C	40-130	350 -640	640-760	940-965	250
	Δm (%)	6.60	51.43	7.05	4.02	
	Peak (°C)	120	610	700	955	
Ce(Bz)₃.2 H₂O	θ°C	45-120	350-625	625-750	-	250
	Δm (%)	6.94	50.84	10.62		
	Peak (°C)	110	570	660		
Pr(Bz)₃.2 H₂O	θ°C	35-120	350-610	610-760	845-900	245
	Δm (%)	6.82	50.93	6.80	4.00	
	Peak (°C)	110	560	675	860	
Nd(Bz)₃.2,5 H₂O	θ°C	40-120	350-630	630-840	880-910	240
	Δm (%)	7.85	50.35	7.06	4.00	
	Peak (°C)	110	500	555	890	
Sm(Bz)₃.2 H₂O	θ°C	45-110	350-630	630-800	530-680	230
	Δm (%)	6.44	51.34	10.48	-	
	Peak (°C)	105	550	690	-	
Eu(Bz)₃.1,5 H₂O	θ°C	35-110	375-580	580-850	-	245
	Δm (%)	4.81	51.65	11.21	-	
	Peak (°C)	105	540	830	-	
Gd(Bz)₃.1,5 H₂O	θ°C	40-105	400-620	620-820	-	250
	Δm (%)	4.64	50.85	11.06		
	Peak (°C)	100	550	760		
Tb(Bz)₃.1 H₂O	θ°C	40-95	400-615	615-910		265
	Δm (%)	3.26	51.21	11.20		
	Peak (°C)	90	555	840		
Dy(Bz)₃	θ°C	400-620	620-910	-	-	270
	Δm (%)	55.44	8.74	-	-	
	Peak (°C)	560	680	-	-	
Ho(Bz)₃	θ°C	400-620	620-965	-	-	280
	Δm (%)	54.49	10.05	-	-	
	Peak (°C)	565	690	-	-	
Er(Bz)₃	θ°C	385-625	625-970	-	-	280
	Δm (%)	55.39	8.41	-	-	
	Peak (°C)	580	700	-	-	
Tm(Bz)₃	θ°C	385-625	625-1040	-	-	280
	Δm (%)	56.35	7.51	-	-	
	Peak (°C)	580	690	-	-	
Yb(Bz)₃	θ°C	400-630	630-1010	-	-	280
	Δm (%)	53.84	9.54	-	-	
	Peak (°C)	580	710	-	-	
Lu(Bz)₃	θ°C	400-630	630-1020	-	-	275
	Δm (%)	54.77	8.09	-	-	
	Peak (°C)	610	700	-	-	
Y(Bz)₃	θ°C	400-620	620-990	-	-	280
	Δm (%)	62.37	12.75	-	-	
	Peak (°C)	590	720,800	-	-	

cases, the presence of carbonaceous residue and evolution of CO_2, indicating the formation of carbonate or a derivative of carbonate, as intermediate. The formation of carbonate or derivative carbonate and carbonaceous residue, undoubtedly was favoured by CO_2 used as purge gas. The for-

mation of intermediate derivative of carbonate had already been observed during the thermal decomposition of other lanthanide compounds [26, 27].

The second step corresponding to endothermic peaks is attributed to the thermal decomposition of the intermediate and carbonaceous residue to lanthanide dioxycarbonate [26, 27]. The last (La, Pr) or the two last (Nd) steps corresponding to endothermic peaks are attributed to the thermal decomposition of the dioxycarbonate to the respective oxide, La_2O_3, Pr_6O_{11}, Nd_2O_3.

Cerium, samarium, gadolinium and terbium compounds

The TG-DTA curves of the cerium and gadolinium as representative of these compounds are shown in Fig. 1. The first mass loss up to 120 °C (Ce), 110 °C(Sm), 105 °C (Gd) and 95 °C (Tb) with the corresponding endothermic peak at 115 °C (Ce), 105 °C (Sm), 100 °C (Gd) and 90 °C (Tb) is due to the dehydration with loss of $2H_2O$ (Ce, Sm), $1.5H_2O$ (Gd) and $1H_2O$ (Tb).

The anhydrous compounds are stable up to 350 °C (Ce, Sm) and 400 °C (Gd, Tb) and the endothermic peak at 250 °C (Ce, Gd), 230 °C (Sm) and 265 °C (Tb) is ascribed to the reversible crystalline phase transition, as already observed [25].

The thermal decomposition of the anhydrous compounds takes place in two steps. The first one accompanied by a small endothermic peak is attributed to the thermal decomposition of these compounds with the formation of a mixture of carbonaceous residue and carbonate or a derivative of carbonate, as intermediate.

The last mass loss corresponding to the endothermic peaks is attributed to the thermal decomposition of the carbonaceous residue and of the intermediate to the respective oxide; CeO_2, Sm_2O_3, Gd_2O_3 and Tb_4O_7.

Europium compound

The TG-DTA curves of the europium compound are shown in Fig. 1. The first mass loss up to 110 °C with the corresponding endothermic peak at 105 °C is due to the dehydration with loss of $1.5H_2O$.

The anhydrous compound is stable up to 375 °C and the endothermic peak at 245 °C is attributed to the reversible crystalline phase transition [25].

The thermal decomposition of the anhydrous compounds takes place in three steps with the two last overlapping ones. The first step corresponding to endothermic peak is attributed to the thermal decomposition of the compound with the formation of a mixture of carbonaceous residue and a derivative of carbonate, as intermediate.

The two last overlapping mass losses corresponding to the endothermic peaks are attributed to the thermal decomposition of the carbonaceous residue and of the intermediate to the respective oxide, Eu_2O_3.

Dysprosium to lutetium and yttrium compounds

The TG-DTA curves of the holmium and ytterbium as representative of these compounds are shown in Fig. 1. these curves show that all the compounds were obtained in the anhydrous state and stable up to 385 °C (Eu, Tm) 400 °C (Dy, Ho, Yb, Lu) and 420 °C (Y) and the endothermic peak at 270 °C (Dy), 275 °C (Lu) and 280 °C (Ho, to Yb, Y) is ascribed to the reversible crystalline phase transition [25].

The thermal decomposition of these compounds occurs in three (Ho to Lu) or four (Dy, Y) steps. The first one corresponding to endothermic peaks is attributed to the thermal decomposition of these compounds with the formation of an intermediate derivative of carbonate and carbonaceous residue. Above 620 °C (Dy to Yb) and 630 °C (Lu, Y) the mass losses corresponding to endothermic peaks are attributed to the thermal decomposition of the intermediate derivative of carbonate followed by the carbonaceous residue, with formation of the respective oxide, Ln_2O_3 (Ln= Dy to Lu, Y). For these compounds the thermal decomposition of the intermediate derivative of carbonate occurs before of the carbonaceous residue, due to the decreasing thermal stability of these intermediates with increasing atomic number of the lanthanide ions, as had already been observed [28]. For this reason the large endothermic event between 850 – 1100 °C attributed to the thermal decomposition of the carbonaceous residue is not observed for the light lanthanide compounds since the carbonaceous residue is evolved before the thermal decomposition of the intermediate derivative of the carbonate.

Conclusions

In the dehydration process of these compounds, no influence of the atmosphere (CO_2 or air) is observed in TG-DTA curves, however the thermal decomposition of the anhydrous compounds significative differences is observed.

The thermal decomposition in air atmosphere, the TG-DTA curves suggest the formation of dioxycarbonate or a mixture of dioxycarbonate and oxide only for La, Nd, Sm and Eu compounds, while in a CO_2 atmosphere the TG-DTA curves suggest for all the compounds the formation of a mixture of carbonate, oxy or dioxycarbonate, as intermediate.

These curves also show that the thermal stability of the anhydrous compounds is greater in CO_2 than in an air atmosphere.

J. R. Locatelli, A. B. Siqueira , C. T. Carvalho, M. Ionashiro. Decomposição térmica dos benzoatos de lantanídeos e ítrio no estado sólido em atmosfera de CO_2.

Resumo: Foram sintetizados no estado sólido os compostos Ln-Bz, onde Ln representa lantanídeos trivalentes e Bz benzoato. Análise termogravimétrica e análise térmica diferencial (TG/DTA) foi usada para estudar a decomposição térmica destes compostos em atmosfera de CO_2.

Palavras chaves: lantanídeos, benzoato, decomposição térmica, atmosfera de CO_2.

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