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THERMAL DECOMPOSITIONS OF Y, La AND LANTHANIDE 3-HYDROXYBENZOATES IN AIR AND NITROGEN ATMOSPHERES

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When heated, the 3-hydroxybenzoates of Y, Sm and Eu(III) decompose in two steps. The hydrates first lose crystallization water and the anhydrous complexes are then transformed to oxides in air, and to mixtures of oxide and C in nitrogen atmosphere. When heated in air, the pentahydrates of La, Pr and Nd are dehydrated in two stages and the anhydrous complexes are then transformed to oxides; when heated in nitrogen, they are dehydrated in one step and then decomposed to mixtures of oxides and C.

The salts of 3-hydroxybenzoic acid are little known. 3-hydroxybenzoates of NH_4, Li, Na, K, Tl(I) and Cd have been obtained as anhydrous salts [1, 2], and these of Rb, Cs, Ca, Cu(II) and UO_2^{2+} as hydrates ones [1–3]. The prepared salts are crystalline, and soluble in water and ethanol. The IR spectra of the Tl(I) [4] and Na [4–6] salts have been studied.

In previous work we reported on the thermal decompositions of heavy lanthanide 3-hydroxybenzoates [7].

As a continuation of our work on the thermal decompositions of rare earth carboxylates, we now report on the thermal decompositions of Y, La and light lanthanide 3-hydroxybenzoates in air and nitrogen atmospheres.

Experimental

Complexes of 3-hydroxybenzoic acid with Y, La and light lanthanides from Ce(III) to Eu(III) were prepared by dissolving freshly precipitated lanthanide hydroxides in an equivalent quantity of 3-hydroxybenzoic acid and crystallizing at room temperature. The precipitates formed were filtered off, washed with distilled water and dried at 30° to constant weight.

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The contents of carbon and hydrogen in the prepared complexes were determined by elemental analysis, using V_2O_5 as oxidizing agent. The contents of rare earth elements were determined by igniting the complexes to the oxides Ln_2O_3, CeO_2 and Pr_6O_{11} at 900°, and from the TG curve. The contents of crystallization water were determined by isothermal heating of the complexes at defined temperatures.

Obtained results revealed that the 3-hydroxybenzoates of Y, La and the light lanthanides were prepared as hydrated compounds with a metal to ligand ratio of 1 : 3. The 3-hydroxybenzoates of Y, Sm(III) and Eu(III) were prepared as tetrahydrates, and these of La, Ce(III), Pr(III) and Nd as pentahydrates (Table 1). The complexes of Y, La, Ce(III), Sm and Eu(III) are cream-coloured, that of Pr green, and that of Nd pink.

Table 1 Analytical data

Complex	% H		% C		% M	
	Calcd.	Found.	Calcd.	Found.	Calcd	Found.
$Y(C_7H_5O_3)_3 \cdot 4H_2O$	4.05	4.36	44.07	43.73	15.33	14.96
$La(C_7H_5O_3)_3 \cdot 5H_2O$	3.93	4.47	39.39	38.48	21.69	21.31
$Ce(C_7H_5O_3)_3 \cdot 5H_2O$	3.92	4.20	39.32	42.07	21.84	21.16
$Pr(C_7H_5O_3)_3 \cdot 5H_2O$	3.92	3.70	39.26	38.78	21.93	21.93
$Nd(C_7H_5O_3)_3 \cdot 5H_2O$	3.91	4.26	39.06	39.03	22.33	22.28
$Sm(C_7H_5O_3)_3 \cdot 4H_2O$	3.97	4.26	39.79	40.13	23.73	22.85
$Eu(C_7H_5O_3)_3 \cdot 4H_2O$	3.64	3.65	39.69	39.18	23.91	23.31

The X-ray diagrams revealed that the prepared 3-hydroxybenzoates are compounds crystallizing in the monoclinic system with large unit cells.

The IR spectra of the prepared complexes were recorded over the range 4000–400 cm^{-1}. These proved similar to one another. Analysis of the IR spectra confirms the compositions of the prepared complexes.

In the IR spectra of the 3-hydroxybenzoates of Y, La and the light lanthanides, broad absorption bands appear with max. at 3420–3340 cm^{-1} and sharp bands at 1620–1600 cm^{-1}, which confirms the presence of crystallization water bound in the outer coordination sphere. The bands of the asymmetrical and symmetrical vibrations of the $—COO^-$ group appear at 1545–1535 cm^{-1} and 1420–1410 cm^{-1}, respectively, with the bands of the metal-oxygen bonds at 430–410 cm^{-1}.

On the basis of the shifts of the absorption bands ν_{asym} and ν_{sym} for these complexes compared to those for the sodium salt, the carboxylate ion is found to be a symmetrical bidentate chelating ligand [8].

Table 2 Frequency of absorption bands of COO^- ion of Na and Y, La and light lanthanide 3-hydroxybenzoates (cm^{-1})

Complex	ν_{as}	ν_{sym}	$\Delta\nu$	ν_{M-O}
Na	1570	1410	160	475
Y	1545	1420	125	430
La	1530	1410	120	410
Ce	1530	1410	120	410
Pr	1535	1415	120	415
Nd	1535	1415	120	425
Sm	1540	1415	125	425
Eu	1540	1415	125	425

The thermal stabilities of the prepared complexes were studied. The TG, DTA and DTG curves were recorded. The measurements were made on an OD–102 derivatograph at a heating rate of 9 deg · min^{-1}. The samples were heated in air and nitrogen atmospheres at the following sensitivities: TG – 200 mg, DTA – 1/10, DTG – 1/5. The nitrogen flowed through gas washers filled with pyrogallol and silica gel, at a rate of 115 $cm^3 \cdot min^{-1}$. The results obtained are presented in Table 3 and Figs 1–3. The natures of the solid products of decomposition were established from the TG curves and confirmed from their IR spectra.

When heated in air atmosphere, the 3-hydroxybenzoates of Y, La and the light lanthanides decompose in different ways. The tetrahydrates of Y, Sm and Eu(III)

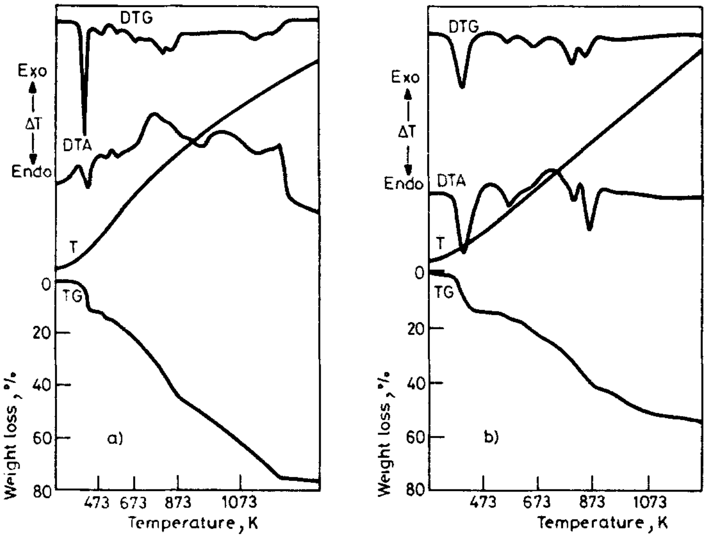

Fig. 1 TG, DTG and DTA curves of $La(C_7H_5O_3)_3 \cdot 5H_2O$. a) in air, b) in nitrogen

Table 3 Temperature range of thermal stability of Y, La and light lanthanide 3-hydroxybenzoates and their decomposition products in air and nitrogen atmosphere

Ln	$Ln(C_6H_4OHCOO)_3 \cdot nH_2O$		Air	$Ln(C_6H_4OHCOO)_3 \cdot H_2O^*$			$Ln(C_6H_4OHCOO)_3$			$Ln_2O_3^{**}$			% C
	Temp. range, K	H_2O n	N_2	Temp. range, K	% calcd.	% found.	Temp. range, K	% calcd.	% found.	Temp. range, K	% calcd.	% found.	
Y	293–353	4	A				433–478	87.41	88.0	1283	19.73	19.0	20.0
	293–353		N				433–533		87.5	1173		39.7	
La	293–353	5	A	403	88.75	89.0	543	85.94	86.0	1183	25.45	25.0	17.5
	293–353		N				463–533		85.6	1253		43.0	
Ce	293–353	5	A	423–433	91.58	91.0	593–603	85.93	85.0	1233	26.83	26.0	17.0
	293–353		N	443–435		91.0	563		85.3	1223		43.8	
Pr	293–353	5	A	423–433	88.79	89.5	503	85.92	86.0	1223	26.50	26.5	8.5
	293–353		N				453–473		86.0	1193		35.0	
Nd	293–353	5	A	423–433	88.84	88.5	493	86.05	85.5	1148	26.0	26.0	3.0
	293–353		N				453–543		85.5	1203		29.0	
Sm	293–353	4	A				463–483	88.63	89.0	1163	27.52	26.5	4.5
	293–353		N				433–463		89.0	1203		32.0	
Eu	293–353	4	A				433–523	88.65	88.5	1173	27.7	27.5	7.3
	293–353		N				433–543		88.5	1233		35.0	

$Ln(C_6H_4OHCOO)_3 \cdot H_2O^*$ — $Ce(C_6H_4OHCOO)_3 \cdot 2H_2O$ in Air
$Ln_3O_3^{**}$ (Ln = Y, La, Nd, Sm, Eu) and CeO_2, Pr_6O_{11}

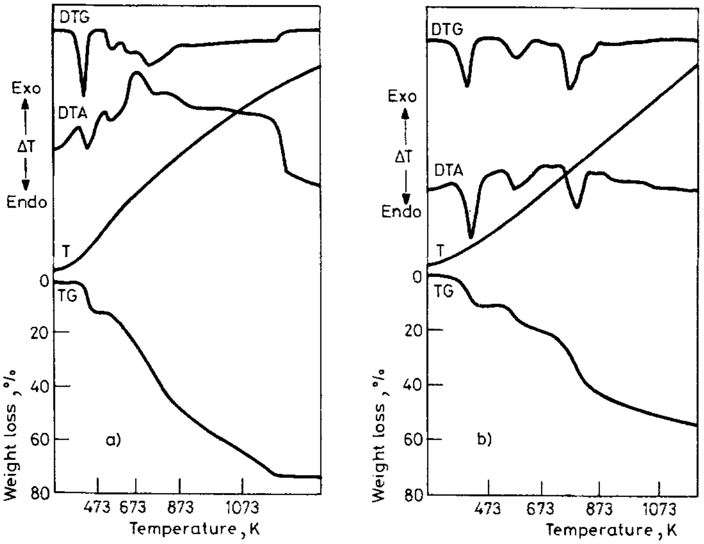

Fig. 2 TG, DTG and DTA curves of $Ce(C_7H_5O_3)_3 \cdot 5H_2O$. a) in air, b) in nitrogen

decompose in two steps (Fig. 3a). They are stable up to 433–463 K, but then lose crystallization water, yielding the anhydrous salts, to the accompaniment of a strong endothermic effect. The anhydrous complexes are stable to 478–523 K, above which they decompose to the oxides Ln_2O_3, which are stable in the temperature range 1163–1283 K.

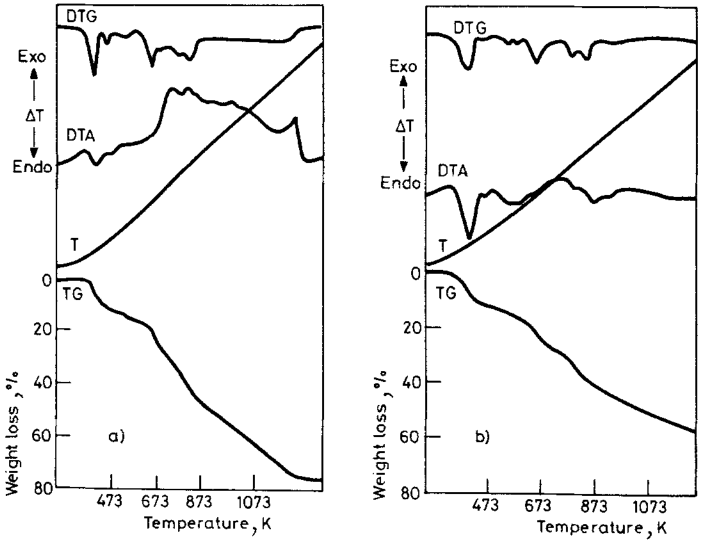

Fig. 3 TG, DTG and DTA curves of $Eu(C_7H_5O_3)_3 \cdot 4H_2O$. a) in air, b) in nitrogen

The complexes of La, Ce(III), Pr(III) and Nd decompose in three steps (Figs 1a, 1b). The pentahydrates of La, Pr and Nd are stable up to 353 K, but at 403–423 K they lose 4 water molecules to give the monohydrates, which are transformed to the oxides Ln_2O_3 and Pr_6O_{11} through the anhydrous salts (Table 3).

The pentahydrate of Ce(III) loses 3 water molecules to yield the dihydrate, which decomposes to the anhydrous complex and then to CeO_2.

The dehydration processes are associated with endothermic effects, and the combustion of the organic ligand with exothermic ones.

When heated in a nitrogen atmosphere, the hydrated complexes of Y, La and the light lanthanides decompose in two steps (Figs 1b, 3b), except for the 3-hydroxybenzoate of Ce(III), which decomposes in three steps (Fig. 2b), similarly as in air. The processes of dehydration and decomposition are accompanied by strong endothermic effects. The final products of decomposition of the complexes of Y, La and the light lanthanides are mixtures of oxides and carbon. The content of carbon in the oxides ranges from 3% for Nd to 20% for Y.

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Zusammenfassung — Die 3-Hydroxybenzoate von Y, Sm und Eu(III) zersetzen sich beim Erhitzen in zwei Schritten. Die Hydrate verlieren zunächst Kristallwasser und die wasserfreien Komplexe werden in Luft in die Oxide und in Stickstoffatmosphäre in ein Gemisch des betreffenden Oxids und Kohlenstoff überführt. Beim Erhitzen in Luft werden die Pentahydrate von La, Pr und Nd in zwei Schritten dehydratisiert und die wasserfreien Komplexe in die Oxide überführt; beim Erhitzen in Stickstoff erfolgt dagegen die Dehydratisierung in nur einem Schritt und Endprodukt der Zersetzung ist ein Gemisch von Kohlenstoff und dem entsprechenden Oxid.

Резюме — Термическое разложение 3-оксибензоатов иттрия, самария и европия протекает в две стадии. Первоначально происходит потеря кристаллизационной воды, а образующиеся при этом безводные соли затем превращаются до окислов в атмосфере воздуха и до смеси окислов и углерода — в атмосфере азота. При нагревании пентагидратов лантана, празеодима и неодима в атмосфере воздуха дегидратация их протекает в две стадии с последующим разложением безводных солей до окислов. В атмосфере азота процесс дегидратации протекает в одну стадию, после которой следует разложение солей до смеси окислов и углерода.