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# THERMAL DECOMPOSITION OF HEAVY LANTHANIDE 3-HYDROXYBENZOATES IN AIR AND NITROGEN ATMOSPHERES

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The conditions of thermal decomposition of heavy lathanide complexes with 3-hydroxybenzoic acid in air and nitrogen atmospheres have been studied. On heating, the complexes of Gd, Dy, Ho, Yb and Lu decompose in three stages. First, the hydrated complexes lose crystallization water and the anhydrous salts heated in air are then transformed to $Ln_2O_3$, or in a nitrogen atmosphere to $Ln_2O_3$ and C. Complexes of Tb(III), Ho and Er are dehydrated in two stages during heating, and the anhydrous complexes are converted in air to $Ln_2O_3$ and $Tb_4O_7$, and in a nitrogen atmosphere to a mixture of oxides and C. The carbon content in the decomposition product ranges between 9.7% for Gd and 19.6% for Ho.

The dehydration of the complexes is accompanied by endothermic effects. The decomposition of 3-hydroxybenzoates is exothermic in air and endothermic in nitrogen.

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 those of Rb, Cs, Ca, Cu(II) and $UO_2^{2+}$ as hydrated ones [1–3]; they are crystalline, and soluble in water and ethanol. The sodium salt fluoresces. The IR spectra of the Tl(I) [4] and Na [4–6] salts have been studied. The frequencies of the absorption bands of the $OCO^-$ groups indicated ionic bonding in the complexes. A search of the available literature showed that 3-hydroxybenzoates of rare earths have not been studied so far. As a continuation of our work on the thermal decomposition of rare earth carboxylates, we now report the thermal decomposition of heavy lanthanide 3-hydroxybenzoates in air and nitrogen atmospheres.

## Experimental

Complexes of 3-hydroxybenzoic acid with heavy lanthanides from Gd to Lu were prepared by dissolving freshly precipitated lanthanide hydroxides in an equivalent quantity of 3-hydroxybenzoic acid and crystallizing at room temperature. The pre-

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cipitates formed were filtered off, washed with distilled water and dried at 30° to constant weight.

The carbon and hydrogen contents of the complexes were determined by elemental analysis with $V_2O_5$ as oxidizing agent. The rare earth element contents were determined by ignition of the complexes to $Ln_2O_3$ or $Tb_4O_7$ at 900° and by thermogravimetry.

The results showed that the complexes of heavy lathanides with 3-hydroxybenzoic acid were prepared as hydrated compounds with a metal to ligand ratio of 1:3. 3-Hydroxybenzoates of Gd, Dy, Tm and Yb were obtained as tetrahydrates, and of Tb(III), Ho, Er and Lu as pentahydrates (Table 1). Complexes of Gd, Dy, Ho, Tm, Yb and Lu were obtained as cream-coloured crystalline solids; that of Tb was greenish, and that of Er pale-pink.

X-ray study confirmed that the complexes are crystalline compounds of low symmetry with large unit cells. They are characterized by different structures and different degrees of crystallinity.

**Table 1** Analytical data

| Complex | H, % | | C, % | | M, % | |
|---|---|---|---|---|---|---|
| | Calcd. | Found | Calcd. | Found | Calcd. | Found |
| $Gd(C_7H_5O_3)_3 \cdot 4H_2O$ | 3.61 | 3.24 | 39.37 | 40.19 | 24.53 | 24.28 |
| $Tb(C_7H_5O_3)_3 \cdot 5H_2O$ | 3.81 | 3.34 | 38.19 | 39.87 | 23.91 | 23.38 |
| $Dy(C_7H_5O_3)_3 \cdot 4H_2O$ | 3.58 | 3.61 | 39.05 | 38.90 | 25.15 | 24.83 |
| $Ho(C_7H_5O_3)_3 \cdot 5H_2O$ | 3.78 | 3.57 | 37.85 | 40.70 | 24.75 | 24.01 |
| $Er(C_7H_5O_3)_3 \cdot 5H_2O$ | 3.76 | 3.31 | 37.72 | 38.93 | 25.01 | 24.92 |
| $Tm(C_7H_5O_3)_3 \cdot 4H_2O$ | 3.55 | 3.35 | 38.66 | 38.05 | 25.89 | 25.34 |
| $Yb(C_7H_5O_3)_3 \cdot 4H_2O$ | 3.53 | 3.33 | 38.42 | 38.71 | 26.35 | 26.34 |
| $Lu(C_7H_5O_3)_3 \cdot 5H_2O$ | 3.72 | 3.24 | 37.29 | 37.31 | 25.87 | 26.38 |

**Table 2** Frequency of absorption bands of $COC^-$ ion of Na and heavy lanthanide 3-hydroxybenzoates ($cm^{-1}$)

| Complex | $\nu_{as}$ | $\nu_{sym}$ | $\Delta\nu$ | $\nu_{M-O}$ |
|---|---|---|---|---|
| Na | 1570 | 1410 | 160 | 475 |
| Gd | 1540 | 1415 | 125 | 425 |
| Tb | 1535 | 1420 | 115 | 430 |
| Dy | 1535 | 1415 | 120 | 425 |
| Ho | 1530 | 1420 | 110 | 425 |
| Er | 1530 | 1420 | 110 | 425 |
| Tm | 1535 | 1420 | 115 | 435 |
| Yb | 1530 | 1420 | 110 | 425 |
| Lu | 1540 | 1425 | 115 | 430 |

The IR spectra of the complexes were recorded in the range 4000–400 $cm^{-1}$. They are similar to one another. Analysis of the IR spectra confirms the compositions of the complexes.

In the IR spectra of the 3-hydroxybenzoates of the heavy lathanides, broad absorption bands appear with max. at 3420–3340 $cm^{-1}$ and sharp bands at 1620–1600 $cm^{-1}$, confirming the presence of crystallization water in the outer coordination sphere. The bands of the asymmetric and symmetric vibrations of the $OCO^-$ group appear at 1540–1530 $cm^{-1}$ and 1425–1415 $cm^{-1}$, respectively (Table 2), and the bands of the metal–oxygen bond at 435–425 $cm^{-1}$.

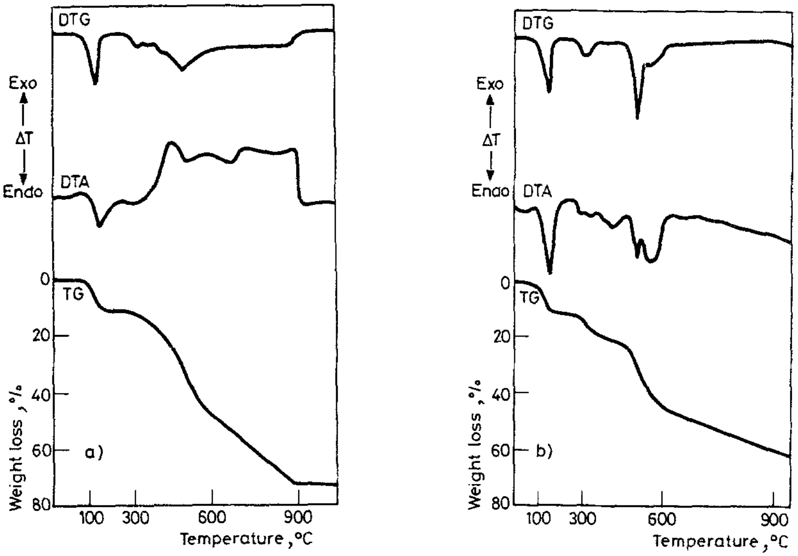

**Fig. 1** TG, DTG and DTA curves of $Gd(C_7H_5O_3 \cdot 4\,H_2O$. a) in air, b) in nitrogen

The displacement of the $\nu_{asym}$ and $\nu_{sym}$ bands of these complexes relative to those for the sodium salt indicate that the carboxylate ion behaves as a bidentate chelating ligand [7].

The thermal stabilities of the complexes were studied. TG, DTA and DTG curves were recorded on an OD-102 derivatograph at a heating rate of 9 deg · $min^{-1}$. The samples were heated in air and nitrogen atmospheres. The results are presented in Table 3 and Figs 1–3. The solid decomposition products were calculated from the weight losses in the TG curves and were confirmed by recording the IR spectra.

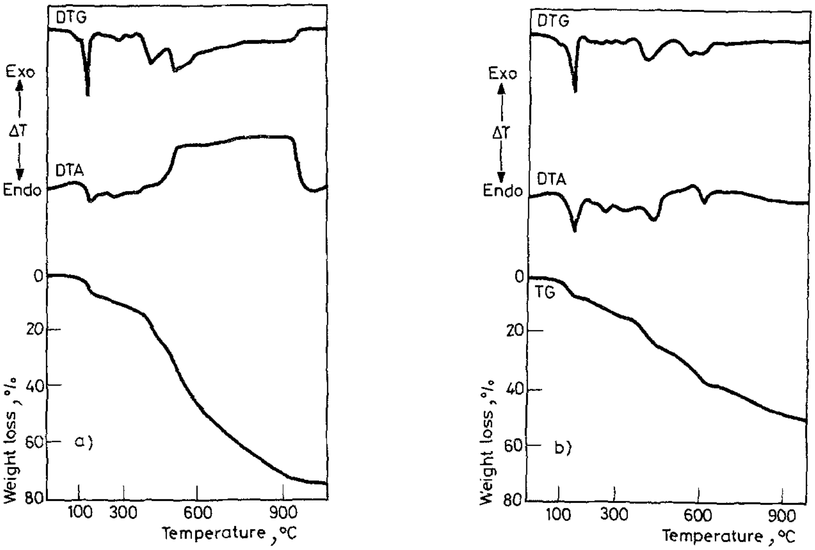

**Fig. 2** TG, DTG and DTA curves of $Ho(C_7H_5O_3)_3 \cdot 5\,H_2O$. a) in air, b) in nitrogen

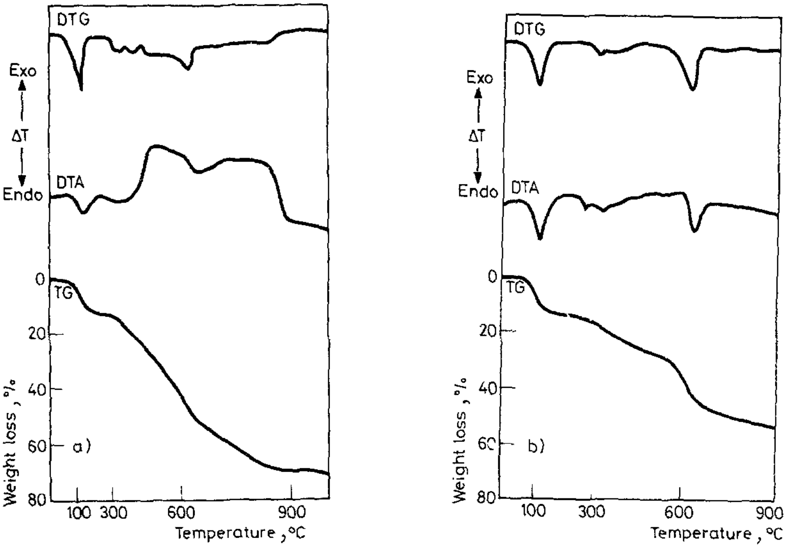

**Fig. 3** TG, DTG and DTA curves of $Lu(C_7H_5O_3)_3 \cdot 5\,H_2O$. a) in air, b) in nitrogen

**Table 3** Temperature range of thermal stability of heavy lanthanide 3-hydroxybenzoates and their decomposition products in air and nitrogen atmosphere

| | $Ln(C_6H_4OHCOO)_3 \cdot n\ H_2O$ | | | $Ln(C_6H_4OHCOO)_3 \cdot 2\ H_2O$ | | | $Ln(C_6H_4OHCOO)_3$ | | | $Ln_2O_3$ * | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ln | Temp. range, °C | $H_2O$ n | Air/$N_2$ | Temp. range, °C | Calcd., % | Found, % | Temp. range, °C | Calcd., % | Found, % | Temp. range, °C | Calcd., % | Found, % | C, % |
| Gd | 20–80 | 4 | A | | | | 160–265 | 88.75 | 88.5 | 900 | 28.29 | 29.0 | 9.7 |
| | 20–80 | | N | | | | 160–285 | | 88.5 | 960 | | 38.0 | |
| Tb | 20–100 | 5 | A | 170–200 | 92.03 | 92.5 | 365–370 | 86.36 | 88.0 | 970 | 28.31 | 27.5 | 17.7 |
| | 20–100 | | N | 160–200 | | 93.0 | 360–370 | | 87.0 | 920 | | 46.0 | |
| Dy | 20–90 | 4 | A | | | | 160–210 | 88.84 | 89.0 | 895 | 28.87 | 28.5 | 17.1 |
| | 20–80 | | N | | | | 160–260 | | 89.0 | 920 | | 46.0 | |
| Ho | 20–90 | 5 | A | 160–190 | 91.89 | 92.5 | 360–380 | 86.48 | 86.7 | 940 | 28.35 | 27.5 | 19.6 |
| | 20–80 | | N | 140–170 | | 92.0 | 360–380 | | 86.0 | 960 | | 48.0 | |
| Er | 20–100 | 5 | A | 165–205 | 91.92 | 92.0 | 370–380 | 86.53 | 86.0 | 930 | 28.60 | 28.5 | 17.4 |
| | 20–100 | | N | 145–200 | | 92.0 | 370 | | 85.0 | 960 | | 46.0 | |
| Tm | 20–80 | 4 | A | | | | 120–280 | 88.95 | 88.3 | 860 | 29.58 | 29.0 | 12.4 |
| | 20–80 | | N | | | | 125–280 | | 88.5 | 960 | | 42.0 | |
| Yb | 20–90 | 4 | A | | | | 140–280 | 89.02 | 90.0 | 920 | 30.02 | 30.0 | 15.0 |
| | 20–70 | | N | | | | 140–280 | | 90.0 | 980 | | 45.0 | |
| Lu | 20–80 | 5 | A | | | | 140–270 | 86.68 | 86.3 | 800 | 29.42 | 29.0 | 12.6 |
| | 20–80 | | N | | | | 140–270 | | 86.0 | 1000 | | 42.0 | |

* $Ln_2O_3$ (Ln = Gd, Dy, Ho, Er, Tm, Yb, Lu) and $Tb_4O_7$.

## Results and discussion

When heated in air, the 3-hydroxybenzoates of heavy lanthanides decompose in different ways. The hydrates of Gd, Dy, Tm, Yb and Lu decompose in two steps (Figs 1a and 3a).

They are stable up to 80–90°, then lose crystalline water to yield the anhydrous salts, this step being accompanied by a strong endothermic effect. The anhydrous complexes are stable up to 210–270°, but decompose to oxides at 800–920°. Lutetium oxide forms already at 800°.

The complexes of Tb(III), Ho and Er decompose in three steps (Fig. 2a). The pentahydrates are stable up to 90–100°, but are transformed at 190–205° to the dihydrates, which are converted to the oxides through the anhydrous salts. The dehydration processes are accompanied by two endothermic effects, but the burning of the organic anion by an exothermic one.

When heated in a nitrogen atmosphere, the hydrated 3-hydroxybenzoates of Gd, Dy, Tm, Yb and Lu decompose in two steps, similarly as in air (Fig. 1b, 3b); the complexes of Tb(III), Ho and Er decompose in three steps (Fig. 2b). The dehydration and decomposition processes are accompanied by strong endothermic effects. The final products of decomposition of lanthanide 3-hydroxybenzoates in a nitrogen atmosphere are mixtures of oxides and carbon. The decomposition products have a high carbon content, ranging from 9.7% for Gd to 19.6% for Ho.

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**Zusammenfassung** — Die Bedingungen der thermischen Zersetzung von Komplexen der schweren Lanthanide mit 3-Hydroxybensoesäure in Luft und Stickstoffatmosphäre wurden untersucht. Beim Erhitzen zersetzen sich die Komplexe von Gd, Dy, Ho, Yb und Li in drei Schritten. Zuerst verlieren die hydratisierten Komplexe Kristallwasser, die wasserfreien Salze ergeben dann in Luft $Ln_2O_3$ und in Stickstoffatmosphäre $Ln_2O_3$ und C als festen Rückstand. Komplexe von Tb(III), Ho und Er werden während des Erhitzens in zwei Stufen dehydratisiert und ergeben bei höheren Temperaturen in Luft $Ln_2O_3$ bzw. $Tb_4O_7$ und in Stickstoffatmosphäre eine Mischung der Oxide mit Kohlenstoff als festen Rückstand. Der Kohlenstoffgehalt des Zersetzungsproduktes liegt zwischen 9.7% für Gd und 19.6% für Ho. Die Dehydratisierung der Komplexe geht mit endothermen Effekten einher. Die Zersetzung von 3-Hydroxybenzoaten ist exotherm in Luft und endotherm in Stickstoffatmosphäre.

**Резюме** — Условия термического разложения комплексов тяжелых лантанидов с 3-оксибензойной кислотой изучены в атмосфере воздуха и азота. Установлено, что комплексы гадолиния, диспрозия, гольмия, иттербия и лютеция разлагаются в три стадии. Сначала гидратированные комплексы теряют кристаллизационную воду, а затем безводные соли превращаются в атмосфере воздуха до окислов, а в атмосфере азота — до окислов и углерода. Дегидратация комплексов тербия, гольмия и эрбия протекает в две стадии и образующиеся затем безводные комплексы превращаются в соответствующие окислы в атмосфере воздуха, тогда как в атмосфере азота — в смеси окислов и углерода. Содержание углерода в продуктах разложения комплексов гадолиния и гольмия составляло соответственно, 9.7 и 19.6%. Дегидратация комплексов сопровождалась эндотермическими эффектами. Разложение 3-оксибензоатов в атмосфере воздуха является экзотермическим процессом, а в атмосфере азота — эндотермическим.