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Thermal decomposition of rare earth element complexes with *o*-phthalic acid in air atmosphere

W. Brzyska and W. Wołodkiewicz

Department of Inorganic and General Chemistry, Faculty of Chemistry, M. Curie Skłodowska University, 20-031 Lublin (Poland)

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Abstract

The thermal decomposition in air of *o*-phthalates of Y and the lanthanides from La(III) to Lu(III) (excluding Pm) was studied. The hydrated complexes $Ln_2(C_8H_4O_4)_3 \cdot nH_2O$ ($n = 2$–16) lose water of crystallization in one (Y, Ce, Sm–Ho, Yb and Lu), two (Pr, Tm) or three steps (La, Nd, Er), then anhydrous complexes decompose directly to oxides or with intermediate formation of oxycarboxylates (La, Pr, Nd). The anhydrous complexes of La–Dy undergo polymorphic transformation on heating.

INTRODUCTION

Rare earth element *o*-phthalates have been known for many years but have not been studied systematically. Rimbach and Killian [1] described the preparation of the *o*-phthalate of Ce(III), Pratt and James [2] on that of Y(III). Riabchikov and Terentieva [3] worked on the preparation of the complexes of some lanthanides in the solid state, whereas Krishnamurthy [4] studied their preparation in aqueous solution. The stability constants of the complexes were determined by using a potentiometric method [4]. Vagina [5] prepared *o*-phthalates of Y, Er and Yb (at pH 7–8) having the general formula $Ln(C_6H_4C_2O_4)OH$ and determined their solubilities in water and hydrochloric acid solutions.

Brzyska [6,7] prepared *o*-phthalates of Y, La–Sm and Gd with the general formula $Ln_2(C_6H_4C_2O_4)_3 \cdot nH_2O$, determined their solubilities in water, solutions of HCl (0.1 M, 0.01 M) and NH_4Cl, and recorded their IR spectra.

Strakhina et al. [8] prepared *o*-phthalates of Eu and Tb [$Ln_2(C_6H_4C_2O_4)_3 \cdot 3H_2O$], determined their thermal stability and recorded their IR spectra. When heated, the complexes are dehydrated and decompose directly to the oxides.

In earlier work we presented the preparation of rare earth *o*-phthalates with a molar ratio of metal to organic ligand of 2:3 [9], their IR and X-ray spectra and their solubilities in water.

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TABLE 1

Data on dehydration of Y and lanthanide *o*-phthalates

Complex	Temperature range of dehydration I (K)	Weight loss (%)		Loss of H_2O (mol)	Temperature range of dehydration II (K)	Weight loss (%)		Loss of H_2O (mol)	Temperature range of dehydration III (K)	Weight loss (%)		Loss of H_2O (mol)	Compound
		Calcd.	Found			Calcd.	Found			Calcd.	Found		
$Y_2L_3 \cdot 4H_2O$	423–508	9.70	9.6	4	---	--	--	--	---	--	--	--	Y_2L_3
$La_2L_3 \cdot 16H_2O$	393–433	6.81	6.6	4	433–473	8.53	8.6	1	543–593	27.12	26.8	11	La_2L_3
$Ce_2L_3 \cdot 6H_2O$	393–498	12.27	13.0	6	---	--	--	--	---	--	--	--	Ce_2L_3
$Pr_2L_3 \cdot 3H_2O$	403–433	4.25	4.2	2	433–493	6.52	6.2	1	---	--	--	--	Pr_2L_3
$Nd_2L_3 \cdot 16H_2O$	373–438	9.94	9.9	6	438–518	21.53	21.0	7	518–593	26.50	27.00	3	Nd_2L_3
$Sm_2L_3 \cdot 4H_2O$	423–483	8.32	8.1	4	---	--	--	-	---	--	--	--	Sm_2L_3
$Eu_2L_3 \cdot 4H_2O$	413–503	8.29	8.1	4	---	--	--	--	---	--	--	--	Eu_2L_3
$Gd_2L_3 \cdot 4H_2O$	423–493	8.19	8.0	4	---	--	--	--	---	--	--	--	Gd_2L_3
$Tb_2L_3 \cdot 4H_2O$	423–503	8.16	8.0	4	---	--	--	--	---	--	--	--	Tb_2L_3
$Dy_2L_3 \cdot 4H_2O$	418–498	8.10	7.8	4	--	--	--	--	---	--	--	--	Dy_2L_3
$Ho_2L_3 \cdot 4H_2O$	438–498	8.05	7.7	4	---	--	--	--	---	--	--	--	Ho_2L_3
$Er_2L_3 \cdot 6H_2O$	373–433	5.78	5.8	3	438–493	9.64	9.9	2	528–613	11.56	11.30	1	Er_2L_3
$Tm_2L_3 \cdot 2H_2O$	463–503	2.08	2.1	1	583–623	4.16	4.0	1	---	--	--	--	Tm_2L_3
$Yb_2L_3 \cdot 3H_2O$	563–633	6.05	5.6	3	---	--	--	--	---	--	--	--	Yb_2L_3
$Lu_2L_3 \cdot 2H_2O$	473–553	4.04	4.0	2	---	--	--	--	---	--	--	--	Lu_2L_3

TABLE 2

Data on thermal decomposition of Y and lanthanide *o*-phthalates

Complex	Temperature range of stability (K)	Temperature of polymorphic transformation (K)	Temperature of intermediate compound formation (K)	Intermediate compound	Weight loss (%)		Temperature of oxide formation [a] (K)
					Calcd.	Found	
Y_2L_3	503–653	–	–	–	–	–	993
La_2L_3	593–673	673	933–973	$La_2O_3 \cdot CO_2$	34.75	34.4	1053
Ce_2L_3	498–643	643	–	–	–	–	1058
Pr_2L_3	493–610	610	843–953	$Pr_2O_3 \cdot 3CO_2$	44.23	44.0	1250
Nd_2L_3	593–673	643	823–903	$Nd_2O_3 \cdot CO_2$	35.59	35.5	1033
Sm_2L_3	483–673	623	–	–	–	–	1053
Eu_2L_3	503–633	633	–	–	–	–	1063
Gd_2L_3	493–653	653	–	–	–	–	1033
Tb_2L_3	503–653	633	–	–	–	–	993
Dy_2L_3	498–643	623	–	–	–	–	963
Ho_2L_3	498–543	–	–	–	–	–	943
Er_2L_3	573–633	–	–	–	–	–	933
Tm_2L_3	618–638	–	–	–	–	–	963
Yb_2L_3	633–653	–	–	–	–	–	983
Lu_2L_3	553–633	–	–	–	–	–	958

[a] Ln_2O_3, CeO_2, Pr_6O_{11}, Tb_4O_7.

As a continuation of our work on the thermal decomposition of rare earth benzenecarboxylates, we now report on the thermal decomposition of Y and lanthanide [from La(III) to Lu(III)] *o*-phthalate hydrates during heating in an air atmosphere.

EXPERIMENTAL

The thermal stabilities of Y and lanthanide [from La(III) to Lu(III) (excluding Pm)] *o*-phthalates having the general formula $Ln_2(C_8H_4O_4)_3 \cdot nH_2O$ (Table 1) were studied in air atmosphere. The measurements were made with a Q-1500 Derivatograph at a heating rate of 10 K min^{-1}. The TG, DTG and DTA curves were recorded. Samples of 100 mg were heated to 1273 K in platinum crucibles at the following sensitivities: TG 100 mg, DTG 500 μV, DTA 500 μV.

Alumina was used as a standard. The samples were also heated isothermally at definite temperature and the thermal curves were recorded to confirm the results. The intermediate products were confirmed by recording the IR spectra and diffractograms.

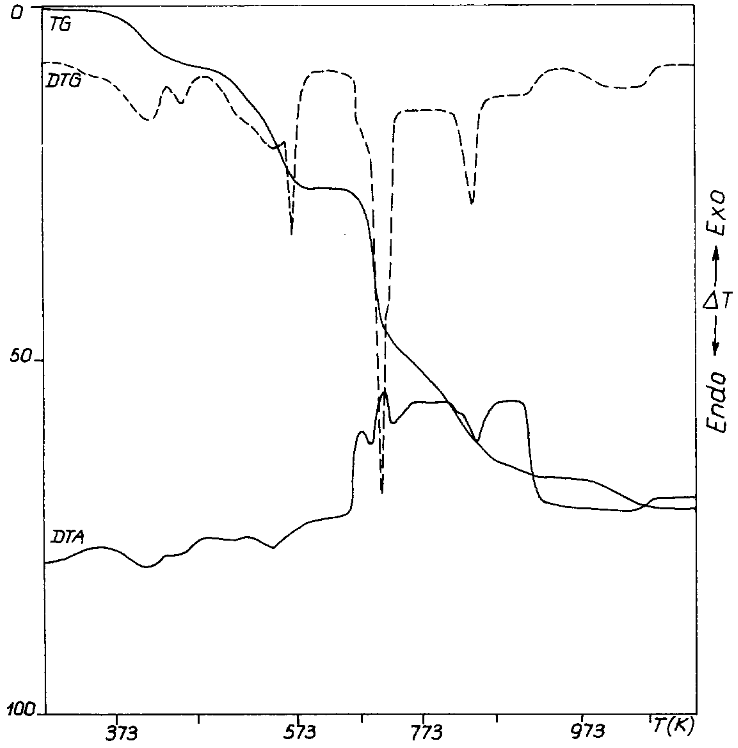

Fig. 1. TG, DTG and DTA curves of $La_2(C_8H_4O_4)_3 \cdot 16H_2O$.

RESULTS AND DISCUSSION

The results presented in Figs. 1–4 and Tables 1 and 2 indicate that the rare earth element *o*-phthalate hydrates prepared here decompose in various ways when heated in an air atmosphere. All the complexes are dehydrated by heating but the process of dehydration occurs in one, two or three steps.

The hydrated complexes of La, Nd and Er are dehydrated in three steps (Fig. 1) and they begin to lose crystallization water at low temperatures (373–393 K). The complexes of Pr(III) and Tm are more stable (Fig. 2). They are stable up to 403 and 463 K, respectively, and are dehydrated in two steps.

The hydrated *o*-phthalates of Y, Ce(III), Sm(III)–Ho, Yb and Lu are dehydrated in one step (Fig. 3). All complexes form anhydrous compounds on heating. The anhydrous complexes of La–Dy exhibit polymorphic changes. On the DTA curves at 610–630 K an exothermic peak is observed (without change of weight on the TG curves).

The structure of the transformation products was confirmed by recording diffractograms. For the complexes of Y and lanthanides from Ho to Lu polymorphic changes are not observed.

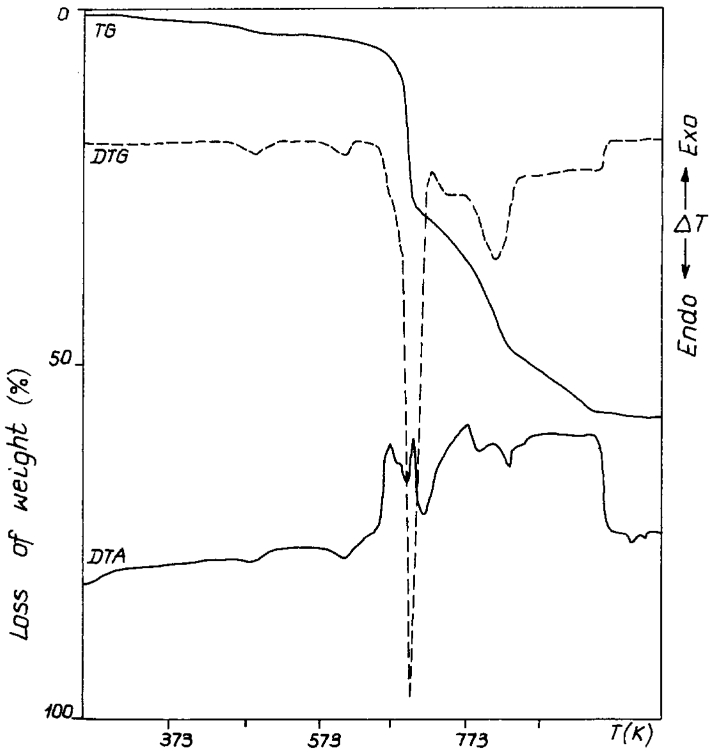

Fig. 2. TG, DTG and DTA curves of $Tm_2(C_8H_4O_4)_3 \cdot 2H_2O$.

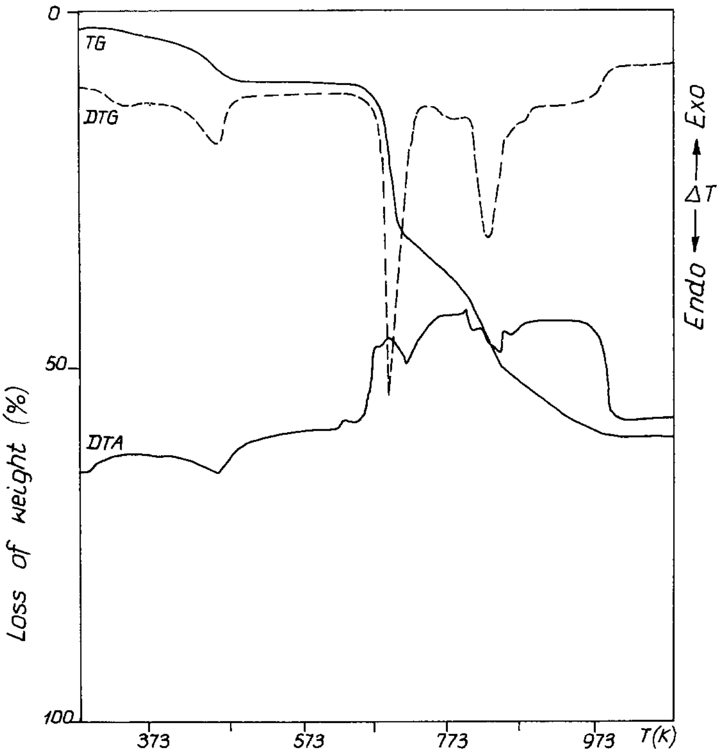

Fig. 3. TG, DTG and DTA curves of $Tb_2(C_8H_4O_4)_3 \cdot 4H_2O$.

The thermal stabilities of anhydrous complexes are variable (Fig. 4). The most stable are the complexes of La, Nd and Sm, which decompose at 673 K, whereas the least stable is the Pr complex (to 610 K). The thermal stabilities of the remaining *o*-phthalates are similar one to another and their temperatures of decomposition have values of 633–653 K.

The process of decomposition and combustion of the organic ligand is connected with a strong exothermic effect. On the basis of the TG curve it is possible to suggest that anhydrous *o*-phthalates decompose directly to oxides (the intermediate products are very unstable and impossible to identify). Only the *o*-phthalates of La, Pr(III) and Nd decompose to oxides with intermediate formation of stable oxycarbonates (Table 2).

Generally, it can be suggested that hydrated *o*-phthalates, when heated in an air atmosphere, are dehydrated in one, two or three steps, and the anhydrous complexes then decompose directly to oxides Ln_2O_3, CeO_2, Tb_4O_7 (only La, Pr, Nd form oxycarbonates as intermediate products).

The temperatures of oxide formation do not change regularly with increasing atomic number of the metal in the lanthanide series. However, it is possible to confirm that the temperatures of light lanthanide (La–Gd)

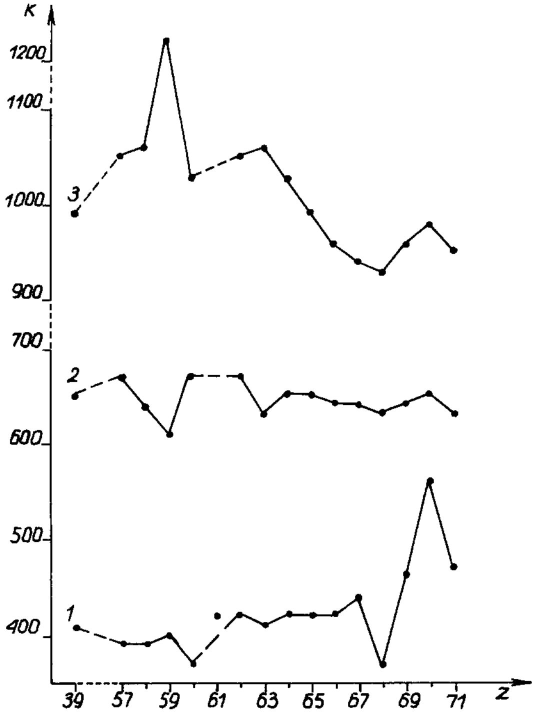

Fig. 4. Relationship between the final temperatures of dehydration T_D and of oxide formation T_T and the atomic number Z of the metal.

oxide formation (1033–1063 K) are higher than those for Y and heavy lanthanides (933–973 K); see Table 2 and Fig. 4.

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