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THERMAL DECOMPOSITION OF YTTRIUM, LANTHANUM AND LANTHANIDE BENZENE-1,3-DIOXYACETATES IN AN AIR ATMOSPHERE

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ABSTRACT

The thermal decomposition in air of benzene-1,3-dioxyacetates of Y, La and lanthanides from Ce^{III} to Lu^{III} was studied. During heating, the hydrated complexes $Ln_2[C_6H_4(OCH_2COO)_2]_3 \cdot nH_2O$ ($n = 7$–12) lose water of crystallisation in one (La–Nd, Eu, Lu) or two steps (Y, Ce, Sm, Gd–Yb), then decompose directly to oxides (Ce) or with intermediate formation of oxycarbonates: $Ln_2O_2CO_3$ (La, Pr, Sm–Ho), $Ln_2O_3 \cdot 0.5CO_2$ (Y, Er–Lu) or two types of oxycarbonates (Nd).

INTRODUCTION

Rare earth element complexes with benzene-1,3-dioxyacetic acid, $C_6H_4(OCH_2COOH)_2$, were previously unknown. In earlier work, we presented the preparation of Y, La and lanthanide (from Ce^{III} to Lu^{III}) benzene-1,3-dioxyacetates with the molar ratio of metal to organic ligand of 2 : 3 and different degrees of hydration [1], their IR and X-ray spectra, solubilities in water and the conductivity of their water solutions.

As a continuation of our work on the thermal decomposition of rare earth carboxylates [2–4], we now report on the thermal decomposition of Y, La and lanthanide benzene-1,3-dioxyacetate hydrates during heating in an air atmosphere.

EXPERIMENTAL

The thermal stabilities of Y, La and lanthanide from Ce^{III} to Lu^{III} benzene-1,3-dioxyacetates with general formula $Ln_2(C_{10}H_8O_6)_3 \cdot nH_2O$ (Table 1) were studied in air atmosphere. The TG, DTG and DTA curves were recorded. The measurements were made with a Q-1500D derivatograph at a heating rate of 10 K min^{-1}. The samples of 100 mg were heated to 1273 K

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TABLE 1

Data on dehydration of Y, La and lanthanide benzene-1,3-dioxyacetates

Complex [a]	Temperature range of dehydration I (K)	Weight loss (%)		Loss of H_2O (moles)	Temperature range of dehydration II (K)	Weight loss (%)		Loss of H_2O (moles)	Weight of residue (%)		Compounds
		Calc.	Found			Calc.	Found		Calc.	Found	
$Y_2L_3 \cdot 10H_2O$	308–403	10.49	10.5	6	403–445	15.73	16.0	3	84.27	84.0	$Y_2L_3 \cdot H_2O$
$La_2L_3 \cdot 10H_2O$	313–468	15.94	16.0	10	–	–	–	–	84.06	84.0	La_2L_3
$Ce_2L_3 \cdot 7H_2O$	308–468	11.69	12.0	7	–	–	–	–	88.31	88.0	Ce_2L_3
$Pr_2L_3 \cdot 12H_2O$	308–468	15.39	15.3	10	–	–	–	–	84.61	84.7	$Pr_2L_3 \cdot 2H_2O$
$Nd_2L_3 \cdot 9H_2O$	308–478	14.44	15.0	9	–	–	–	–	85.56	85.0	Nd_2L_3
$Sm_2L_3 \cdot 8H_2O$	318–405	11.20	11.5	7	405–463	12.89	13.5	1	87.11	86.5	Sm_2L_3
$Eu_2L_3 \cdot 12H_2O$	313–458	12.08	12.5	8	–	–	–	–	87.92	87.5	$Eu_2L_3 \cdot 4H_2O$
$Gd_2L_3 \cdot 10H_2O$	313–413	10.80	10.5	7	413–468	13.89	13.5	2	86.11	86.5	$Gd_2L_3 \cdot H_2O$
$Tb_2L_3 \cdot 12H_2O$	313–405	8.98	9.5	6	405–463	14.93	14.5	4	85.07	85.5	$Tb_2L_3 \cdot 2H_2O$
$Dy_2L_3 \cdot 9H_2O$	308–393	9.32	9.0	6	393–483	13.98	13.5	3	86.02	86.5	Dy_2L_3
$Ho_2L_3 \cdot 9H_2O$	308–395	9.28	9.0	6	395–445	13.92	14.0	3	86.08	86.0	Ho_2L_3
$Er_2L_3 \cdot 9H_2O$	323–413	9.25	9.5	6	413–455	13.87	14.0	3	86.13	86.0	Er_2L_3
$Tm_2L_3 \cdot 7H_2O$	313–393	7.93	7.5	5	393–433	11.09	11.0	2	88.90	89.0	Tm_2L_3
$Yb_2L_3 \cdot 10H_2O$	318–433	3.06	2.6	2	455–503	6.01	5.6	2	93.99	94.4	$Yb_2L_3 \cdot 6H_2O$
$Lu_2L_3 \cdot 10H_2O$	313–443	13.48	13.0	9	–	–	–	–	86.52	87.0	$Lu_2L_3 \cdot H_2O$

[a] $L \equiv C_6H_4(OCH_2COO)^{2-}$.

in platinum crucibles with the following sensitivities: TG, 100 mg; DTG, 500 μV; DTA, 500 μV. The paper speed was 2.5 mm min^{-1}. Al_2O_3 was used as a standard. The samples were also heated isothermally at 473–493 K and the thermal curves were recorded to confirm the results. The intermediate products were confirmed by recording IR and X-ray spectra.

RESULTS AND DISCUSSION

The results, shown in Figs. 1–8 and Tables 1 and 2, indicate that the rare earth benzene-1,3-dioxyacetate hydrates prepared decompose in various ways when heated. They are stable up to 308–323 K, and then become dehydrated in one or two steps. The complexes of La, Ce^{III}, Pr^{III}, Nd, Eu^{III} and Lu are dehydrated in one step whereas those of the remaining elements decompose in two steps, forming the anhydrous complexes of La, Ce, Nd, Sm, Dy, Ho, Er and Tm, and the hydrated complexes of Y, Pr^{III}, Eu^{III}, Gd, Tb, Yb and Lu (Table 1).

From these results, it is possible to suggest that the water of crystallisation molecules are bonded in different ways: with an anion (lost at 393–443 K in the first dehydration step); in the inner sphere of the complexes (lost at

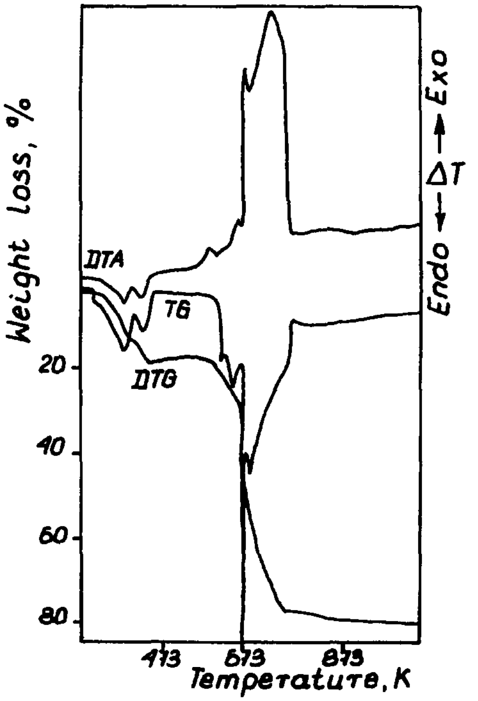

Fig. 1. TG, DTG and DTA curves for $Y_2(C_{10}H_8O_6)_3 \cdot 10H_2O$.

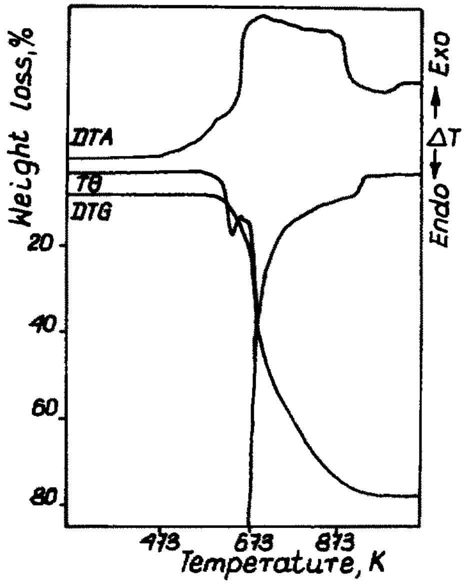

Fig. 2. TG, DTG and DTA curves for $Y_2(C_{10}H_8O_6)_3 \cdot H_2O$.

433–503 K); and the coordination water which is strongly bonded with a metal ion (lost simultaneously with decomposition). Benzene-1,3-dioxyacetates of La–Nd are dehydrated in one step, the final dehydration tempera-

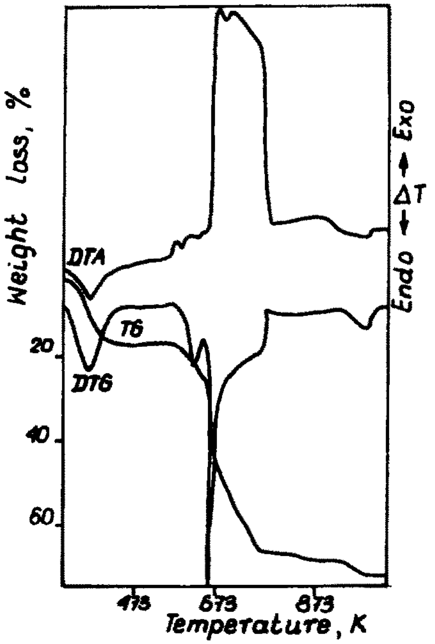

Fig. 3. TG, DTG and DTA curves for $La_2(C_{10}H_8O_6)_3 \cdot 10H_2O$.

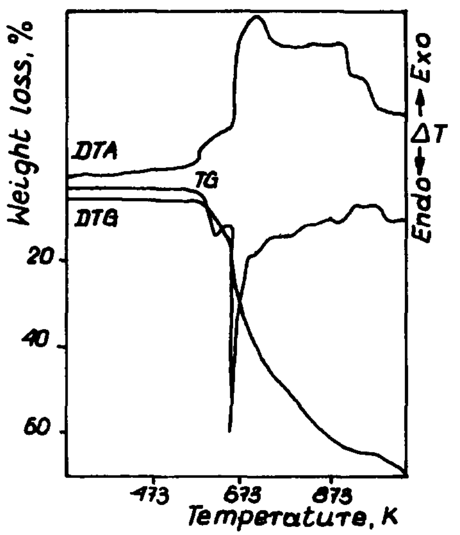

Fig. 4. TG, DTG and DTA curves for $La_2(C_{10}H_8O_6)_3$.

tures indicating cation hydration [5]. Comparing the final temperatures of dehydration of the various complexes, it is clear that water of crystallisation molecules are most strongly bonded in Yb and Dy complexes and least

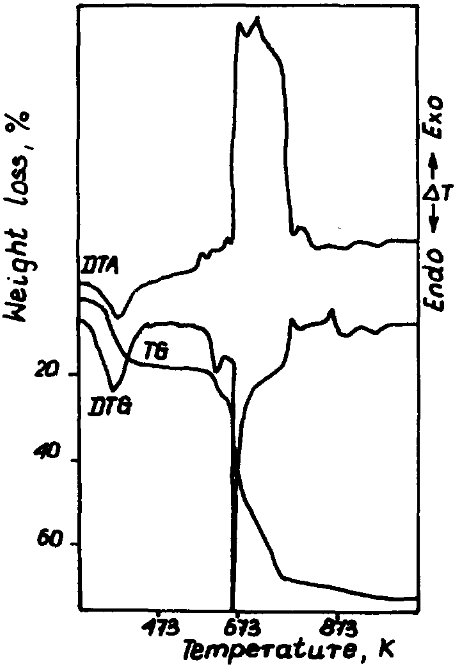

Fig. 5. TG, DTG and DTA curves for $Nd_2(C_{10}H_8O_6)_3 \cdot 9H_2O$.

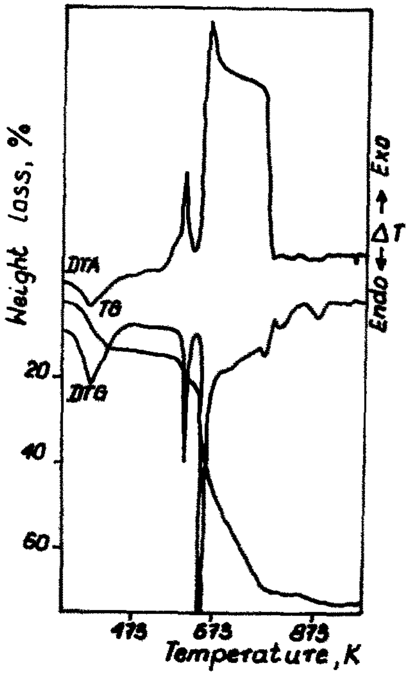

Fig. 6. TG, DTG and DTA curves for $Eu_2(C_{10}H_8O_6)_3 \cdot 12H_2O$.

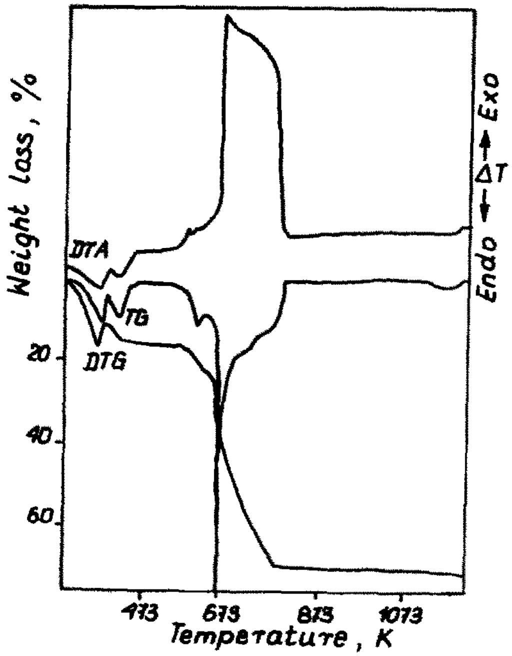

Fig. 7. TG, DTG and DTA curves for $Tb_2(C_{10}H_8O_6)_3 \cdot 12H_2O$.

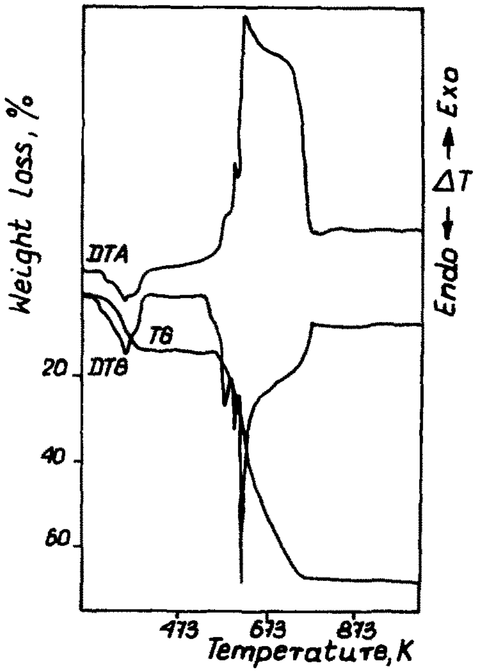

Fig. 8. TG, DTG and DTA curves for $Lu_2(C_{10}H_8O_6)_3 \cdot 10H_2O$.

strongly bonded in Tm, Ho, Lu and Y complexes. For a full interpretation of the nature of the bonding of the water molecules, it is necessary to define the coordination and molecular structure of the complexes on the basis of an X-radiographic study of the monocrystals.

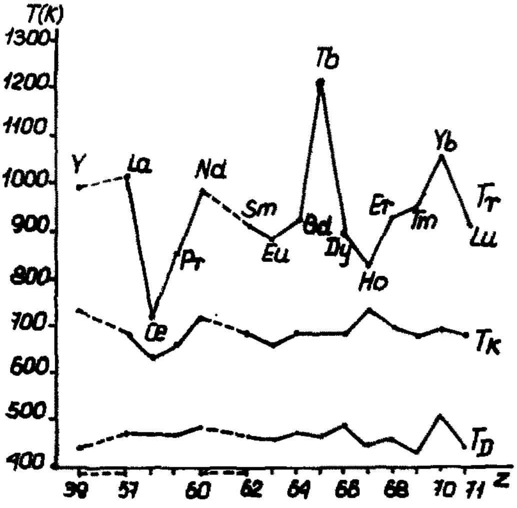

Fig. 9. Relationship between the final temperatures of dehydration T_D, of the exothermic DTA peak T_k and of the oxide formation T_T, and the atomic number Z of the metal.

TABLE 2

Data on decomposition of Y, La and lanthanide benzene-1,3-dioxyacetates

Complex [a]	Temperature range of decomposition to $Ln_2O_2CO_3$ (K)	Weight of residue ($Ln_2O_2CO_3$) (%)		Temperature range of decomposition to $Ln_2O_3 \cdot 0.5CO_2$	Weight of residue ($Ln_2O_3 \cdot 0.5CO_2$) (%)		Exothermic peak on DTA (K)	Temperature of oxide formation (K)	Weight of residue (Ln_2O_3, CeO_2, Pr_6O_{11}, Tb_4O_7) (%)	
		Calc.	Found		Calc.	Found			Calc.	Found
$Y_2L_3 \cdot H_2O$	–	–	–	543–755	24.05	24.5	668, 733	998	21.91	22.0
La_2L_3	768–933	32.71	33.0	–	–	–	678	1021	28.82	29.0
Ce_2L_3	–	–	–	–	–	–	603	713	31.91	32.0
$Pr_2L_3 \cdot 2H_2O$	533–783	31.94	32.5	–	–	–	681	853	29.09	29.0
Nd_2L_3	543–758	33.88	34.5	758–851	31.92	31.5	671, 715	978	29.96	30.0
Sm_2L_3	548–788	35.21	34.5	–	–	–	681	913	31.18	31.0
$Eu_2L_3 \cdot 4H_2O$	538–768	32.20	32.5	–	–	–	583, 653	898	29.51	29.5
$Gd_2L_3 \cdot H_2O$	558–781	34.81	35.0	–	–	–	681	918	31.06	31.0
$Tb_2L_3 \cdot 2H_2O$	531–795	33.97	33.0	–	–	–	683	1211	30.98	31.0
Dy_2L_3	533–791	35.96	35.5	–	–	–	678	895	32.16	32.5
Ho_2L_3	558–748	36.23	35.5	–	–	–	668, 728	828	32.45	32.5
Er_2L_3	–	–	–	545–803	34.59	34.0	693	983	32.72	32.5
Tm_2L_3	–	–	–	493–798	35.89	35.5	633, 678	955	33.95	34.0
$Yb_2L_3 \cdot 6H_2O$	–	–	–	503–948	34.71	34.5	688	1053	32.87	32.5
$Lu_2L_3 \cdot H_2O$	–	–	–	553–795	34.92	34.5	678	918	33.09	33.0

[a] $L \equiv C_6H_4(OCH_2COO)^{2-}$.

The decomposition of the ligand begins at 433–503 K. The ignition of the organic ligand is accompanied by one or two exothermic effects with DTA maxima at 583–733 K. The complexes decompose during heating to oxides with the formation of intermediate oxycarboxylates $Ln_2O_3 \cdot CO_2$ ($Ln \equiv La$, Pr–Ho) at 748–933 K and $2Ln_2O_3 \cdot CO_2$ ($Ln \equiv Y$, Nd, Er–Lu) at 755–948 K (Table 2). Neodymium complex decomposes to Nd_2O_3 with intermediate formation of $Nd_2O_2CO_3$ and $2Nd_2O_3 \cdot CO_2$.

The anhydrous cerium(III) complex directly decomposes, as expected, to the oxide CeO_2. The final decomposition products, Ln_2O_3, CeO_2, Pr_6O_{11} and Tb_4O_7, are formed in the temperature range 713–1211 K. The temperature of oxide formation (T_T) in the lanthanide series changes irregularly with increasing atomic number (Fig. 9). The temperature of CeO_2 formation has the lowest value (713 K), whereas the temperature of Tb_4O_7 formation has the highest (1211 K), as observed during the decomposition of many other series of lanthanide complexes.

The results indicate that the thermal decomposition of hydrated rare earth benzene-1,3-dioxyacetates can be presented in the following manner:

$$Ln_2L_3 \cdot nH_2O \rightarrow Ln_2L_3 \cdot mH_2O \rightarrow Ln_2O_2CO_3 \rightarrow Ln_2O_3$$

$$\text{for } Ln \equiv La, Pr, Sm\text{–}Ho \text{ and } n > m \qquad (1)$$

$$Ln_2L_3 \cdot nH_2O \rightarrow Ln_2L_3 \cdot mH_2O \rightarrow Ln_2O_3 \cdot 1/2CO_2 \rightarrow Ln_2O_3$$

$$\text{for } Ln \equiv Y, Er\text{–}Lu \qquad (2)$$

$$Ce_2L_3 \cdot 7H_2O \rightarrow Ce_2L_3 \rightarrow CeO_2 \qquad (3)$$

$$Nd_2L_3 \cdot 9H_2O \rightarrow Nd_2L_3 \rightarrow Nd_2O_2CO_2 \rightarrow Nd_2O_3 \cdot 1/2CO_2 \rightarrow Nd_2O_3 \qquad (4)$$

Generally, it can be suggested that hydrated rare earth element benzene-1,3-dioxyacetates, when heated in air atmosphere, dehydrate losing all or some water molecules, and then decompose directly to oxides (Ce) or with intermediate formation of oxycarbonates of different compositions.

The final temperatures of complex dehydration (T_D), the temperatures of the exothermic decomposition peak (T_k) and the temperatures of oxide formation (T_T) change irregularly with increasing atomic number Z of the metal (Fig. 9). The results indicate that the ytterbium complex is the most stable and that of thulium is the least stable. Taking account of the thermal properties of the yttrium complex, it is possible to group it with the heavy lanthanides.

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